Modelling and Simulation of Gas adsorption in Shale Gas Reservoirs

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The thesis is submitted in partial fulfilment of the requirements for the award of the degree of

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Declaration

Whilst registered as a candidate for the above degree, I have not been registered for any other research award. The results and conclusions embodied in this thesis are the work of the named candidate and have not been submitted for any other academic award

John Senam Fianu
March 2019
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Dedication

To my Dad, Livingstone Kwasi Fianu.
Abstract

Gas adsorption accounts for a large portion of total gas in place in most shale gas reservoirs. However, the mechanism of contribution of gas adsorption to total gas recovery from shale gas reservoirs is hardly understood. Gas adsorption can be expressed both as a function of pressure and temperature. In most studies of gas adsorption, it is only expressed at a single temperature by using Langmuir isotherm. Very often, erroneous calculations are obtained for gas in place and prediction of production performance since the isotherm used might not represent the true reservoir temperature. Very few adsorption models have addressed gas adsorption as a function of both pressure and temperature with majority of the models currently used in reservoir simulation and gas in place calculation ignoring the dependence of gas adsorption on temperature. Therefore, the use of temperature-dependent models for shale gas adsorption is crucial not only because it accounts for the effect of temperature in gas adsorption/desorption but also for conducting numerical reservoir simulation where the need for thermal stimulation could be explored as an enhanced recovery mechanism in shale gas reservoirs.

On the other hand, in material balance calculations for unconventional reservoirs such as coal bed methane and shale gas, temperature-dependent gas adsorption models can be incorporated in analytical methodologies to predict useful information such as gas in place calculations and future production performance analysis once data is obtained for adsorption capacities at several temperatures. This would ensure accurate representation of gas adsorption throughout the reservoir and better predictions of gas in place, pressure and future production performance.

This thesis presents new methodology for incorporating temperature-dependent gas adsorption models into material balance calculations for unconventional gas reservoirs and also explores the use of microwave heating as a thermal stimulation strategy for enhancing gas recovery in shale gas reservoirs. A dual porosity–dual permeability model is developed for the system of shale gas with the account of both viscous and Knudsen diffusion in the matrix. This is coupled with the microwave heating by solving Maxwell’s equation for the electric field using a finite difference time domain methodology. Furthermore, a coupled
electromagnetic–thermal model is developed to investigate the production of gas from shale gas reservoir using microwave heating as a novel enhanced gas recovery technique. Simulation results indicate higher production of gas when microwave heating is used through the elevation of formation temperature around the waveguide prompting desorption of gas into the well compared with when no thermal stimulation is used. The findings from this work can provide a better insight into modelling gas adsorption in shale formations and open avenues for obtaining higher ultimate estimated recoveries from these unconventional reservoirs through the use of microwave heating.
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Chapter 1 Introduction

1.1 Motivation

Due to the high adsorption rate of most shale gas reservoirs, critically analysing and understanding the adsorption processes, as well as its contribution to the overall recovery of gas, is crucial. Also, by investigating the gas adsorption phenomenon, one can gain an understanding of well performance, shale characterisation and the optimisation of fracture design in shale gas reservoirs (Yu et al., 2015; Lane et al., 1991, 1989).

Shale gas is increasingly becoming an abundant source of energy for the world. It has already revolutionised the energy industry in the USA. Recent advances and knowledge in the production of shale gas have made it possible for it to be produced cheaply, and as a consequence, have contributed to gas prices falling relative to oil prices. Different countries in the world are eagerly advancing their quest to exploit this source of energy that some years ago was deemed unfavourable in exploring for oil and gas.

As an unconventional reservoir, it is characterised by low permeability, which makes the economic development of this resource risky, requiring higher investment. To reduce this risk, a combination of horizontal drilling and hydraulic fracturing has allowed for easy access to the natural gas by providing a permeable pathway through which the gas can flow.

Other unique features of this unconventional resource present challenges to its development. Large amounts of gas are adsorbed on the shale matrix as well as being stored in the pore networks of the shale. The presence of natural fractures also plays an important role in the production of natural gas from shale gas reservoirs. Where these fractures are present, there must be an extensive network of intersecting fractures to be able to contribute towards production. Diffusion in the nano-pore network of the shale and the concept of non-Darcy flow are among several other characteristics of shale gas reservoirs that pose a challenge to its development.

A large surface area of shale/coal means that more gas can be adsorbed compared to that stored by compression in the pore matrix. Production forecast in shale gas reservoirs without the inclusion of adsorbed gas will be less accurate than forecast made when the effects of gas adsorption are included (Lane et al., 1991, 1989).
Adsorption plays an important role in accounting for the original gas in place (OGIP) of shale gas reservoir. The desorbed gas also contributes towards production, even though for some shale plays, like the Barnett\(^1\), the contribution of gas desorption towards production is small and only relevant at the later stage of the well’s life (Cipolla et al., 2010).

According to Cipolla et al. (2010), the contribution from adsorbed gas makes up a low percentage of the overall gas recovery due to the ultra-low permeability of the rock. He also observed that the impact of desorption decreases when the network fracture spacing is smaller using the Barnett shale play. Therefore, it is expected that gas desorption will play a small role in well performance, and this will usually occur at the later life of the well when pressures in the tight matrix have become very low. Frantz et al. (2005) also concluded that in the Barnett shale, desorption is not significant for well performance.

The contribution of adsorption to shale gas performance was further analysed by Yu et al. (2015). This was done by conducting experimental measurements of methane adsorption from the Marcellus shale\(^2\). They concluded that the adsorption of methane on the Marcellus shale deviated from the Langmuir isotherm but obeyed the Brauner, Emmet and Teller (BET) isotherm. This implies that gas adsorption in the Marcellus shale reservoir behaves like multi-layer adsorption rather than mono-layer adsorption assumed for the Langmuir isotherm. Contribution from the BET isotherm model shows an increase in overall gas recovery compared to use of a Langmuir isotherm.

Heller and Zoback (2014) noted the critical effect of adsorption of methane on the production capacity of the reservoir. The adsorption of methane is controlled by the composition and microstructure of the rock. The adsorbed phase is also pressure dependent and with a depleting reservoir, the adsorbed phase contributes to additional gas production. Heller and Zoback (2014) pointed out that certain factors such as desorption pressure, kinetics and effective stresses affect the contribution of desorbed gas to the total production. Furthermore, Heller and Zoback (2014) studied the adsorption of methane and Carbon

\(^1\) Barnett Shale is a geological formation located in the North central Texas primarily for shale gas drilling

\(^2\) Marcellus Shale is a sedimentary rock that stretches through Pennsylvania to West virgin also noted for shale gas drilling
Dioxide (CO₂) on various shale samples in order to understand adsorption in gas shales. Their studies focused on measuring the adsorptive capacities of four shale samples as well as samples of carbon, illite and kaolinite. Their experiments proved that in all the samples, CO₂ proved to have better affinity to shale, and that the adsorptive capacity of shale with CO₂ is indeed two to three times larger than that with methane.

Mengal and Wattenbarger (2011) studied the effect of adsorbed gas in shales using a set of techniques previously employed for the evaluation of tight gas reservoirs. This included reviewing previous literature that utilised end of transient time and boundary dominated flow methods to estimate original gas in place. Mengal and Wattenbarger (2011) included the concept of adsorbed gas in their studies. By including adsorption into their study, they reasoned that at very late times, the well is more likely to undergo boundary dominated flow, and it is at this point that desorption from shale normally takes place. By reviewing analytical solutions from previous research works aimed at estimating OGIP (Anderson et al., 2010; Ibrahim et al., 2006; Ibrahim and Wattenbarger, 2003), Mengal and Wattenbarger (2011) included desorbed gas in all of the methods that ignored gas adsorption effects. By applying these combined models to field data, they were able to analyse results with and without adsorption. The results of their research showed that desorption plays an important role in determining the OGIP calculations, and it also affects the recovery factor of the field. Ignoring desorption will therefore lead to inaccurate estimates of OGIP and recovery factors. They were able to show that OGIP estimates increased by 30% when adsorbed gas was included in the estimation; however, recovery factor estimates were found to have decreased by 17% when adsorbed gas was included in the calculation.

Modelling gas adsorption is therefore crucial when conducting numerical simulation studies. The adsorption capacity of shale gas reservoirs depends on both the pressure and temperature. Several isotherm models have been explored to represent the adsorption of gas onto shale and coal. Amongst which is the Langmuir isotherm (Langmuir, 1916), which has been widely used to explore the pressure dependence of gas onto shale.

The Langmuir isotherm assumes that the adsorbed gas behaves as an ideal gas under isothermal conditions. Hence there is a dynamic equilibrium, at constant temperature and pressure, between the adsorbed and non-absorbed gas.
Modelling of temperature dependence has been largely ignored in most studies, with only a handful of researchers focussing on the pressure and temperature dependency of adsorbed gas on the shale.

1.1.1 Adsorption Phenomenon
Adsorption is often seen as exothermic process where the gas molecules or atoms adhere to the surface of a rock due to the imbalance in the surface energy. This process often results in a thin layer of the adsorbate on the surface of the adsorbent. The adsorbate is referred to as the gas molecules while adsorbent is the surface or rock that the gas adheres to. Hence adsorption is often referred to as a surface phenomenon. The gas that adsorbs onto the rock surfaces can also desorb from the surface especially at very low pressures or high temperature. This is often referred to as desorption. The process of adsorption and desorption is reversible due to the weak “Van Der Waals” attraction forces that occurs between the gas molecules and the rock surface.

There are two main types of adsorption known as physiosorption and chemisorption. Physiosorption is a reversible process which occurs when molecular forces (Van Der Waals) between adsorbate and adsorbent is relatively weak. This type of adsorption normally has a low enthalpy 25-45KJ/mol which means the adsorbate has low kinetic energy and the process can occur at low temperature (Sing et al., 1985).

Chemical adsorption is an irreversible process and occurs when there is a chemical attraction force between the adsorbate and adsorbent which result in strong chemical bond between molecules. Unlike physiosorption, it occurs within a single layer between the two phases and this indicate a stronger adsorption in terms of attraction forces and result in high adsorption entropy (200-400KJ/mol), it can occur at high temperature and hence requires an activation energy for starting the adsorption process (Ho and McKay, 1998).

1.1.2 Adsorption in Shale Rock Reservoirs
Shale reservoirs are naturally fractured and possess layered matrix composed of micropores. High amount of gas is sorbed onto the surface of these micropores and the rest is trapped free gas. Gas in shale is found in three ways: it can be within the pore spaces, held within natural rock fractures or adsorbed onto the matrix of the rock. The gas held in natural fractures in produced directly while the adsorbed gas is released when downhole pressure is
decreased. The structure of pore spaces in shale provides great surface area which allow shale-pores to adsorb high amount of natural gas. Various production models (Javadvour et al., 2007) are used for gas production built on the assumptions that production is measured by a constant diffusivity coefficient from spherical bodies connected via large fracture network.

1.2 Problem statement and Research Gaps
Most of the published studies on gas adsorption in shale gas reservoirs have mainly considered adsorption as a function of pressure, with the Langmuir isotherm widely used as the adsorption model in these applications (Arri et al., 1992; Mengal and Wattenbarger, 2013; Yu et al., 2015, 2014; Yu and Sepehrnoori, 2014; Zhang et al., 2015). One of the reasons for this is the ease with which the Langmuir model can be incorporated into most reservoir simulators. However, with this choice of adsorption model, there can be no examination of thermal stimulation as an enhanced recovery method.

Only a handful of researchers have considered thermal stimulation in shale gas reservoirs or (until recently) the use of microwave heating as a heat source. The choice of temperature dependent adsorption model has been made with little consideration to which model gives the best accuracy in modelling gas adsorption.

Furthermore, where microwave heating has been used, the mathematical model of the shale gas has failed to consider the non-Darcy effect of flow in shale gas reservoirs and hence does not accurately represent the physical system of shale gas reservoirs.


Therefore, the focus of this research will be to address these gaps by first reviewing different adsorption models that incorporate temperature to find the best model for a set of shale gas adsorption data and second, developing a coupled electromagnetic-thermal model for shale gas reservoirs. The work will also focus on developing a new methodology for incorporating temperature dependent gas adsorption model into a material balance simulator for unconventional gas reservoirs.
1.3 Research Questions
In the course of this research, the choice of methodology, as well as the results obtained, have been guided by the following questions:

- How well can gas adsorption models predict shale gas adsorption capacities, and what models are best for single, multi-component and temperature dependent gas adsorption on shale gas reservoirs?
- Can temperature dependent gas adsorption models be used in analytical material balance calculations for unconventional gas reservoirs?
- What contribution can gas adsorption make to overall total production?
- Can a temperature dependent model be used in place of the Langmuir model in numerical simulations involving thermal stimulation, and which temperature dependent model gives the best accuracy in modelling gas adsorption?
- What factors influence production in a shale gas involving thermal stimulation, and what thermal stimulation strategies exist for shale gas reservoirs?
- Is microwave heating suitable for enhanced shale gas recovery, and what factors influence microwave heating in shale gas recovery?

1.4 Aim of study
The principal aim of this thesis is to examine the modelling of shale gas reservoir considering the use of temperature-dependent adsorption models, in order to give accurate representation of adsorption phenomenon. The thesis also examines the simulation of gas adsorption production in shale gas reservoirs with microwave heating as enhanced gas recovery method (EGR).

1.5 Objectives
- Review applications of gas adsorption models in shale gas reservoirs. Different gas adsorption models are able to predict differently on gas adsorption data. The choice of adsorption model would therefore depend on how well the model is able to fit the adsorption data and whether it can be used in single or multicomponent systems.
- Develop a new methodology for predicting gas in place, average pressure and future gas production, using material balance calculations for unconventional gas reservoirs.
The new methodology should be able to account for gas adsorption at multiple temperatures.

- Develop a numerical simulation model to analyse the contribution of gas adsorption to shale gas reservoirs.
- Investigate the application of thermal stimulation in shale gas reservoirs, using microwave heating as the heat source.

1.6 Methodology
In order to address these questions, several methodologies have been used to provide answers to these questions. Both analytical and numerical models have been used, some sourced from literature sources, whilst others are new methods developed to address these fundamental questions.

Several types of nonlinear regression techniques have been proposed and used to identify an optimal model for gas adsorption on various adsorbents. The techniques involve minimising error distribution between the experimental data and the predicted results. Thus, several error functions have been used in the non-linear regression, to try to optimise the adsorption model for any particular set of experimental data. A more statistically robust method involving sum of normalised error (SNE) has been used throughout the adsorption modelling to obtain an optimised adsorption model. These error functions include sum of squared error (SSE), absolute relative error (ARE), sum of absolute error (SAE), Marquardt’s percent standard deviation (MPSD) and hybrid fractional error (HYBRID).

Analytical material balance methods have been used to determine gas in place, average pressures and future production predictions for unconventional gas reservoirs. Several methodologies have been proposed for material balance in unconventional reservoirs, with earlier methodologies focused on King’s Method. However, the choice of methodology used throughout this thesis for analytical calculations of material balance follows an approach by Ahmed and Roux (2006), with modifications made to include temperature dependent adsorption models.

Numerical modelling was chosen as the preferred method in those parts of the thesis relating to simulations of shale gas. This choice is obvious because of the set of nonlinear partial differential equations involved in describing the physical system. A combination of Newton’s
method and iterative methods was used to solve the system of equation concerning the shale gas system. The finite difference method was used to discretize the medium. In terms of solving the electromagnetic equations, finite difference time domain methodology was used.

The whole set of equations involving shale gas systems, heat equations and Maxwell equations has been coupled together to describe a coupled electromagnetic –thermal model for shale gas systems. A segregated approach was employed in the solution of the systems of equations to arrive at the final solutions. Convergence limits have all been incorporated into the simulation program written in MATLAB. The detailed methodology is presented in the relevant chapters of this thesis.

1.7 Thesis Layout
Following the compilation style PhD thesis guidance, each chapter has been presented as a standalone with dedicated, specific objectives. However, the chapters work in combination to present the modelling and simulation of gas adsorption in shale gas reservoirs.

Chapter 2: This chapter provides a complete overview of gas adsorption in shale gas reservoirs. It primarily provides details of most used adsorption models in the petroleum industry by focussing on single component models and multi component models. The chapter ends by applying the adsorption models discussed to a set of adsorption data to investigate their predictability and accuracy.

Chapter 3: An overview of temperature dependent modelling and its application is the main theme of this chapter. Firstly, the chapter goes into detail by examining the different forms of temperature dependent adsorption models and why they are relevant in modelling gas adsorption. It also discusses the limitations of using the Langmuir isotherm in modelling gas adsorption. Finally, a complete shale gas adsorption dataset sourced from literature provides the basis for modelling temperature dependent gas adsorption.

Chapter 4: New methodology that incorporates temperature dependent gas adsorption modelling into material balance calculations is introduced in this chapter. A review of different mathematical methods for material balance calculations in unconventional gas reservoirs is conducted, with particular emphasis on Ahmed and Roux's methodology. A
comparison is made of the new methodology with the Ahmed and Roux method for gas in place calculations and future production results.

**Chapter 5:** This chapter discusses the use of numerical simulation in shale gas reservoirs first by comparing models with and without gas adsorption in a mathematical model of shale gas. The role of several factors, such as matrix porosity and fracture permeability, is also examined. Validation of the proposed mathematical model for shale gas system is shown, using results from earlier literature. Finally, the chapter introduces the concept of thermal stimulation by coupling the heat equation with the shale gas system. The source term is left as generic and production results are examined with and without a heat source.

**Chapter 6:** This chapter reviews the concept of thermal stimulation in shale gas reservoirs. Microwave heating is chosen as the heat source for simulation work involving thermal stimulation of shale gas reservoirs. The chapter presents mathematical formulations of Maxwell’s equation and solution methods. Finite difference time domain as a numerical method for solving the set of Maxwell equation is used and later coupled with the heat equation and the shale gas model developed in previous chapter. Several factors that influence microwave heating and gas recovery, such as microwave frequency, are also examined.

**Chapter 7:** Finally, a summary of all the preceding chapters and their results is discussed in this chapter. Recommendations for future work are also provided in this chapter.
Chapter 2
Modelling of Optimised Gas Adsorption in Shale Gas Reservoirs with Advanced Error Analysis

2.1 Introduction
Shale gas reservoirs are characterised by gas adsorption on shale matrix and free gas stored within the pores of the matrix. Both free gas and adsorbed gas make up a large portion of the original gas in place (OGIP) of these reservoirs, with gas adsorption estimated to be about 20-85% of the total gas in place (Curtis, 2002). Gas adsorption plays an important role in the estimations of the overall gas in place which, and so, in turn, is crucial when developing these resources for future production. Langmuir isotherm has remained one of the most popular models used in representing the relationship between the amount of gas adsorbed and pressure. However, several other models have also been developed that can also represent the adsorption process in most of these shale reservoirs (Ahmadpour et al., 1998; Bazan et al., 2008; Charoensuppanimit et al., 2016; L. Chen et al., 2017; Clarkson et al., 2013; Clarkson and Haghshenas, 2013; Guo et al., 2017; Sandoval et al., 2017; Tang et al., 2017; Y. Wang et al., 2015). To ensure accurate representation of the amount of gas adsorbed, these models need to be evaluated and compared with the experimental data for the gas adsorption in the shale matrix. Since each shale rock might show unique properties, it may not be possible to select a single model to represent the adsorption process in all the shale formations. For instance, it has been reported that the Brunauer, Emmet and Teller (BET) model represents the adsorption process in Marcellus shale better than Langmuir isotherm, based on different samples within the formation (Yu et al., 2015). However, this may not necessarily be the case for other shales.

Gas adsorption modelling involves applying a set of different adsorption models to acquired experimental shale gas adsorption data. These models can be grouped as single component systems or multi-component systems. Under the single component system, a single gas such as methane is used as the adsorbed gas on shale. The advantage of using single component models is that they are very simple to use in the calculation of adsorbed gas amount. This is especially useful when conducting numerical simulations involving the calculation of
adsorption in shale gas reservoirs. For this reason, single component models can be found in a variety of reservoir simulations of shale gas systems. However, this simplification is not valid because in most cases, the formation gas is a mixture containing more than one component (Wang et al., 2015). In shale gas systems, methane, carbon dioxide (CO₂) and other gases can be found, therefore, modelling the gas adsorption in such systems requires adsorption models capable of addressing the multi-component gas mixture present.

There are lots of factors that can account for the adsorption capacity of methane on shale. These factors include, but are not limited to, the total organic content (TOC), the level of thermal maturity of the shale, Kerogen content, pressure and temperature. Experimental studies have suggested that a plot of adsorbed gas quantity versus TOC will show a proportional relationship, with high TOC of shale leading to high adsorption capacity (Chalmers and Bustin, 2008; Lu et al., 1995; Ross and Bustin, 2007; Ross and Marc Bustin, 2009; Zhang et al., 2012). Low reservoir pressure will correspond to a much lower adsorbed quantity due to the fact that higher binding energy is required for gas adsorption (Guo et al., 2013; Raut et al., 2007).

Several works on adsorption modelling have been conducted without taking into consideration the choice of error function used in optimising the adsorption model (Chareonsuppanimit et al., 2012; Clarkson et al., 2013; Fianu et al., 2018; Tang et al., 2017; Yang et al., 2017). This often results in only one set of adsorption constants for the adsorption models being used, without any serious interrogation into how accurately the set of adsorption constants fits the adsorption model to experimental data. According to Sreńsczek-Nazzal et al., 2015, very few detailed studies have been conducted that compare the accuracy of the error functions used in modelling gas adsorption and the accuracy of the predicted isotherm parameters. No study, however, has compared different error functions on modelling gas adsorption in shale gas reservoirs. In minimising the difference between the experimental data and the predicted results from the adsorption models, several error functions have been proposed and applied to predict optimal isotherms, including sum of square error (SSE), average relative error (ARE), sum of absolute error (SAE), Marquardt’s percent standard deviation (MPSD) and hybrid fractional error (HYBRID) (Allen et al., 2003; Ho et al., 2002; Kumar and Porkodi, 2007; Sreńsczek-Nazzal et al., 2015).
2.1.1 Types of gas adsorption Isotherm

Gas adsorption involves gas molecules adhering to the surfaces of an adsorbent. This process can be represented by many different isotherms. These isotherms can be basically classified into 6 groups defined by the International Union of Pure and Applied Chemistry (IUPAC) for physical adsorption. Due to the weak Van der Waal forces that characterise the interaction of the gas molecules, gas adsorption is normally referred to as physical adsorption and hence a reversible process allowing for both adsorption and desorption.

The following descriptions of each of the isotherm types have been given by Sing et al., (1985) and are graphically represented in Figure 2.1.

Type I is described as the isotherm for microporous adsorbents in which the pore size is smaller than the molecular diameter of the sorbate molecule (Ruthven, 1984). They have relatively small external surfaces; examples being activated carbons and molecular zeolites.

Type II is associated with non-porous or macroporous absorbents. This is normally referred to as BET isotherms. For non-porous adsorbents, the adsorption mechanism is monolayer formation where the adsorbate is assumed to adhere on a single layer followed by multilayer adsorption in which case multiple layers are assumed to be present for the adsorption process (Clarkson and Haghshenas, 2013) (See Figure 2.2). At low pressure, it becomes concave and then turns linear when it reaches one third of the isotherm as pressure decreases indicating monolayer coverage completion. We can also see from Figure 2.1 that the graph then turns to be convex indicating multilayer formation.

The Type III isotherm is convex over its entire range and therefore does not exhibit a point B. Point B indicates the end of monolayer coverage and the beginning of multilayer adsorption. This type of isotherm is common in nonporous and microporous adsorbents, the isotherm indicates unrestricted multilayer formation process, it forms because the interactions between adsorbate’s molecules are stronger than the interactions between adsorbent and adsorbate. The isotherm for types II and III occurs for wide-ranging pore sizes. Type II and III isotherms show a continuous progression from monolayer to multilayer adsorption, with Ruthven (1984) noting the high capacity of adsorption at very high temperatures being due to capillary condensation that occurs in pores of increasing diameter.
Type IV has a hysteresis loop which is associated with capillary condensation taking place in mesopores. As shown in Figure 2.1, the initial part of the isotherm follows the same path as type II where monolayer to multilayer adsorption takes place. Type IV occur in many mesoporous industrial adsorbents. Type IV isotherm is similar to Type II isotherm at low relative pressures; however, Type IV isotherm starts decreasing when high pressure is reached and beyond that the slope becomes horizontal to a constant adsorption value.

Type V according to Sing et al., (1985) is the least common, and it is related to type III isotherm where the interaction between the adsorbent and adsorbate is weak. The isotherm is convex to relative pressure, yet Type V isotherm reaches a plateau at high relative pressure. This type of isotherm is common in mesoporous or microporous adsorbents.

Type VI isotherms show a stepwise multi-layer adsorption on a non-uniform porous surface, with the sharpness of the steps dependent on the system and the temperature.

![Figure 2.1: Types of adsorption isotherm (Yang, 2013)](image)

When the adsorption model can only be applied to a single component system, such as methane, it is normally classified under single/pure component modelling, otherwise referred to as multi-component models. A brief summary of all the models discussed in the preceding...
sections under both single component and multi-component models have been summarised in Table 2.1.

2.2 Pure Component Adsorption Models

2.2.1 Langmuir Isotherm

One of the key assumptions of Langmuir isotherm is that there must be a homogeneous surface and no interaction between the neighbouring molecules. This is, however, a difficult concept to apply even in coal or shale systems, because their internal organic matter is chemically heterogeneous (Clarkson and Haghshenas, 2013). Also, the monolayer volume is assumed to be invariant to temperature. According to Clarkson et al., (1997), several studies have shown this assumption to be inaccurate, since the monolayer amount do vary with temperature. Langmuir isotherm is given by the formula below

\[
V = \frac{V_L P}{P + P_L}, \quad \text{...................................................(2.1)}
\]

\( V \) = volume of adsorbed gas at pressure \( P \),

\( V_L \) = Langmuir volume or maximum gas adsorption at infinite pressure and

\( P_L \) = Langmuir pressure corresponding to one half of the Langmuir volume. In order to convert the gas content from \textit{scf} / \textit{ft}^3 to \textit{scf} / \textit{ton} the bulk density of shale is needed.

The assumptions under which Langmuir isotherm was developed make its limitation obvious especially when applied to real systems; however, it has been found to provide good approximations to experimental data on microporous materials (Bell and Rakop, 1986; Clarkson et al., 1997; Mavor et al., 1990).

Due to the presence of multiple gas in shale reservoirs, there is competitive adsorption with the gases competing to adhere on the same adsorption site. Carbon dioxide (CO\textsubscript{2}) is found to have the most affinity to adsorption on coal and shales. Predicting accurate gas in place, reserves and rates becomes even more important when there is the presence of multicomponent gas. An extension of the Langmuir model known as Extended Langmuir has been proposed, to accurately predict adsorption in the presence of other gases.
2.2.2 BET Isotherm

Stephen Brunauer, P.H. Emmet and Edward Teller developed in 1938 the BET isotherm, in which they assumed that the adsorption layers on the surface of the organic carbon were infinite. Unlike Langmuir isotherm, which assumed monolayer adsorption, BET isotherm extended Langmuir’s application to include a multilayer adsorption.

With several key assumptions, such as homogeneous surface, no lateral interactions between molecules, and number of layers becoming infinite at saturation pressure, BET isotherm is considered a better fit to describe the adsorption processes in shale gas reservoir. BET isotherm occurs in a non-porous or a macroporous material (Kuila and Prasad, 2013). The general form of the BET isotherm can be given as

$$V(P) = \frac{V_m C}{1-P/P_o} \left[ 1 - \left( \frac{P}{P_o} \right)^n + \frac{n \left( \frac{P}{P_o} \right)^{n+1}}{1 + C - 1 \left( \frac{P}{P_o} \right)} \right]$$

$$V_m = \text{maximum adsorption gas volume when the entire absorbent surface is being covered with a complete monolayer}$$

$$C = \text{constant related to the net heat of adsorption}$$

$$P_o = \text{saturation pressure of the gas}$$

$$n = \text{maximum number of adsorption layers.}$$

When \( n =1 \), the equation will be reduced to the Langmuir isotherm and when \( n = \infty \), the equation reduces to

$$V_L = \frac{V_m CP}{(P_o - P) \left[ 1 + \left( C - 1 \right) \frac{P}{P_o} \right]}$$

The BET isotherm has been described as successful only for a limited range of data and has also been found to be inaccurate when used to make mixture predictions (Danner and Wenzel, 1969; Kaul, 1984).
Yu et al., (2015) investigated the contribution of adsorption on Marcellus shale by analysing several experiments of methane adsorption and found that gas adsorption in Marcellus shale deviated from the Langmuir isotherm but obeyed the BET isotherm. Although the BET matched the experimental data more accurately than the Langmuir model, other adsorption models, since proven to be better fits to shale/coal experimental data sets such as Dubinin-Astakhov (D-A) and the Vacancy Solution Model (VSM), were not tested. Figure 2.2 shows a comparison between Langmuir and BET models for gas adsorption.

![Comparison of Langmuir and BET models for gas adsorption](image)

Figure 2.2: Comparison of Langmuir and BET models for gas adsorption

### 2.2.3 Potential Theory Approach

The Potential theory concept, first introduced by Polanyi in 1914, explains that the surface force field is represented by an equipotential contour above the surface, and that the space between each contour corresponds to a definite adsorbed volume. Thus the cumulative volume of the adsorbed space, $W$, is a function of the chemical potential of the gas, $\varepsilon$. (Yang, 1997) (See figure 2.3). According to this theory, adsorption can be measured through the equilibrium between the chemical potential of a gas near the surface and the chemical potential of the gas from a large distance away. In terms of application, the Polanyi theory can be applied at much higher $P/P_o$ (between 0.1-0.8 MPa) compared with that of BET (between 0.05-0.35 MPa)

$$ W = f(\varepsilon) \tag{2.4} $$
Polanyi referred to this function as the characteristic curve; he assumed that the adsorption potential is independent of temperature. Thus, it is possible to predict the adsorption of gases onto the solids at different temperatures once the characteristic curve has been defined at one temperature. The characteristic curve, therefore, represents the relationship between the adsorption potential and the distance from the solid surface.

The adsorption potential is related to the vapour pressure by

$$\varepsilon = RT \ln \left( \frac{P_e}{P} \right)$$

(2.5)
2.2.4 Dubinin – Radushkevich (D-R) and Astakhov (D-A) Equations

One of the widely used equations for describing experimental data of the adsorption of gases on microporous solids is the D-R equation. This equation was proposed by Dubinin and Radushkevich for solids with homogeneous structure of micropores with later extensions to non-homogeneous microporous structures by Dubinin –Astakhov equations.

The D-R adsorption model is a pore-filling model which does not assume monolayer surface coverage (Sakurovs et al., 2007) (See figure 2.4). Dubinin and Radushkevich’s theory of micropore volume filling was based on the Polanyi concept of a characteristic curve (Gil and Grange, 1996). Dubinin used adsorption of zeolites to prove his theory of volume filling mechanism (Do, 1998). The D-R equation is expressed as

\[ W = W_o \exp \left[ - \left( \frac{RT}{\beta E} \ln \frac{P}{P_o} \right)^2 \right] \] ..........................(2.6)

\( W \) = volume adsorbed volume,

\( W_o \) = micropore volume

\( E \) = energy of adsorption

\( \beta \) = affinity of the sorbent for the gas.

A more general form of the equation is the D-A equation written in the form

\[ W = W_o \exp \left[ - \left( \frac{RT}{\beta E} \ln \frac{P}{P_o} \right)^m \right] \] .................................(2.7)

When \( m \) is equal to 2, the D-A equation reduces to the D-R equation. The additional parameter \( m \) allows for some flexibility of modelling (Clarkson and Haghshenas, 2013; Kapoor et al., 1990), compared with the two-parameter D-R equation.

Dubinin equations can be used to represent adsorption data at different temperatures. The characteristic energy is independent of pressure, and a plot of the fractional loading versus the adsorption potential for different temperatures will collapse into one curve, called the characteristic curve (Do, 1998). Talu and Myers (1988) noted that the D-R equation is not
thermodynamically consistent in Henry's law region (limit of zero loading). When the pressure reduces to zero, the D-R equation is not able to return to Henry’s Law.

Kapoor et al., (1989) modified the D-R equation to include Henry’s law limits that are applicable to pressure ranges from 0 to saturation pressure. The modification of the D-R equation makes it useful for prediction of multicomponent adsorption equilibria.

Figure 2.4: monolayer (top) and pore filling mechanism (bottom) of Langmuir and Dubinin models (Clarkson and Hagshenas, 2013)

The D-R method provides a better fit to adsorption data than the Langmuir method, even though they both have the same number of parameters (Clarkson and Bustin, 2000).

According to Sakurovs et al., (2007), D-R cannot be used to model the adsorption of gases at temperatures or pressures where the gases are supercritical and the saturation pressure is undefined. For instance, methane’s critical temperature is 190.6K and hence in shale gas reservoirs, methane is expected to be in the supercritical state. Methane will therefore not exhibit a saturated vapour pressure under supercritical conditions.

Sakurovs et al., (2007) proposed a general DR equation that replaced the saturation pressure term with an adsorbed density and gas density term in order for the isotherm to be applied to supercritical conditions. The modified isotherm can, therefore, be applied to a much wider
temperature and pressure range. Sakurovs et al., (2007) used experimental data from Australian bituminous coals to fit the modified D-R equation.

2.3 Multicomponent Adsorption Models

Many models have been proposed for modelling the prediction of mixed gas adsorption on coal and shale. These models usually use single component isotherm data to predict multicomponent adsorption. Two of the simplest models used are the Extended Langmuir Model (EL) and the Ideal Adsorbed Solution Theory (IAST). However, EL models are found to be the simplest model in predicting multicomponent adsorption.

Due to the complexities of multi-component adsorption isotherm tests, such as difficulties in measurement and time consumption, predictions are rather made from single component adsorption isotherms, and the adsorption capacities of each component in the mixture are predicted at a temperature and pressure. This process, according to Wang (2016), involves using the single component adsorption model for fitting the experimental data and to obtain model parameters. The parameters are then applied to the prediction models to calculate the multicomponent mixture adsorption equilibrium. Figure 2.5 shows the procedure for obtaining binary prediction from pure component modelling.
Figure 2.5: Illustration showing prediction of binary gas adsorption from pure component isotherms (Modified from Clarkson and Bustin, 2000)
2.3.1 Extended Langmuir Model
An extension to the Langmuir isotherm was developed by Markham and Benton (1931) and called the Extended Langmuir Model. This model has been used widely in the prediction of multicomponent adsorption. Most commercial reservoirs prefer the use of this model, due to its simplicity and ease of use. This model extends the Langmuir model to include a multi-component system, by taking into consideration the partial pressures and molar composition.

One of the main critiques of this model is the issue of thermodynamic inconsistency. A thermodynamically consistent model implies that the sorption limit must be equal for all the components (Clarkson and Haghshenas, 2013). Therefore, the Langmuir sorption constants for the pure components must be equal for thermodynamic consistency (Arri et al., 1992).

The equation below is used to represent the EL model for multi-component systems (Arri et al., 1992)

\[
V_a = \sum_{i=1}^{n} \frac{V_{Li}}{P_{Li}} (P_g y_i) + \sum_{j=1}^{n} \frac{1}{P_{Lij}} (y_j P_g)
\]

\[
V_{Li} = \text{Langmuir volume constant for pure component I, (SCF/Ton)}
\]

\[
P_{Li} = \text{Langmuir pressure constant for pure component I, (psia)}
\]

\[
y_i = \text{Gas phase composition of component I, (fraction)}
\]

\[
P_g = \text{Gas phase pressure, (psia)}
\]

\[
V_i = \text{Adsorbed volume of component I, (SCF/Ton)}
\]

The EL method works well especially in CBM reservoirs when the compositional changes are minimal. The majority of the gas in such reservoirs is methane and there is little effect of compositional changes. However for shale gas reservoirs, due to compositional changes as a result of primary depletion and enhanced recovery phases, the use of EL method will fall short of accurately describing the desorption process. According to Manik et al., (2002), the EL method is a purely empirical formulation that ignores thermodynamic equilibrium between gas components in the free and adsorbed gas phases.
Arri et al., (1992) modified a reservoir simulator to use EL isotherm for describing the equilibrium relationship between the free and sorbed gas. By measuring the sorption of various binary gas compositions at different pressures and fixed temperature on coal samples, they were able to show that the use of EL isotherm provided a reasonable correlation to the data. However Arri et al., (1992) realised that at very high pressures, the EL isotherm loses its accuracy and under-predicted the binary sorption data. The extended Langmuir equation is found to be inadequate overall in predicting adsorption equilibrium, even though it offers simplicity in adsorption calculations (Tien, 1994).

2.3.2 Ideal Adsorbed Solution Theory (IAST)

Ideal adsorbed solution theory can be used to predict binary adsorption equilibrium for various mixtures from pure component adsorption data. This theory was first proposed by Myers and Prausnitz in 1965. For multi-component adsorption prediction, it has quickly established itself as one of the favoured methods. One key assumption under which the IAST was derived is that the adsorbed mixture behaves like an ideal adsorbed solution. This is similar to Raoult's law for a bulk solution.

\[ p y_i = p^o_i (\pi)x_i \] ..........................(2.9)

\( p^o_i \) is the vapour pressure of the pure component I, at the same spreading pressure and same temperature \( T \), as the adsorbed mixture.

\( x_i \) = sorbed phase gas mole fraction

\( \pi \) = spreading pressure, where the spreading pressure is defined as the reduction in the surface tension of the surface as the adsorbate spreads over the surface (Ruthven, 1984). The relationship between \( p^o_i \) and \( \pi_i \) is expressed as

\[ \pi_i = \frac{\pi_i A}{RT} = \int_0^{p^o_i} \frac{n_x(p)}{p} dp \] ..........................(2.10)

\( n_x(p) \) = pure component isotherm

\( A \) = specific surface area of the adsorbent.
The condition below needs to be satisfied for both adsorbed mole fractions and mole fractions of the free gas.

\[ \sum_{j=1}^{N} y_j = 1 \]  \hspace{1cm} (2.11)

\[ \sum_{j=1}^{N} x_j = 1 \]  \hspace{1cm} (2.12)

Total adsorbed gas in the mixture is given as

\[ \frac{1}{n_t} = \frac{\sum_{i=1}^{n} x_i}{\sum_{i=1}^{n} n_i} \]  \hspace{1cm} (2.13)

The amount of each component adsorbed in the mixture is given as

\[ n_i = n_j x_j \]  \hspace{1cm} (2.14)

Any pure component adsorption isotherm could be used in the above equation to evaluate the spreading pressure. Clarkson and Bustin (2000) argued that for IAS fitting to experimental data, a more accurate pure component isotherm should be applied.

The successful calculations of IAS depend on the correct fitting of the single component data in regions of low pressure and at very high pressures where pure hypothetical pressure lies (Do, 1998). Errors in these regions would lead to significant errors in multicomponent calculations.

One key advantage of the use of this theory is the fact that it can allow any type of single component isotherm to be used for the prediction of the multicomponent equilibria, as long as it fits the experimental data over the range of pressures (Richter et al., 1989).

Several researchers (Hall et al., 1994; Stevenson et al., 1991) have found that when compared with the extended Langmuir isotherm, the IAS theory is more accurate for mixed gas adsorption, especially on dry coal.

The model does not require the use of any mixture data and is independent of the actual mode of physical adsorption (O’Brien and Myers, 1985). The theory is based on the
hypothesis that both the free gas and adsorbed gas phase equilibrium is similar to the vapour-liquid equilibrium (Manik et al., 2002).

There are several models which have been proposed for modelling adsorption that can be said to be either thermodynamically consistent or inconsistent. Most of these models have been utilised in coalbed methane reservoirs; more recently, a lot of these models have been applied to shale gas reservoirs.

For ideal and non-ideal gas mixtures, as well as homogeneous and heterogeneous surfaces, IAST method has been found to be the preferred method in studying adsorption equilibria, due to the fact that it is thermodynamically consistent (Ahmadpour et al., 1998; Chen et al., 2011). The equation below describes the thermodynamic equilibrium between adsorbed and free gas phases, using the ideal adsorbed phase assumption (Rajput, 2016). Fugacity may be used to account for non-ideality of the gas phase where the activity coefficient is considered to be greater than one.

\[
P_{g}y_{i}\phi_{i}^{*} = P_{i}^{o}\phi_{i}^{o,x_{i}}^{a} \quad \text{......................................................... (2.15)}
\]

Where

\[P_{g} = \text{gas phase pressure (psia)}\]
\[y_{i} = \text{Gas phase composition of component i (fraction)}\]
\[\phi_{i} = \text{Fugacity coefficient of pure component i in the gas phase, (dimensionless)}\]
\[P_{i}^{o} = \text{Standard state pressure of pure component i in the gas phase (psia)}\]
\[\phi_{i}^{o} = \text{Fugacity coefficient of pure component i in the gas phase at standard condition (dimensionless)}\]
\[x_{i}^{a} = \text{Molar composition of component i in adsorbed phase (fraction)}\]

Chen et al., (2011) studied adsorption equilibria of pure methane and ethane gases and their binary mixtures on activated carbon by comparing their isotherm data, using the sips equation for pure component isotherm and the extended sips equation, as well as IAST, for binary
equilibria. They found out that IAST performed better when predicting data on highly heterogeneous carbon samples.

Successful calculations of the IAS require single component data to be fitted accurately for low pressure and high-pressure regions where the hypothetical pressure lies. According to Do (1998), large errors will occur in multicomponent calculations if these regions are in error.

2.3.3 Vacancy Solution Model
The vacancy solution model by Suwanayuen and Danner (1980) treats the adsorbed phase as a mixture of adsorbed species and their vacancies (Kaul, 1984). That is, it assumes two solutions in the system, made up of the gas phase and the adsorbed phase. The surface is considered to be made up of a vacancy (species \( \nu \)) and adsorbed species (species 1) (Yang, 1997). The vacancy is defined as “vacuum entity occupying a space that can be filled by an adsorbate molecule” (Kaul, 1984). The vacancies are an imaginary entity with the same size as the adsorbate. In order to account for the non-ideality of the system, the activity coefficient obtained from pure component data is used. The VSM has been found to be applicable to all gas adsorption systems (Suwanayuen and Danner, 1980); in view of this, its application could be said to be suitable for shale and coal bed methane systems. There are however limited applications of this model in shale gas systems.

Using Wilson equation to define the activity coefficient, the Wilson – VSM isotherm equation can be obtained for the single component as

\[
P = \left[ \frac{n^v_i}{b_i} \theta \right] \Lambda_{1v} \left[ 1 - (1 - \Lambda_{1v}) \theta \right] \exp \left[ -\frac{\Lambda_{1v} (1 - \Lambda_{1v}) \theta}{1 - (1 - \Lambda_{1v}) \theta} - \frac{(1 - \Lambda_{1v}) \theta}{\Lambda_{1v} + (1 - \Lambda_{1v}) \theta} \right] \quad \text{......... (2.16)}
\]

With the provision of adsorption data, the four parameters \( n^v_i, b_i, \Lambda_{1v}, \Lambda_{1v} \) could be determined through non-linear regression analysis. \( P \) refers to pressure whilst \( \theta \) is the fractional coverage.

The activity coefficient for \( i \) and \( \nu \) is given by the Wilson equation below

\[
\ln \gamma_i = 1 - \ln \left[ \sum_j X_j \Lambda_{ij} \right] - \sum_i \left[ \frac{X_i \Lambda_{ik}}{\sum_j X_j \Lambda_{ij}} \right] \quad \text{........................... (2.17)}
\]
Vacancy solution model can be used for both single component and multicomponent adsorption isotherms.

Using a set of data on activated carbon and zeolites, Suwanayuen and Danner (1980) successfully predicted adsorption phase diagrams for binary mixtures, using the VSM. By ignoring the adsorbate-adsorbate interactions, excellent predictions were obtained for binary adsorption of light hydrocarbons such as methane and ethane.

VSM has proved to be successful when applied to predict multicomponent adsorption isotherms, especially for high surface coverage interactions. This was demonstrated by Kaul (1984) when he reviewed different isotherm models in predicting both single and multicomponent adsorption isotherms. For low coverage multicomponent data prediction, Kaul (1984) found that both IASM and VSM were sufficient; however, the VSM provided accurate predictions of high coverage multicomponent data from both single and binary data using different adsorbate on two different adsorbents involving molecular sieve and activated carbon. Low surface coverage implies that the adsorbate molecules are less likely to interact with each other and hence the adsorbed phase can be treated as ideal, whereas the opposite occurs for high surface coverage.

The vacancy solution theory was criticised by Talu et al., (1988) for its inconsistency in the binary selectivity predictions in Henry’s law limit. Bhatia and Ding (2001) noted that the error in the model by Suwanayuen and Danner (1980) was the result of the incorrect treatment of vacancies in the surface equation. They proposed a thermodynamically consistent approach that is instead based on the mass-action principle.

For multicomponent adsorption calculations, the general form of the VSM is given as

\[ \phi_i y_i P = \gamma_i x_i n_i^{\lambda_i} \frac{n_i^{\lambda_i} \Lambda_i^3}{n_m^{\lambda_i} b_i} \exp(\Lambda_i - 1) \exp\left(\frac{\pi a_i}{RT}\right) \]  \hspace{1cm} (2.18)

The fugacity coefficient is set to unity for gas adsorption at moderate pressures. This equation is normally solved by trial and error to obtain \( y_i \) and \( n_i^{\lambda_i} \).
**Table 2.1: Summary of gas adsorption models used in coal/shale gas reservoirs**

<table>
<thead>
<tr>
<th>MODEL</th>
<th>DESCRIPTION</th>
<th>ADVANTAGES/LIMITATION</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>First developed by Irving Langmuir in 1916. The model postulates that gas</td>
<td>It cannot be applied to the real system due to shale systems having heterogeneous surface however good approximations have been found for microporous materials. It assumes that the Langmuir volume is temperature invariant but this is not the case. At higher pressures, the model fails to apply adequately.</td>
<td>Langmuir 1916.</td>
</tr>
<tr>
<td>Isotherm</td>
<td>behaves as an ideal gas under isothermal conditions. Key assumption being a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>homogeneous surface and no interaction between neighbouring sites. Monolayer</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>coverage is also assumed.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET Model</td>
<td>Developed by Brunaur, Emmet and Teller in 1938. This model assumes that the</td>
<td>Not applicable for multicomponent systems can only be used at a single temperature. It is only suitable for ideal systems.</td>
<td>Brunauer, Emmet and Teller 1938</td>
</tr>
<tr>
<td></td>
<td>adsorption layers on the surface of the organic carbon were infinite. Unlike</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir, multilayer adsorption coverage is assumed. It has proved useful in the</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>determination of surface area of materials.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


### Potential Theory

Introduced by Polanyi in 1914. It assumes gas molecules move according to potentials like that of gravity or electric field.

Uses the concept of the characteristic curve, which is independent of temperature. Adsorption is measured through an equilibrium between the chemical potential of a gas near the surface and that of the gas from a distance away.

Mostly applicable at higher $P/P_0$, unlike Langmuir and BET. $P=\text{pressure, } P_0=\text{vapour pressure}$. The characteristic curve allows for successful prediction of adsorption of gases at different temperatures. Makes an assumption about ideal gas. Used in the design of adsorption systems and for binary gas predictions under different temperatures, thereby saving time and cost of experiments.

Polanyi 1914

<table>
<thead>
<tr>
<th>D-R and D-A Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used for describing experimental data of the adsorption of gases on microporous solids. It is a pore filling model which does not assume monolayer coverage</td>
</tr>
<tr>
<td>It is useful for representing assumption at different temperature. It has also being found to be thermodynamically inconsistent in Henry’s region</td>
</tr>
</tbody>
</table>

Dubinin (1975)

### MULTI-COMPONENT MODELS
<table>
<thead>
<tr>
<th>Model</th>
<th>Description</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Extended Langmuir Model</strong></td>
<td>An extension of the Langmuir model developed by Markham and Benton 1931 for binary gas adsorption. This model considers the partial pressures and molar composition of the adsorbates in its calculation. Purely empirical formulation that ignores thermodynamic equilibrium between the gas components in the free and adsorbed gas phase.</td>
<td>This model has been criticised for not being thermodynamic consistent. For thermodynamic consistency, the sorption limit must be equal for all the components. Most preferred model for use due to its simplicity and ease of use in commercial simulators.</td>
</tr>
<tr>
<td><strong>Ideal Adsorbed Solution</strong></td>
<td>First proposed by Myers and Prausnitz in 1965 for the prediction of binary adsorption equilibrium for various mixtures from pure component adsorption data. Derived from the fact that the adsorbed gas behaves like an ideal adsorbed solution similar to Raoult's law for bulk solutions.</td>
<td>Does not require the use of any mixture data and it is independent of the actual mode of physical adsorption. It can allow any type of single component isotherm to be used for the prediction of multicomponent equilibria. It however assumes an ideal gas system for its formulation. Requires rigorous thermodynamic calculations.</td>
</tr>
<tr>
<td><strong>Vacancy Solution Model</strong></td>
<td>Suwanayuen and Danner developed the vacancy solution model which basically treats the adsorbed phase as a mixture of adsorbed species and their vacancies. The vacancies are an imaginary entity with the same size as the adsorbate. Accounts for non-ideality of the system by introducing an activity coefficient.</td>
<td>Has been criticised by Talu et al 1988 for its inconsistency in the binary selectivity prediction in Henry's law limit. Suitable for predicting both single and multi-component adsorption isotherms. Kaul 1984 found that it was insufficient for low coverage multicomponent predictions. Very successful for multi-component predictions at high surface coverage interactions.</td>
</tr>
</tbody>
</table>

Markham and Benton (1931)

Myers and Prausnitz (1965)

Suwanayuen and Danner (1980)
<table>
<thead>
<tr>
<th><strong>TEMPERATURE DEPENDENT MODELS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exponential Model</strong></td>
</tr>
<tr>
<td><strong>Bi-Langmuir Model</strong></td>
</tr>
<tr>
<td><strong>D-R and D-A Model</strong></td>
</tr>
</tbody>
</table>
2.4 Methodology

2.4.1 Procedure for the Estimation of Parameters
Several nonlinear regression techniques have been used to identify the optimal isotherm for gas adsorption on various adsorbents. These nonlinear regression methods involve minimizing the error distribution between the experimental data and the predicted results (Kumar, 2006). For the selection of optimum isotherm, the use of nonlinear regression has been found to be the best (Ho, 2004). The method of least squares, is a key technique used by many researchers in predicting the optimum isotherm (Kumar, 2006; Kumar et al., 2008) and has also been found to be the most widely used (Kumar, 2007; Kumar and Porkodi, 2006). Some other widely used nonlinear regression methods include hybrid fractional error function (HYBRID), Marquardt’s percent standard deviation (MPSD), sum of the squared (SSE), sum of the absolute errors (SAE) and absolute relative error (ARE) (Foo and Hameed, 2009; Ho, 2004; Kumar, 2006; Kumar et al., 2008; Porter et al., 1999; Wong et al., 2004). In this study Excel solver have been used for non-linear regression with an objective function defined based on the formula of the error function. This approach is highly dependent on the value of the initial guess chosen. To improve the accuracy of the selection of the initial guess, several computations have been done for the same exercise to gain some confidence on the choice of parameters obtained. The second approach has been to compare the result of the parameters obtained for other adsorption models using similar error function and if they are close to each other, to conclude on the accuracy of the final parameters obtained and of the choice of initial guess chosen.

2.4.2 Error Function Analysis
Average Relative Error Function (ARE)
Absolute average deviation (AAD%) or Average relative error (ARE) has been used extensively by various researchers to find the optimum model for a set of adsorption data on coal and shale (Charoensuppanimit et al., 2015; Clarkson, 2003; Clarkson et al., 1997; Clarkson and Haghshenas, 2013; Kapoor et al., 1989). Even though it has been reported to have a tendency to under- or overestimate the experimental data, it minimizes the fractional error distribution across the sample concentration range (Foo and Hameed, 2009; Kapoor and Yang, 1989).
\[ \% AAD = 100 \times \text{ABS} \left( \frac{\sum_{i=1}^{N} \left( \frac{n_{\text{cal}} - n_{\text{exp}}}{n_{\text{exp}}} \right)^2}{N} \right) \]  
\[ \text{…………………………(2.19)} \]

\[ n_{\text{cal}} = \text{calculated adsorbed concentration,} \]
\[ n_{\text{exp}} = \text{experimental adsorption data,} \]
\[ N = \text{number of data points for the isotherm.} \]

**Sum of Squared Error Function (SSE)**

This is probably the most common of all the error functions. It is given as

\[ SSE = \left( \sum_{i=1}^{N} n_{\text{cal}} - n_{\text{exp}} \right)^2 \]  
\[ \text{…………………………(2.20)} \]

**Sum of Absolute Error Function (SAE)**

This is very similar to Sum of Squared Error and is given as

\[ SAE = \sum_{i=1}^{N} \left| n_{\text{cal}} - n_{\text{exp}} \right| \]  
\[ \text{………………………….. (2.21)} \]

**Marquardt’s Percent Standard Deviation (MPSD)**

This is often seen as an ideal error function in most adsorption studies (Foo and Hameed, 2009; Sreńcsek-Nazzal et al., 2015). It can be expressed as

\[ MPSD = 100 \sqrt{\frac{1}{N - r} \sum_{i=1}^{N} \left( n_{\text{cal}} - n_{\text{exp}} \right)^2} \]  
\[ \text{………………… (2.22)} \]

**Hybrid Fractional Error Function (HYBRID)**

At low-pressure values, the HYBRID function improves the overall fitting of the model to the experimental data, compared to some of the other error functions, such as SSE.

\[ HYBRID = \frac{100}{N - r} \sum_{i=1}^{N} \left( \frac{n_{\text{cal}} - n_{\text{exp}}}{n_{\text{exp}}} \right)^2 \]  
\[ \text{………………………… (2.23)} \]
**Sum of Normalised Error (SNE)**

Non-linear regression is mostly preferred to linear regression due to inherent bias resulting from linearization (Ho et al., 2002; Porter et al., 1999). Porter et al., (1999), proposed the use of statistically robust method of sum of normalised error. They argued that due to the different set of isotherm parameters produced by the different error criteria, results can be obtained by finding normalised results for each parameter set for each isotherm model and combining them. The procedure involves obtaining the value of errors for each error function for each set of isotherm constants and dividing by the maximum errors for that error function (Nazzal et al., 2015). Each parameter is obtained by minimising the error functions across the gas pressures, by using Microsoft Excel Solver add-in.

**Sum of Normalised Error Procedure**

The sum of normalised error procedure has been summarised in steps 1 to 10 of Figure 2.6. In Appendix 2, a sample calculation is provided using the steps shown in Figure 2.6.

---

**Figure 2.6 : Procedure for calculating SNE**
2.5 Experimental Data

Obtaining experimental data for shale gas modelling is a challenging task due to the low adsorption capacities and the range of pressure and temperature under which experiments are conducted (Sandoval et al., 2017). Reports of inconsistent results from measurements observed at higher pressures, and the lack of available quality database, have also contributed to challenges in this area. In particular, very limited experimental binary gas adsorption data on shale are available. Due to this scarcity of available data, adsorption capacity on activated carbon is used by many researchers to model the performance of an adsorption model in predicting binary mixtures of gas adsorption capacities on shale. Fitzgerald et al., (2006) argue that experimental uncertainty in the use of activated carbon is lower compared to coal, which has a similar structure to shale. Also, because coal/shale has a more complex structure pore to activated carbon, the adsorption on activated carbon can serve as a reference for more complicated adsorption/desorption on coal/shale (Ren et al., 2017).

Model comparison is essential in the study of their capabilities and limitations when fitting pure component isotherms, as well as for predicting multi-component systems. Adsorption data about Methane, Carbon dioxide and Nitrogen on New Albany shale have been obtained from the literature (Chareonsuppanimit et al., 2012) to model single component gas adsorption. New Albany shale is one of a number of organic-rich shales of the upper Devonian and lower Mississippian age in North America. Its formation consists of brown, black and green shale with minor beds of dolomite and sandstone (Chareonsuppanimit et al., 2012). The formation is also thought to be a major source of oil shale. The adsorption data for New Albany shale have been provided in Appendix 2. The results obtained for the single component modelling is based on these data. For the purpose of showing the performance of the different binary adsorption models, data about activated carbon from Szepesy and Illes (1963) have been used. For temperature dependent models, pure component data about shale obtained at several temperatures in Green River shale (Zhang et al., 2012) have been used to evaluate the different models and their performance. Data relating to the Green River shale have been provided in Appendix 2.
2.6 Results and Discussion

2.6.1 Single component modelling of New Albany Shale

Table 2.2-2.5 the error analysis involving the use of SNE. The values obtained by the use of SNE have been compared to identify parameters of the isotherms that can provide the most accurate match to the measured data on New Albany shale. The bold numbers represent the minimum SNE for each of the isotherms and their associated optimum parameter set for different gas adsorption is shown in Appendix Table 11-16.

The Langmuir isotherm parameters for New Albany shale for Methane, Carbon dioxide and Nitrogen were obtained using non-linear regression technique and shown in Table 11-16 of Appendix 2. Similar values can be easily observed for the different error functions used in that analysis. The SNE values are very similar for the different gas adsorption, with the exception of methane, which showed a much higher SNE for SAE compared with the other error functions. Also, the Langmuir parameter constants \( V_L \) and \( b \) are quite similar in magnitude. Overall, we can see that the Langmuir isotherm provided a good fit to the New Albany datasets. ARE provided the best match parameters for Langmuir isotherm of Methane and CO\(_2\), whilst SSE gave the best match for the case of nitrogen adsorption using Langmuir isotherm. Overall, the Langmuir isotherm is recommended for modelling the experimental data for New Albany shale for methane and CO\(_2\). As can be observed in Figure 2.7, the Langmuir isotherm fits very well with the experimental data, regardless of which error function is chosen. The BET isotherm constants and error analysis using the different error functions are shown in Table 2.3 and in Appendix 2 Table 2.12 for methane, CO\(_2\) and nitrogen adsorption. It can also be observed that the parameters for BET for all the error functions are very similar, with only slight variations. Likewise, the SNE values are very much similar. Comparing the SNE values, it can be concluded that SSE for methane and ARE for CO\(_2\) and nitrogen provided the best BET fit for the experimental data for New Albany shale.

Non-linear modelling of D-A equation with different error functions also showed similar values for the D-A constants (see Appendix 2 Table 2.13). However, for nitrogen adsorption, MPSD showed a much higher value for \( W_o \) compared with the rest of the error functions. Comparing the SNE also shows that ARE is a much better fit for methane gas adsorption using D-A, whereas HYBRID error function showed the closest fit for CO\(_2\) adsorption and nitrogen
adsorption. Observing Figures 2.6 - 2.9 shows that D-A model was however not the best for modelling methane, CO\textsubscript{2} and nitrogen adsorption on New Albany shale.

Appendix 2 Table 2.14 and Table 2.5 presents the VSM parameters and the error analysis using different error functions. Overall, just like previous adsorption models, the model parameters for VSM were very similar to all the error functions used. In terms of the SNE comparison, it is noticeable that SSE showed consistently higher values for methane, CO\textsubscript{2} and nitrogen adsorption on shale, whereas the remaining SNE for the other error functions were generally quite similar. MPSD was the best error function to be used for methane adsorption, whilst SAE was found to be best for CO\textsubscript{2} adsorption. ARE was also found to be most suited for modelling nitrogen adsorption using VSM on New Albany shale.

Of the overall 12 different results for SNE calculations, SSE and Hybrid produced parameter sets showing the minimum sum of normalised error in only 2 of the results. ARE provided 6 minimum SNE out of the total 12, proving to be the most consistent error function to be used in shale gas adsorption modelling. Finally, SAE and MPDS provided only a single result showing minimum SNE for all the results generated. From observation of Tables 2.2 - 2.5 and Figures 2.7 - 2.10, it can also be deduced that Langmuir isotherm provides the best overall fit for the data on all of the gas adsorption involving methane and CO\textsubscript{2}, with the exception of nitrogen adsorption, where D-A proved to be the best fit for the experimental data. Adsorption modelling for CO\textsubscript{2} was difficult to achieve especially at very higher pressures. This implies that, the different adsorption models might struggle to represent accurately CO\textsubscript{2} adsorption in the New Albany shale. Figure 2.8 confirms that BET isotherm cannot be used for modelling CO\textsubscript{2} adsorption on New Albany shale data, even though there was a better match for methane and nitrogen adsorption using BET. Due to the inherent heterogeneity of shale which might be different for different shale reservoirs, data obtained for one shale should not be assumed to be representative for all shale reservoirs. In that respect, the results of this thesis are only applicable to the data obtained about shale from these reservoirs. These data have been provided in Appendix 2. Adsorption models might predict differently with different data.
Table 2.2: SNE for Non-Linear Langmuir Isotherm

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>2.0456</td>
<td>2.0083</td>
<td>5</td>
<td>2.1427</td>
<td>2.2411</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>4.2552</td>
<td>3.6307</td>
<td>4.0848</td>
<td>4.2752</td>
<td>4.2320</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>3.9504</td>
<td>4.0152</td>
<td>4.1666</td>
<td>4.0152</td>
<td>4.2265</td>
</tr>
</tbody>
</table>

Figure 2.7: Experimental data for methane, CO2 and nitrogen for Langmuir isotherm obtained by SSE, ARE, SAE, MPSD and HYBRID
Figure 2.8: Experimental data for methane, CO₂ and nitrogen for BET isotherm obtained by SSE, ARE, SAE, MPSD and HYBRID

Figure 2.9: Experimental data for methane, CO₂ and nitrogen for Dubinin Astakhov obtained by SSE, ARE, SAE, MPSD and HYBRID
Figure 2.10: Experimental data for methane, CO$_2$ and nitrogen for VSM obtained by SSE, ARE, SAE, MPSD and HYBRID
### Table 2.3: SNE for Non-Linear BET

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>SNE</td>
<td>4.668</td>
<td>4.7349</td>
<td>4.7410</td>
<td>4.8365</td>
</tr>
<tr>
<td>CO₂</td>
<td>SNE</td>
<td>4.9481</td>
<td>3.9526</td>
<td>4.8955</td>
<td>4.9129</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>SNE</td>
<td>4.0081</td>
<td>3.9433</td>
<td>4.2248</td>
<td>3.9650</td>
</tr>
</tbody>
</table>

### Table 2.4: SNE for Non-Linear Dubinin-Astakhov isotherm

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>SNE</td>
<td>3.5769</td>
<td>3.5619</td>
<td>4.7807</td>
<td>3.5619</td>
</tr>
<tr>
<td>CO₂</td>
<td>SNE</td>
<td>4.3903</td>
<td>4.5538</td>
<td>4.7416</td>
<td>4.5539</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>SNE</td>
<td>3.4763</td>
<td>3.9055</td>
<td>3.8840</td>
<td>3.9055</td>
</tr>
</tbody>
</table>

### Table 2.5: SNE for Non-Linear Vacancy solution model

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>SNE</td>
<td>4.6122</td>
<td>4.1126</td>
<td>4.4328</td>
<td>4.1071</td>
</tr>
<tr>
<td>CO₂</td>
<td>SNE</td>
<td>4.6145</td>
<td>3.9830</td>
<td>3.6623</td>
<td>3.9830</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>SNE</td>
<td>4.9796</td>
<td>3.98022</td>
<td>3.9921</td>
<td>3.9884</td>
</tr>
</tbody>
</table>
3.2 Multi-Component Modelling of Ethane and Methane Adsorption on Activated Carbon (Szepesy and Illes, 1963)

Adsorption data for methane and ethane on activated carbon at a temperature of 293.15 k have been reported by Szepesy and Illes (1963). Pressures for pure component adsorption data were extended up to 124 KPa. The use of pure adsorption models to represent adsorption data is significant when modelling shale gas reservoir simulation. Very often, Langmuir equation has been used to represent pure adsorption data due to the ease with which it can represent the data, and also because of its use in numerical reservoir simulators. In order to conduct binary gas adsorption modelling, results from pure components are used to obtain adsorption prediction. For this study, VSM and Langmuir's isotherm has been used to conduct the pure component adsorption modelling, and later used in carrying out the binary adsorption prediction. The results from single component modelling using Langmuir and VSM are shown in Tables 2.6 and 2.7.

Table 2.6: SNE for binary mixture of methane and ethane (Langmuir isotherm)

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>4.9668</td>
<td><strong>4.9169</strong></td>
<td>4.9358</td>
<td>4.9358</td>
<td>4.9235</td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>4.2434</td>
<td>4.5727</td>
<td>4.3382</td>
<td>4.5728</td>
<td><strong>4.2024</strong></td>
</tr>
</tbody>
</table>

In both Appendix 2 Table 2.15 and 2.16, the individual Langmuir and VSM parameters are very similar, irrespective of the error function that was used. For methane adsorption, the sum of normalised error was minimum for ARE compared to the rest of the error function when Langmuir isotherm was used as the adsorption model (See Table 2.6). ARE also proved to be the best fit for ethane adsorption when modelling with VSM (See Table 2.7). The HYBRID error function was however found to fit the model better when using Langmuir isotherm, whilst it was found to be a worse fit for methane adsorption using VSM. MPSD was the most appropriate error function to be used in methane adsorption when using VSM. The results from Tables 2.6 and 2.7 also indicate that VSM would be the preferred adsorption model to be used in modelling single component adsorption for this data set.
### Table 2.7: SNE for binary mixture of methane and ethane (Vacancy solution model)

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>1.7534</td>
<td>1.6184</td>
<td>1.6436</td>
<td>1.6092</td>
<td>5</td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SNE</td>
<td>4.0883</td>
<td>3.4805</td>
<td>3.5592</td>
<td>3.6697</td>
<td>3.6697</td>
</tr>
</tbody>
</table>

Binary gas adsorption modelling can now be undertaken once pure component adsorption model fitting has been completed. Throughout this study, EL, IAS and the VSM have been used. The different multi-component adsorption models have already been discussed in the previous section. Figures 2.10 and 2.11 show the predictions of the binary gas-phase diagrams for each of the models at a pressure of 101 Kpa. The phase diagrams shown in Figures 2.10 and 2.11 show the plots of mole fraction of both ethane and methane in the adsorbed phase versus mole fractions in the free gas phase (non-sorbed), while Figure 2.12 is the plot of mole fraction of methane in sorbed phase versus the total gas adsorption. The predictions show that each of the multi-component adsorption models was able to fit closely to the experimental binary adsorption data. The Extended Langmuir showed the worst fit compared with both the Ideal adsorbed solution and the Vacancy solution model. The Vacancy solution model was, however, able to fit more accurately for predicted equilibrium compositions in Figures 2.10 - 2.12. EL predicted more ethane in the sorbed phase in Figure 2.10 and more methane in the free gas phase, as shown in Figure 2.11 more than what the experimental data showed.
Figure 2.10: Predicted equilibrium composition diagram showing free gas phase versus the sorbed phase for Ethane

Figure 2.11: Predicted equilibrium composition diagram showing free gas phase versus the sorbed phase for methane
For model calculations of EL and IAS, the free gas phase compositions have been inputted and the adsorbed phase mole fraction predicted. However, for VSM, the adsorbed mole fraction was inputted and the free mole gas phase was calculated. To be able to express the relative adsorption of components within an adsorption system, separation factor calculations are useful (Hartman et al., 2011). Separation factor calculations also help to understand gas storage mechanism especially in cases of carbon capture and sequestration. Most often, the higher the separation factor, the stronger the relative adsorption compared with other components (Ruthven, 1984). In a binary system of carbon dioxide and methane, carbon dioxide is expected to exhibit a much higher separation factors indicating an affinity to the shale than methane.

One other use of separation factor calculations is to help decide on which gas component to be used in enhanced gas recovery method. Competitive adsorption means gas with a smaller relative adsorption to the shale will be released, whereas those with a stronger relative

Figure 2.12: Total volume of mixtures adsorbed at pressures of 101 Kpa for Case 1
adsorption will be adsorbed. Since methane has a much smaller relative adsorption compared with other heavier gas components, enhanced gas recovery method such as injecting heavier components into shale gas reservoirs could help to produce more of the adsorbed methane. In this study, all the models predict a higher selectivity ratio or separation factor for ethane than for methane (see Figure 2.14). According to Ruthven (1989), the separation factor measures the affinity of the adsorbent for component $i$ relative to the component $j$. This can be expressed as

$$\alpha_{ij} = \frac{y_i}{y_j}$$

![Figure 2.14: Separation factor calculations for mixtures for case 1 corresponding to a 0.519-mole fraction of ethane.](image)

The separation factor for the Extended Langmuir (EL) shows a constant value compared to the other models that show variable separation factors. This is because, for the EL model, the separation factor is not a function of pressure or composition (Ruthven, 1984). Figure 2.14
shows the separation factor calculations for a mixture corresponding to 0.519 mole fraction of ethane.

**2.7 Summary**

This chapter has critically reviewed the different adsorption models used in the prediction of methane adsorption in shale gas reservoirs by grouping them under single and multi-component adsorption models. It has further investigated the application of adsorption models on shale gas reservoirs using a statistically robust method. Comparison was made between different categories of adsorption models, allowing for the choice of adsorption model to be selected based on evaluating different error functions, such as SSE, SAE, ARE, MPSD and HYBRID.

By adopting a more statistically robust approach using the sum of normalised errors to minimise the error distributions for each adsorption model adopted, an optimised adsorption model was selected and used in the modelling of gas adsorption in shale gas reservoirs.

Based on the results from the analysis, ARE proved to be the most accurate in terms of predicting the minimum sum of normalised error, and would therefore provide the best fit to the experimental data. In all, 6 of the results provided minimum SNE for ARE calculations, whereas 2 of the results showed minimum SNE for both SSE and Hybrid. Overall, the Langmuir model gave the most accurate predictions for single component modelling, compared with other models. In Binary mixture studies, VSM proved to give accurate results and fitted the data more appropriately compared with IAS and EL models. ARE proved to be the best fit for ethane adsorption when modelling with VSM. The HYBRID error function was however found to fit the model better when using Langmuir isotherm, whilst it was found to be a worse fit for methane adsorption using VSM.
**Nomenclature**

\[ V = \text{the volume of adsorbed gas} \]

\[ P = \text{Gas pressure} \]

\[ V_L = \text{Langmuir volume or maximum gas adsorption at infinite pressure} \]

\[ P_L = \text{Langmuir pressure corresponding to one half of the Langmuir volume} \]

\[ V_m = \text{maximum adsorption gas volume} \]

\[ C = \text{constant related to the net heat of adsorption} \]

\[ P_o = \text{the saturation pressure of the gas} \]

\[ n = \text{maximum number of adsorption layers} \]

\[ W = \text{volume adsorbed volume} \]

\[ W_o = \text{micro pore volume} \]

\[ E = \text{energy of adsorption} \]

\[ \beta = \text{affinity of the sorbent for the gas} \]

\[ V_{Li} = \text{Langmuir volume constant for pure component I, (SCF/ton)} \]

\[ P_{Li} = \text{Langmuir pressure constant for pure component i , (psia)} \]

\[ y_i = \text{Gas phase composition of component I, (fraction)} \]

\[ P_g = \text{Gas phase pressure, (psia)} \]

\[ V_i = \text{Adsorbed volume of component I, (SCF/ton)} \]

\[ p_i^o = \text{vapour pressure of the pure component} \]

\[ x_i = \text{sorbed phase gas mole fraction} \]

\[ \pi = \text{spreading pressure} \]

\[ n_A(p) = \text{pure component isotherm} \]

\[ \Lambda = \text{specific surface area of the adsorbent}. \]
\( P_g \) = gas phase pressure (psia)

\( y_i \) = Gas phase composition of component i (fraction)

\( \phi_i \) = Fugacity coefficient of pure component i in gas phase, (dimensionless)

\( P_i^o \) = Standard state pressure of pure component i in gas phase (psia)

\( \phi_i^o \) = Fugacity coefficient of pure component i in gas phase at standard condition (dimensionless)

\( x_i^a \) = Molar composition of component i in adsorbed phase (fraction)

\( n_{\text{cal}} \) = calculated adsorbed concentration,

\( n_{\text{exp}} \) = experimental adsorption data

\( N \) = number of data points for the isotherm.

\( r \) = number of parameters in adsorption model

\( i, j \) = gas components

\( n_i^\infty \) = maximum number of moles of i in surface phase

\( \theta \) = fractional coverage

\( \Lambda_{1v}, \Lambda_{1r} \) = Wilsons parameters for interaction between vacancy and adsorbate

\( b_i \) = Henry’s law constant for component one

\( \phi_i \) =fugacity coefficient of l in bulk gas mixture

\( \gamma_{i}^{l} \) = activity coefficient of l in adsorbed phase vacancy solution

\( n_{in}^l \) =total number of moles of mixture in phase

\( n_i^{l,\infty} \) =maximum number of i in surface phase

\( n_{m}^{l,\infty} \) = maximum number of moles of l in surface phase
\( a_i \) = partial molar surface area of \( i \)

\( T \) = temperature of adsorption system

\( R \) = Universal gas constant

\( r \) = Number of isotherm parameters, dimensionless
Chapter 3
Temperature-Dependent Gas Adsorption Modelling in Shale Gas Reservoirs

3.1 Introduction
There are different factors controlling the adsorption capacity of methane on shale. These include, but are not limited to, total organic carbon, pressure, temperature, thermal maturity, moisture and shale clay minerals (Guo et al., 2013). Total Organic Carbon (TOC) is seen as a primary factor that contributes to the adsorption capacity of shale. TOC refers mainly to the amount of organic carbon present in shale and is a key indicator of the ability of shale to generate hydrocarbons. Previous experimental studies have reported high TOC of shale, resulting in a higher capacity for the adsorbed gas (Chalmers and Bustin, 2008; Lu et al., 1995; Ross and Bustin, 2007; Ross and Bustin, 2009; Zhang et al., 2012).

The adsorption capacity of shale can also be affected by pressure. Higher reservoir pressure corresponds to a higher adsorption capacity. Raut et al., (2007) point out that with low pressure, higher binding energy is required for gas adsorption, and hence the adsorbed content decreases compared with when the pressure is very high. In terms of production from shale gas reservoirs, the low matrix permeability of shale reservoirs implies that considerable time will be needed for the average pressure to drop to a level where gas desorption becomes significant, by which time the economic shut in limits of the well must have been reached (Cipolla et al., 2010). Therefore, dependence on pressure depletion alone for ultimate recovery of gas adsorbed on the shale matrix will contribute less towards overall gas production in the well.

One other decisive factor contributing to the adsorption capacity is temperature. The process of shale gas adsorption results in an exothermic reaction. Thereby, shale gas adsorption capacity is expected to decrease with increasing temperature. The temperature dependence of adsorption capacity is greatly controlled by the isosteric heat, which also depends on the surface coverage. Many experimental studies have been conducted on the influence of temperature on adsorbed shale gas content (Charoensuppanimit et al., 2015; S. Chen et al.,
Guo et al., (2013) reported that adsorbed gas content increased with increasing pressure under isothermal conditions, whereas the gas content decreased under isobaric conditions for increases in temperature. Guo et al., (2013) obtained adsorption isotherms at different temperatures and also at different pressure points for shale samples of the Ordos Basin, China. Their studies also noted that, for low pressure and temperature zones, pressure had a much greater effect on the adsorbed gas content. For high pressure and temperature zones, however, the effect of temperature on the adsorbed gas content was dominant.

The amount of gas in a shale gas reservoir is affected by the existence of geothermal gradients. There are temperature differentials at different depths in the reservoir, and due to the effect of temperature on the gas adsorbed, the gas in place will differ at each depth. Temperatures are usually at near critical or supercritical regions of the adsorbed gas, hence adsorption models should be able to provide reliable predictions of the temperature dependence of adsorption in these regions (Charoensuppanimit et al., 2015).

### 3.2 Temperature-dependent Langmuir volume or Saturation loading

Since gas adsorption is an exothermic reaction, the heat produced is normally dissipated towards the immediate surroundings. The ratio of the change that occurs in the adsorbate’s enthalpy to the change in the adsorbed amount is normally referred to as the heat of adsorption. The adsorption equilibrium constant, $b(T)$ normally represented by the Van’t Hoff expression, is temperature-dependent (Zhu et al., 2006):

$$ b = b_0 \exp \left( - \frac{\Delta H_{\text{ads}}}{RT} \right) \quad \ldots \ldots \quad (3.1) $$

$\Delta H_{\text{ads}} = \text{adsorption enthalpy change for a component.}$

Langmuir isotherm remains one of the most commonly used adsorption models in coal/shale gas simulation, with most commercial simulators, such as CMG and Schlumberger Eclipse, implementing gas adsorption modelling using Langmuir isotherm.

The expression for the adsorption on the microporous adsorbent is given as

$$ V = V_L \frac{bp}{1 + bp} \quad \ldots \ldots \quad (3.2) $$

where $V_L$ refers to the theoretical maximum Langmuir volume.
This equation can be written in terms of saturation loading as the temperature-independent form used in this study:

\[
\text{Langmuir 3: } V = q_{so} \frac{b_p}{1 + b_p} \quad (3.2a)
\]

where \( q_{so} \) is the saturation loading similar to the Langmuir volume.

While the adsorption equilibrium constant \( b \) is temperature-dependent, as can be seen in equation (3.1), the Langmuir volume or saturation loading for the Langmuir isotherm is considered constant and does not change with temperature. This assumption has been made by several researchers. Zhu et al., (2006) in their studies of zeolites stated that “saturation loading should be constant and independent of operating temperature”. Do (1998) conducted studies with the temperature-dependent form of the Sips isotherm. The results from the fitting of the Sips isotherm to several temperatures showed that the saturation loading at different temperatures was the same as the reference temperature, indicating the temperature independence of the saturation loading. Furthermore, a new adsorption model was proposed by Do and Do (1997) for heterogeneous solids and tested with isotherm data for various adsorbates on activated carbon and zeolites. They concluded that the thermal expansion parameter for the saturation capacity is very small, implying that the saturation loading is independent of temperature.

Other researchers, however, have strongly supported the idea of temperature dependence of the saturation loading (Koresh, 1982). According to Malek and Farooq (1996), the temperature dependence of saturation loading accounts for the thermal expansion of the adsorbed phase, leading to decreasing monolayer coverage at very high temperatures.

Various temperature-dependent equations have been proposed for saturation loading, but the exact functional form and the thermodynamic consistency of the parameters have not been completely validated (Helminen et al., 2000a). Hwang et al., (1997) proposed the dependence of the saturation loading on temperature as

\[
q_s = a_1 + a_2 \frac{1}{T} \quad \ldots \ldots \ldots \ldots \ldots (3.3)
\]

An empirical equation to describe the temperature-dependent saturation loading was given (Cochran and Danner, 1985; Malek and Farooq, 1996) as

\[
q_s = q_{so} \exp\left(-\frac{q_1}{T}\right) \quad \ldots \ldots \ldots \ldots (3.4)
\]
with \( q_1 = 0 \) if the saturation loading is not temperature-dependent.

\( q_{so} \) is temperature-independent constant.

There have been other works on petroleum applications, including methane adsorption on coal and shale. Ji et al., (2014) conducted experiments on shale samples from the southeastern Ordos Basin in China to ascertain the effects of TOC, maturity, clay mineral and thermodynamic conditions, such as pressure and temperature, on the methane sorption capacity. A positive correlation was found to exist between the sorption capacity of the samples and the TOC, whereas the clay mineralogy content of the samples had minimal effect on their adsorption capacity. Ji et al., (2014) developed a computational algorithm that allowed for the calculation of methane sorption capacity as a function of TOC, temperature and pressure. They found that with an increase in temperature, the Langmuir pressure increases exponentially, while the Langmuir volume undergoes a linear decrease. Ye et al., (2016) also proposed an exponential relation to describe the temperature dependence of the Langmuir volume, based on analyzing experimental data for gas adsorption capacity on different shales. The dependence of temperature of the Langmuir volume has been attributed to the isosteric heat of adsorption by several researchers (Ji et al., 2014; Lu et al., 1995; Rexer et al., 2013; Ye et al., 2016; Zhang et al., 2012).

The effects of temperature on the adsorption capacity of shale have also being explored by Guo et al., (2013). According to them, shale adsorption capacity decreases with increase in temperature. They showed that the desorption curve showed hysteresis for a particular set of adsorption data, and that this was due to thermodynamic reasons, such as the isosteric heat capacity of the adsorption process being greater than that of the desorption process. The adsorption isotherm curve is described by the Langmuir equation, whereas the desorption isotherm is described by an equation proposed by Ma et al., (2014):

\[
V = \frac{V_{1,bp}}{1 + bp} + C_1 \tag{3.5}
\]

Where \( C_1 \) is described as the residual adsorption capacity.

According to Guo et al., (2013), isosteric heat and isothermal adsorption capacity show a good linear relationship, given as
\[ q_{st} = a \cdot n + b \] .................................(3.6)

By determining the isosteric heat from the Clausius-Clapeyron equation, adsorption isotherms can be predicted from different temperatures. The Clausius-Clapeyron equation is given as

\[ \frac{1}{p} \frac{dp}{dT} = \frac{q_{st}}{RT^2} \] .................................(3.7)

Integrating and rearranging will result in

\[ \ln p = -\frac{q_{st}}{RT} + c_3 \] .................................(3.8)

Where \( c_3 = c_2 + \ln p_o \)

They proposed the formula below to be used for predicting adsorption isotherm at different temperatures

\[ p_2 = \exp \left( \ln p_1 + \frac{a \cdot n + b}{RT_1} - \frac{a \cdot n + b}{RT_2} \right) \] .................................(3.9)

\( a, b \) are obtained from the linear relation between the isosteric heat capacity and adsorption capacity, \( n \). \( p_2 \) refers to the pressure under the condition of \( T_2 \).

This model therefore allows the calculation of adsorption capacity using the isosteric heat curve and adsorption /desorption model at a single temperature. Guo et al., (2013) argue that since the production of shale gas is due to desorption, including desorption models into production forecast and numerical simulation will ensure accurate estimations.

\subsection*{3.3 Temperature-dependent Langmuir Models}

Equation (3.1), (3.3) and (3.4) can be applied to the classical Langmuir isotherm to obtain several temperature-dependent Langmuir Models. These equations can be expressed as follows

\[ \text{Langmuir 1: } V = \left( a_1 + \frac{a_2}{T} \right) \left( \frac{bp}{1+bp} \right) \] .......(3.10)

\[ \text{Langmuir 2: } V = q_{so} \exp \left( \frac{-q_1}{T} \right) \left( \frac{bp}{1+bp} \right) \] .........(3.11)
Where \( b = b_0 \exp \left( -\frac{\Delta H_{\text{ads}}}{RT} \right) \).

Due to the heterogeneity of most adsorbent’s, the assumption of a homogenous surface by Langmuir isotherm does not apply. Shale is considered to be an extremely heterogeneous adsorbent (Chen et al., 2017). In this case, the use of an adsorption model such as Freundlich equation combined with Langmuir equation can be applied, by which the adsorbent’s heterogeneity can be successfully represented (Helminen et al., 2000). However, very few works have been found concerning the application of combined Langmuir and Freundlich equation in modelling shale gas adsorption data. An expression for the Langmuir–Freundlich equation is given (Helminen et al., 2000) as

\[
\text{Langmuir Freundlich 3: } q = \frac{q_{bp}^n}{1 + bp^n} \quad \text{......... (3.12)}
\]

The parameter \( n \) represents the surface heterogeneity and has been added to the Langmuir equation without any proper physical meaning (Do, 1998; Helminen et al., 2000a; Ruthven, 1984). Higher values of \( n \) (greater than one) represent a highly heterogeneous adsorbent.

By combining the temperature-dependent saturation equations (3.3) and (3.4) with equation (3.12), the following temperature-dependent Langmuir–Freundlich equations can be proposed, involving the temperature-dependent parameter \( b \).

\[
\text{Langmuir Freundlich 1: } V = \left[ a_1 + \frac{a_2}{T} \right] \left( \frac{bp^n}{1 + bp^n} \right) \quad \text{......... (3.13)}
\]

\[
\text{Langmuir Freundlich 2: } V = q_{w} \exp \left( -\frac{q_{w}}{T} \right) \left( \frac{bp^n}{1 + bp^n} \right) \quad \text{......... (3.14)}
\]

### 3.4 Modified Vacancy Solution

Clarkson (2003) discusses the suitability of the Dubinin equations to microporous solids and points out that for Dubinin-Polanyi theory, part of its additional suitability to coal is its prediction of the temperature dependence of adsorption. Thus, by developing a new model that combines the vacancy solution theory and Dubinin-Polanyi theories, multicomponent adsorption predictions could be made, and also predictions of adsorption capacity at different temperatures. Clarkson (2003) uses the Dubinin–Astakhov (D-A) equation to generate activity coefficients as a function of the degree of pore filling for the pure component gas. For multicomponent gas adsorption at different temperatures, this new model of adsorption
offers the ability to predict multicomponent adsorption data from pure component data collected at a single temperature. The plot of $\theta$ vs $A$ or characteristics curve is temperature invariant, which implies that once $E$ and $n$ are derived at a single temperature, different temperatures could be easily derived. Thus once $D$ is obtained from regression of the single isotherm data, and an activity coefficient as a function of the degree of pore filling is obtained, $D$ can be recalculated for both component gases at the new temperature, assuming $E$ is temperature invariant.

$$D = \frac{E_o \beta}{RT} \quad \text{........................................ (3.15)}$$

$$E = E_o \beta \quad \text{........................................ (3.16)}$$

$$A = RT \ln \left( \frac{P_o}{P} \right) \quad \text{........................................ (3.17)}$$

$E_o$ is the characteristic energy of adsorption for standard vapour, $J/mol$

$\beta$ is similarity coefficient which is dimensionless.

$A$ is specific surface area of adsorbent

$n$ is constant in Dubinin-Astakhov equation.

$\theta$ is saturation loading, dimensionless.

Clarkson (2003) applied this new model to only one experimental binary gas adsorption data set. Applications of this model to other, varied data sets would help to ascertain the robustness of this new adsorption model.

### 3.5 Simplified Local Density (SLD)

The simplified local density model has been successfully applied in many studies and in particular extended to application in shales by Chareonsuppanimit et al., (2012). They argue that this method offers distinct advantages in providing predictions for a spectrum of adsorption phenomena, from adsorption to permeability, on coal and shale. For instance, Pan and Connell (2007) integrated the swelling model to account for adsorption-induced swelling of coals. These advantages, according to Chareonsuppanimit et al., (2012), are crucial for
more realistic reservoir simulations. Charoensuppanimit et al., (2015) improved the temperature dependency of the SLD model by incorporating a new temperature dependency for the adsorbed phase volume that was based on the volume–expansivity approach proposed by Do (1998). By comparing results from the new temperature dependency model to those of the original SLD, significant improvement could be observed over a larger range of temperature. The modified SLD model is therefore suitable for modelling supercritical and near critical gas adsorption. The adsorbed phase volume was related to temperature by the expression

\[ \int_{V_{v_{ads},T}}^{V_{v_{ads}}} \frac{dV}{V} = -\int_{T_n}^{T} \delta dT \]  

(3.18)

\[ V_{ads} = V_{v_{ads},T} \exp(-\delta(T - T_0)) \]  

(3.19)

Where \( V_{ads} \) is the adsorbed phase volume, \( V_{v_{ads},T} \) is the adsorbed phase volume at reference temperature \( T_0 \) and \( \delta \) is the thermal expansion coefficient.

For reservoir simulation, adsorbed phase densities are commonly required, and Charoensuppanimit et al., (2015) showed that the prediction of the adsorbed phase densities by the new model was much closer to that of methane and nitrogen, compared to other models that predicted the densities.

### 3.6 Bi-Langmuir Model

Lu et al., (1995) claimed that Langmuir isotherm is insufficient in describing the adsorption in Devonian shale gas reservoirs. They noted that temperature dependence is very often ignored but plays an important role, especially during thermal stimulation as a recovery method. In fact, both pressure and temperature are major factors in determining the amount of adsorbed gas on the shale. Investigating adsorption as a function of pressure and temperature showed that the effects of temperature are significant (Lu et al., 1995). They reported a general reduction in the adsorption capacity of shale at increased temperatures. Bi-Langmuir model was used to reconcile the data obtained from samples that were used in the experiment. Although Langmuir model might be suitable to represent gas/shale isotherms measured at a single temperature, Bi-Langmuir model was thought to be more suitable for representation of multiple temperatures. Lu et al., (1995) argue that the assumption of
homogeneous adsorbent in the Langmuir model may not be suitable for a gas/shale system, due to the fact that different materials, such as clay minerals and kerogen, may contribute to gas desorption.

Bi – Langmuir model, written in the following form, is used to describe gas adsorption on an adsorbent having two discrete, sharp peaks of adsorption energy distribution. One term of the equation describes the gas adsorption on clay minerals, whilst the other term accounts for gas adsorption on kerogen.

\[
\frac{N_{\text{ads}}}{N_m} = f_1 \frac{k_1(T) p}{1 + k_1(T) p} + (1 - f_1) \frac{k_2(T) p}{1 + k_2(T) p} \quad \text{…………….} \quad (3.20)
\]

\[
k(T) = k_0 T^{-1/2} \exp\left(-E / RT\right) \quad \text{……………………………}(3.21)
\]

Where,

- \( f_1 \) = fraction of adsorption site
- \( k_{1,2} \) = adsorption equilibrium constant
- \( N_{\text{ads}} \) = amount of adsorbed gas per unit volume adsorbent
- \( N_m \) = Amount of adsorbed gas at monolayer coverage
- \( E_1 \) = Adsorption energy

### 3.7 Exponential Model

Ye et al., (2016) conducted similar studies on the temperature dependence of gas adsorption. Their studies proposed a new, improved Langmuir model that was used in evaluating gas adsorption capacity of shale under various pressures and temperatures. Gas adsorption is considered as an exothermic process and hence increasing temperature will restrain the gas adsorption process, thus causing a general reduction in the amount adsorbed as temperature increases (Lu et al., 1995; Ye et al., 2016).

The constant Langmuir volume \( V_L \) was modified to be a function of temperature and thereby an exponential model was proposed that relates \( V_L \) to temperature as

\[
V_L = V_e \exp\left(-D_e T\right) \quad \text{……………..} \quad (3.22)
\]

The final exponential model derived, expressing a temperature-dependent Langmuir model, can be defined as
\[ V = \frac{V_s \exp(-D_r T)}{p + \sqrt{T} / \left[ A \exp\left(\frac{B}{T}\right)\right]} \]  \hspace{1cm} (3.23)

\( V_s \) = theoretical maximum adsorption capacity

\( D_r \) = Reduction coefficient related to temperature increase

The coefficients \( V_s, D_r, A, B \) in equation (3.23) can be determined by fitting the experimental adsorption data.

An exponential relationship between temperature and Langmuir volume can be observed from Figure 3.1, where at increasing temperature, the Langmuir volume decreases exponentially.

**Figure 3.1: The Langmuir volume constant vs Temperature for typical shale samples (Ye et al., 2016)**

Ye et al., (2016) analysed published gas sorption data on shales from the USA, China, and Canada and concluded that an improved Langmuir model that incorporates the effect of temperature is able to describe shale gas sorption capacity under the effect of temperature and pressure. Ji et al., (2012) compared the Exponential model with the linear model and the classical Langmuir model. The comparison was based on the use of average relative error. Their results showed the exponential model as the most efficient model with the least error when predicting gas adsorption at different temperatures.

Table 3.1 and Table 3.2 summarises the overall temperature dependent models derived in this chapter. Modified Vacancy Solution (MVS) and SLD have not been included in the Tables.
because it was not considered further in the analysis section of this thesis. It was felt that these two models required computationally complex solutions that would have made their subsequent inclusion in numerical studies difficult.

**Table 3.1: Langmuir and Langmuir Freundlich Isotherm**

<table>
<thead>
<tr>
<th>Model Name</th>
<th>Model Equations</th>
<th>Equation No.</th>
<th>Fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir 3</td>
<td>( V = \left( \frac{q_{so} bp}{1 + bp} \right) )</td>
<td>2a</td>
<td>( q_{so}, \Delta H_{ads}, b_0 )</td>
</tr>
<tr>
<td>Langmuir Freundlich 3</td>
<td>( V = \left( \frac{q_{so} bp^n}{1 + bp^n} \right) )</td>
<td>7</td>
<td>( q_{so}, n, \Delta H, b_0 )</td>
</tr>
</tbody>
</table>

**Table 3.2: Variations of temperature-dependent Langmuir equations**

<table>
<thead>
<tr>
<th>Model Name</th>
<th>Model Equations</th>
<th>Equation No.</th>
<th>Fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir 1</td>
<td>( b = b_0 \exp \left( -\frac{\Delta H}{RT} \right) )</td>
<td>5</td>
<td>( a_1, a_2, \Delta H_{ads}, b_0 )</td>
</tr>
<tr>
<td>Langmuir 2</td>
<td>( V = q_{so} \exp \left( -\frac{q_1}{T} \right) \left( \frac{bp}{1 + bp} \right) )</td>
<td>6</td>
<td>( q_{so}, q_1, \Delta H, b_0 )</td>
</tr>
<tr>
<td>Langmuir Freundlich 1</td>
<td>( V = \left( a_1 + \frac{a_2}{T} \right) \left( \frac{bp^n}{1 + bp^n} \right) )</td>
<td>8</td>
<td>( a_1, a_2, n, \Delta H_{ads}, b_0 )</td>
</tr>
<tr>
<td>Langmuir Freundlich 2</td>
<td>( V = q_{so} \exp \left( -\frac{q_1}{T} \right) \left( \frac{bp^n}{1 + bp^n} \right) )</td>
<td>9</td>
<td>( q_{so}, q_1, n, \Delta H_{ads}, b_0 )</td>
</tr>
</tbody>
</table>

Other Temperature dependent Models
Selecting a model that is capable of predicting most accurately the adsorption data at different temperatures becomes essential when isotherm estimations are needed at temperatures for which no adsorption data exist. If validated, based on the measurements made in laboratory conditions for certain temperatures, such a model can be used to predict gas adsorption behavior at any other reservoir temperature.

The use of temperature-dependent Langmuir volume/saturation loading when describing gas adsorption avoids the repeated matching of Langmuir constants for each isotherm (Ye et al., 2016). This can lead to more accurate representation of gas adsorption in the reservoir, and also makes it easier to be applied in reservoir simulation where temperature effects are considered.

Furthermore, evaluating gas adsorption as a function of both pressure and temperature using different temperature-dependent adsorption models will allow for the possibility of employing thermal stimulation techniques to enhance the recovery of gas from shale reservoirs.

Incorporating temperature-dependent adsorption model has already been explored by several authors (Lin et al., 2015; Wang, 2016). Wang (2016) included Bi-Langmuir model into an unconventional simulator for thermal stimulation purposes. Their work showed that by using a temperature-dependent adsorption model, the potential to increase gas recovery rose significantly through thermal stimulation. This was achieved by altering the shale gas adsorption/desorption behavior through the elevation of formation temperature.
3.8 Materials and Methods

3.8.1 Shale Gas Data
Experimental data of samples obtained from different shale gas reservoirs have been compiled and adsorption isotherms have been obtained for 11 different samples at different temperatures, ranging from 25°C to 90°C. Four main reference sources have been used to collect the data used in this thesis (Guo, 2013; Ji et al., 2014; Lu et al., 1995; Zhang et al., 2012). Lu et al., (1995) obtained samples from the Devonian shale with reported mineral compositions consisting mainly of clay minerals and organic materials, principally kerogen, with compositions ranging from 0 to 15%, depending on the sample (Luffel et al., 1996). Two shale samples from the Gas Research Institute and one illite sample were used in their adsorption measurements, at four different temperatures, of 25°C, 37.7°C, 50°C and 60°C. Zhang et al., (2012) collected 2 different sets of samples of organic rich shales. These included the Green River Formation (Eocene, Utah) and Woodford shale (Upper Devonian) for the first set of samples, with the second set collected from the Barnett shale cores. Methane sorption capacity for these different samples were obtained at three different temperatures, of 35.4°C, 50.4°C and 65.4°C. Samples from the Ordos Basin in China were collected and used to obtain methane adsorption measurements at different temperatures, of 30°C, 40°C, 50°C, 60°C and 90°C (Guo, 2013; Ji et al., 2014).

A similar method to that used in Chapter 2 section 2.4 has been adopted for identifying the optimal model for gas adsorption, using the temperature-dependent form of Langmuir isotherm. From the results in chapter 2, it was identified that Absolute Relative Error (ARE) or Absolute Average Deviation (AAD%) provided the most consistent best fit for the experimental data. Hence this error function has been used in evaluating the temperature dependent models. It can also be recognised that several researchers (Guo, 2013; Ji et al., 2014, Lu et al., 1995; Zhang et al., 2012) have opted for the use of AAD% over other error functions consistently over time. AAD% was found to be most accurate for majority of the data used in this thesis, thus the rest of the research have been conducted using AAD% to optimise the different adsorption models.

The percentage average relative error has been defined as
\[
% AAD = 100 \times \text{ABS} \left( \frac{\sum_{i=1}^{N} \left( \frac{n_i^{\text{cal}} - n_i^{\text{exp}}}{n_i^{\text{exp}}} \right)}{N} \right) 
\]

Where,

- \( n_i^{\text{cal}} \) is the calculated adsorbed concentration,
- \( n_i^{\text{exp}} \) is the experimental adsorption data,
- \( N \) is the number of data points for the isotherm.

### 3.9 Results and Discussion

Tables 3.3 and 3.4 display the results for the regression carried out on all 11 shale samples used in the study. The results from the regression has been analysed using the Absolute Average Deviation (AAD %) error approach to determine which models gives the least error. The model with the least absolute average deviation error can be said to be the best model for representing the adsorption capability of the sample. Six different models based on the temperature-dependent Langmuir volume, and three models of temperature-independent Langmuir volume, have been compared (see Table 3.3 and 3.4).

In Table 3.3, absolute average deviations have been obtained for models with temperature-dependent Langmuir volume. By comparing these models, it can be ascertained that the Langmuir–Freundlich 2 and the Exponential model were able to give the least error for a majority of the data. Langmuir-Freundlich model 2 predicted most accurately for shale samples from Green river formation, Barnett shale Tarrant A3, Blakely 1 and Ordos Basin A and B in China. On the other hand, three of the shale samples, from Woodford shale, Ordos Basin YY33-2, Ordos Basin YY34-1 and Antrim-7, were most accurately predicted by the Exponential model.

Langmuir model 1 failed to predict most accurately the gas adsorption for any of the shale samples evaluated. The AAD% for Langmuir 1 was notably higher in most of the results when compared with the rest of the temperature-dependent models, ranging from 0.49 % -7.48 %. Similarly, Langmuir 2 could predict only one of the samples (CSW2) most accurately.

However, when the Freundlich model was combined with Langmuir model, the results of the modelling improved, with Langmuir-Freundlich 2 model giving a very small average absolute
deviation error for five of the samples. This could also be attributed to the extra parameter present in the Langmuir–Freundlich model. The more parameters that are present in the model, the greater the likelihood of the model predicting more accurately. Furthermore, the Langmuir-Freundlich model is better able to describe the heterogeneity of the shale sample than the classic Langmuir model.

Similar comparison has been made for the models with temperature-independent Langmuir volume. These models include Langmuir 3, Langmuir-Freundlich 3 and the Bi-Langmuir model (see Table 3.4). Comparing the values obtained for all three models, it can be observed that Langmuir-Freundlich 3 model provided the least error for six of the shale samples, compared with three and two for Langmuir 3 and Bi-Langmuir model respectively.

Most of the shale data have been adequately described by the combination of both the Langmuir and Freundlich models. Thus Langmuir-Freundlich 2 and Langmuir-Freundlich 3 proved to be better models in describing the adsorption process in the shale formations. Since most of these shales are deemed to be highly heterogeneous, with mixtures of clay minerals like quartz and kerogen compositions of type I or II, the combined Langmuir-Freundlich models are best for modelling gas adsorption. The Exponential model also proved to fit adequately most of the data compared with the Langmuir models. Hence the choice of model would depend on how highly heterogeneous the shale sample is, and since Langmuir model assumes a homogeneous surface, the preferred choice of combined Langmuir and Freundlich would best describe the adsorption process in most shales.

In order to compare how well the temperature-dependent and -independent forms of the Langmuir volume models compare to each other when applied to the same datasets, Table 3.3 was combined with Table 3.4 and the model with the least error was chosen to be the most accurate representation of the gas adsorption data on the shale samples. Seven of the data sets were accurately described by the temperature-independent Langmuir volume models, compared to only four by the temperature-dependent models. However, the error difference was minimal.

Due to the large number of graphs generated for the representation of the modelling process, only results showing Woodward shale have been presented. The best fitting parameters for all the models have been provided in Appendix 3 (see Table 3.5-3.12) for checking the models’ applicability to the data.
The $R^2$ method to measure the level of accuracy of the fit for Woodford shale shows very close approximation to one, meaning all the models could adequately fit the gas adsorption process in Woodford shale (see Figure 3.2-Figure 3.9). This was not the case when the $R^2$ was evaluated for the rest of the data (see Table 3.5-3.12 in Appendix 3), as some of the models could not adequately describe the gas adsorption process. In particular, models like Langmuir 1 and 2 failed to describe adequately for some of the adsorption data, as the $R^2$ shows in Tables 3.5 to 3.12.
Figure 3.2: Modelling methane adsorption using Langmuir 1 model on experimental data of Woodford shale

Figure 3.3: Modelling Methane adsorption using Langmuir 2 model on experimental data from Woodford shale
Figure 3.4: Modelling methane adsorption using Langmuir-Freundlich 1 model on experimental data from Woodford shale

Figure 3.5: Modelling methane adsorption using Langmuir-Freundlich 2 model on experimental data from Woodford shale
Figure 3.6: Modelling methane adsorption using Exponential model on experimental data from Woodford shale

Figure 3.7: Modelling methane adsorption using Bi-Langmuir model on experimental data from Woodford shale
**Figure 3.8:** Modelling Methane adsorption using Langmuir 3 model on experimental data from Woodford shale

**Figure 3.9:** Modelling Methane adsorption using Langmuir Freundlich 3 model on experimental data from Woodford shale
### Table 3.3: Absolute Average Deviation (AAD%) for models with temperature-dependent volume

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>Langmuir 1</th>
<th>Langmuir 2</th>
<th>Langmuir-Freundlich 1</th>
<th>Langmuir-Freundlich 2</th>
<th>Exponential</th>
<th>No. of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>0.49 %</td>
<td>0.48 %</td>
<td>2.66 %</td>
<td>0.07 %</td>
<td>0.33 %</td>
<td>33</td>
</tr>
<tr>
<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
<td>2.68 %</td>
<td>2.67 %</td>
<td>2.99 %</td>
<td>3.72 %</td>
<td>1.13 %</td>
<td>40</td>
</tr>
<tr>
<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>1.11 %</td>
<td>1.13 %</td>
<td>0.32 %</td>
<td>0.22 %</td>
<td>2.18 %</td>
<td>39</td>
</tr>
<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>9.28 %</td>
<td>9.23 %</td>
<td>4.07 %</td>
<td>4.00 %</td>
<td>7.82 %</td>
<td>42</td>
</tr>
<tr>
<td>Ordos Basin YY33-2</td>
<td>Ji et al 2014</td>
<td>1.53 %</td>
<td>2.74 %</td>
<td>5.75 %</td>
<td>2.25 %</td>
<td>0.97 %</td>
<td>35</td>
</tr>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>6.95 %</td>
<td>10.63 %</td>
<td>7.57 %</td>
<td>2.00 %</td>
<td>0.76 %</td>
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<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>5.57 %</td>
<td>6.81 %</td>
<td>0.46 %</td>
<td>0.25 %</td>
<td>5.76 %</td>
<td>42</td>
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<tr>
<td>Ordos Basin B</td>
<td>Guo 2014</td>
<td>7.14 %</td>
<td>6.30 %</td>
<td>0.63 %</td>
<td>0.45 %</td>
<td>0.94 %</td>
<td>39</td>
</tr>
<tr>
<td>Ordos Basin C</td>
<td>Guo 2014</td>
<td>7.48 %</td>
<td>5.74 %</td>
<td>0.11 %</td>
<td>5.82 %</td>
<td>0.26 %</td>
<td>36</td>
</tr>
<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.971 %</td>
<td>0.32 %</td>
<td>2.60 %</td>
<td>1.84 %</td>
<td>0.85 %</td>
<td>40</td>
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<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.976 %</td>
<td>0.83 %</td>
<td>1.71 %</td>
<td>0.77 %</td>
<td>0.66 %</td>
<td>40</td>
</tr>
<tr>
<td>Sample</td>
<td>Reference</td>
<td>Langmuir 3</td>
<td>Langmuir-Freundlich 3</td>
<td>Bi-Langmuir</td>
<td>No.of Data</td>
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<td></td>
</tr>
<tr>
<td>-----------------------------</td>
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</tr>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>0.42 %</td>
<td>0.06 %</td>
<td>2.01 %</td>
<td>33</td>
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<tr>
<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
<td>2.68 %</td>
<td>1.03 %</td>
<td>4.12 %</td>
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<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>1.05 %</td>
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<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>9.21 %</td>
<td>4.09 %</td>
<td>3.56 %</td>
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<td></td>
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</tr>
<tr>
<td>Ordos Basin YY33-2</td>
<td>Ji et al 2014</td>
<td>1.79 %</td>
<td>1.92 %</td>
<td>8.96 %</td>
<td>35</td>
<td></td>
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</tr>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>6.48 %</td>
<td>2.79 %</td>
<td>8.71 %</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>3.82 %</td>
<td>0.09 %</td>
<td>6.46 %</td>
<td>42</td>
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<td>Ordos Basin B</td>
<td>Guo 2014</td>
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<td>Ordos Basin C</td>
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<td>5.79 %</td>
<td>5.28 %</td>
<td>36</td>
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<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.69 %</td>
<td>2.31 %</td>
<td>0.71 %</td>
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<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.73 %</td>
<td>0.22 %</td>
<td>0.14 %</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Temperatures can also be extrapolated to conditions that might be outside laboratory conditions, to review how the models might predict gas adsorption. This is only possible because of the use of temperature-dependent models. Extrapolation to temperatures outside laboratory conditions is useful especially in simulation studies where thermal application is involved. For enhanced shale gas recovery studies, the use of temperature dependent-models is key for prediction of gas where temperature variation can significantly affect the amount of gas adsorbed. Undertaking simulation studies would require validating the models before extrapolation to higher temperatures. The experimental adsorption data for Sample YY33-2 at 30°C, 40°C, 50°C and 60.4°C have been used for the establishment and calibration of the models.

Since extrapolation is necessary especially for numerical simulation involving thermal application, this study have used isotherm data at 70°C for YY33-2 to get some idea about the importance of model selection in extrapolation of temperature. Both temperature-dependent Langmuir volume models and temperature-independent Langmuir volume models have been extrapolated to 70°C to confirm how well the models predict gas adsorption for validation and extrapolation purposes (See Figure3.10 and Figure3.11).

The Exponential model from Figure 10 shows a much more accurate fit of the extrapolation to 70°C for the shale data of YY33-2. This implies that subsequent extrapolation is more likely to give better approximation to gas adsorption at temperatures outside laboratory conditions. With the exception of the Exponential model that gave a better validation, both Langmuir 1 and 2 gave an exaggerated prediction, whereas the combined Langmuir and Freundlich models’ prediction was close to the experimental data.

For temperature-independent Langmuir volume models, the validation of the extrapolation with the actual data was not very accurate. All three models either under-predicted or over-predicted the results (see Figure 3.11). This could be because, for the shale sample YY33-2, the temperature-independent Langmuir volume models do not describe the adsorption process well, compared with the temperature-dependent Langmuir volume models.

The results from Figures 3.10 and 3.11 show that care must be taken in the choice of model and the representation of temperature effects on adsorption, due to the different predictions offered by the models. Although some of the results are not exactly far off from the range of data at 70°C, caution is still expected to be exercised in the use of these models, as results
might be an over- or under-estimation of the actual adsorbed gas at temperatures for which there are no experimental data.
Figure 3.10: Extrapolated and validation at 70°C of shale sample YY33-2 using temperature-dependent Langmuir Volume models.
Figure 3.11: Extrapolation and validation at 70°C of shale sample YY33-2 using temperature-independent Langmuir Volume models
3.10 Summary

This chapter introduces the use of temperature-dependent adsorption modelling in prediction of gas adsorption capacities. By examining different temperature dependent adsorption models and their predictive performances, the choice of an accurate model to be used in shale gas reservoir becomes easier and removes error associated when modelling shale gas adsorption.

This chapter has focused on applying 8 different temperature-dependent adsorption models to a wide range of shale gas adsorption data sets. Temperature-dependent models have been further grouped into models that have temperature-dependent Langmuir volume and those that expresses a constant Langmuir volume. Analysis of temperature-dependent Langmuir volume showed that the majority of the data were successfully represented when using the combined Langmuir–Freundlich 2 model, and also the Exponential model. Langmuir 1 and 2 showed the least accuracy for all the data evaluated when used in modelling the gas adsorption on the experimental shale gas data studied. Temperature-independent Langmuir volume also proved able successfully to fit the gas adsorption data presented, and in some cases, when compared with the temperature-dependent Langmuir volume models, it predicted the gas adsorption most accurately. Validation and extrapolation of all the models for shale sample YY33-2 showed varying prediction to actual data at 70°C, though models with temperature-dependent Langmuir volume offered much closer prediction than the temperature-independent Langmuir volume models. This implies that care and caution must be exercised when selecting a particular model for representation of gas adsorbed at temperatures for which no data are available. Temperature-dependent models are important because they offer an ability to accurately describe gas adsorption at multiple temperatures and also to be implemented in numerical simulation studies where thermal stimulation is required for enhanced shale gas recovery process.

Nomenclature

\( \Delta H_{ads} \) = adsorption enthalpy change for component

\( b \) = adsorption equilibrium constant

\( V_L \) = theoretical maximum Langmuir volume.
\( q_{so} \) = saturation loading similar to the Langmuir volume

\( C_1 \) = residual adsorption capacity

\( p_2 \) = pressure under the condition of \( T_2 \)

\( n \) = surface heterogeneity

\( E_o \) = characteristic energy of adsorption for standard vapor, \( J/mol \)

\( \beta \) = similarity coefficient which is dimensionless

\( A \) = specific surface area of adsorbent

\( n \) = constant in Dubinin-Astakhov equation

\( \theta \) = saturation loading, dimensionless

\( V_{ads} \) = adsorbed phase volume

\( V_{ads,0} \) = adsorbed phase volume

\( T_0 \) = reference temperature

\( \delta \) = thermal expansion coefficient

\( f_1 \) = fraction of adsorption site

\( k_{1,2} \) = adsorption equilibrium constant

\( N_{ads} \) = amount of adsorbed gas per unit volume adsorbent

\( N_m \) = Amount of adsorbed gas at monolayer coverage

\( E_1 \) = Adsorption energy

\( V_s \) = theoretical maximum adsorption capacity

\( D_T \) = Reduction coefficient related to temperature increase

\( n_{cal} \) = calculated adsorbed concentration

\( n_{exp} \) = experimental adsorption data

\( N \) = number of data points for the isotherm
Chapter 4

Material Balance Calculations for Unconventional Gas Reservoirs Using Temperature-Dependent Gas Adsorption Models

4.1 Introduction

The material balance equation has been an important tool for making future reservoir predictions, especially future production forecasts, in conventional reservoirs. It is seen as one of the most powerful tools used in reservoir engineering (Canal and Rosbaco, 1992). Material balance models use pressure and production data to determine the volume of hydrocarbons that is present. They have been used primarily in the estimation of original hydrocarbons in place, and also in determining expected ultimate recovery and remaining reserves in a reservoir.

In estimating original gas in place (OGIP) and initial reservoir pressure, several methods, including those of Kings (1993), Jensen and Smith (1997), Seidel (1999), Ahmed and Roux (2006), Moghadam et al., (2011) and Firand (2011), have been proposed. These methods have utilised the application of the P/Z plot, which requires as the input data cumulative gas production, average reservoir pressure and the properties of the produced gas (Seidle, 1999).

The success and usefulness of the P/Z plot in conventional reservoirs led to its application in unconventional reservoirs, such as coal bed methane and shale/tight gas reservoirs. Despite its usefulness, the P/Z plot may give inaccurate results when applied directly to unconventional reservoirs such as coal/shale. This is because in its conventional form, it does not include other sources of gas storage, such as connected reservoirs or adsorption, which are present in coal/shale reservoirs (Moghadam et al., 2011). This has led to the modification of P/Z plot in order for it to be suitable for application to unconventional reservoirs, especially coal / shale gas reservoirs.

Unconventional reservoirs such as coal/shale are characterised by gas adsorption, hence incorporating adsorption into the derivation of the P/Z method is necessary for accurate prediction of hydrocarbons in place for such reservoirs. This requires an adsorption model that can correctly represent the adsorption phenomenon within these reservoirs. Langmuir
isotherm represents this phenomenon for the traditional P/Z plot used in unconventional gas reservoirs. Despite the limitations of Langmuir isotherm, such as adsorption being a function of only pressure, it remains the only model currently incorporated in most P/Z plots to evaluate the production performance of unconventional gas reservoirs using material balance. Several P/Z methodologies have been developed for use in unconventional reservoirs with the use of classic Langmuir isotherm.

Section 4.2 of this chapter comprises a review of different modifications of the P/Z plot used to determine the original hydrocarbons in place and the estimation of the initial pressures. Several of the modified material balance equations for unconventional gas reservoirs can also be used in the prediction of future gas production.

In section 4.3, an attempt has been made to modify the material balance method used in unconventional gas reservoirs to include temperature-dependent models. The chapter concludes with analysis and discussion of the modified methodology used on data from an unconventional gas reservoir.

**4.2 P/Z plot methodology used for unconventional gas reservoirs**

**4.2.1 King’s Method**

King (1993, 1990) was one of the first researchers to modify the P/Z plot for non-volumetric behaviour of coal seam gas and shale gas reservoirs. With the conventional P/Z plot developed mainly for use in volumetric reservoirs (where the pore volume of the reservoir is assumed to be constant, or there is no influx of water into the system), King (1990) offered a different methodology where the effect of adsorption can be incorporated.

An underlying assumption that was used by King was that there must exist an equilibrium between the free gas and the adsorbed gas. The desorption process in the reservoir is described by a strictly pressure-dependent relation. With this assumption, the method could only be applied when the well was shut in, or for flowing wells that experience rapid desorption. The key assumptions used by King in developing the material balance for coal/shale reservoirs are summarised below:

1. Gas is adsorbed primarily in the matrix and free gas exists mostly within the cleats/fractures
2. The compressibility of water and rock, as well as water production, is considered.

3. The coal/shale follows Langmuir isotherm.

4. Adsorption is at pseudo-steady state period.

King proposed the material balance equation in the form:

\[ G_p = \frac{V_{b2} \phi Z_{wT} Z_c}{p_{wT}} \left[ \frac{p_i}{Z_i} - \frac{p}{Z^*} \right] \] ........................................(4.1)

\[ Z^* = \frac{Z}{\left[ 1 - c_p (p_i - p) \right] (1 - S_{wavg}) + \frac{ZRTC}{\phi_i p}} \] ........................................(4.2)

King also proposed an iterative solution to obtain the bulk volume of the secondary porosity, which is denoted by \( V_{b2} \).

\[ C_E = \frac{p_{sc}}{Z_{sc} RT_{sc} Z_c} \left( \frac{V_i p}{p_L + p} \right) \] ...........................................(4.3)

This refers to the adsorption isotherm in terms of lb-moles/ft\(^3\)

The average water saturation was defined by King as:

\[ S_{avg} = \frac{5.615 W_p}{\phi V_{b2}} \] ...........................................(4.4)

The \( Z^* \) consists of two denominator terms: the first represents the free gas in the cleats/natural fractures, while the second term is the ratio of the adsorbed gas to the free gas.

According to Seidle (1999), King’s method was found to be suitable only for under-pressured coal and not for under-saturated coals, and when the method was applied to coal wells, it was found that erroneous results were obtained. That is, unrealistic results were obtained for initial pressure and gas in place calculation when King’s method was applied to production data.

**4.2.2 Jensen and Smith Modified Method**

A modified method for material balance in unconventional gas reservoirs was proposed by Jensen and Smith (1997) after King’s method. It offered a more practical basis for evaluation.
of the estimated recovery and the remaining reserves in the reservoir. Their methodology used only a few parameters, such as the Langmuir pressure, together with the reservoir pressures and cumulative production, to make its estimates. Their approach was seen to be more useful for reservoirs that are highly dominated by adsorption. This meant that water and free gas that exist in the cleats/natural fractures is considered to be negligible, and the effect of water saturation was ignored.

\[ Z^* = \frac{Z}{p_a V_{Ld} (1 - a - w) p_{sc} T Z} \]  
\[ \frac{32.037 \phi Z_{sc} T_{sc} (p + p_L)}{\rho \phi} \]  

…………………(4.5)

and the modified gas material balance was thus given as:

\[ \frac{p}{p + p_L} = \frac{p_i}{p_i + p_L} \left( 1 - \frac{G_r}{G_i} \right) \]  

…………………(4.6)

4.2.3 Seidle Method – Modified King Method

Seidle (1999) modified King’s method after realising the limitations of his iterative method when applied to actual production data. By assuming constant water saturation over time, instead of an averaged water saturation over the drainage area as employed by King, Seidle (1999) modified the iterative solution proposed by King and offered a direct approach to calculating initial gas in place, estimated recovery and remaining reserves. Thus Equation 4.4 was no longer needed. Seidle (1999) believed that the water saturation of coal deposits remains relatively constant over a long period of time, with saturation changes in the order of 0.35 over a 10-year simulation. The \( Z^* \) was found to be insensitive to changes in the water saturation, thus iterations of drainage area had little effect on the value of \( Z^* \); this is because the ratio of the sorbed gas to the free gas in Equation 4.2 is often larger than the water saturation. Seidle (1999) verified his approach on production data that were problematic for the original King method, and found that it provided accurate solutions.
4.2.4 Ahmed and Roux Method

Ahmed and Roux (2006) proposed a new, enhanced material balance methodology that enabled the calculation of the original gas in place, as well as predicting the average reservoir pressure and future reservoir performance. It removed the reliance on the iterative solution that was proposed by King (1993, 1990) by providing a simple method of obtaining the initial gas in place through expressing the material balance as an equation of a straight line.

\[ G_p = G + G_F - G_A - G_R \] \hspace{1cm} (4.7)

\( G_p \) = cumulative gas produced, \( G \) = gas originally adsorbed, \( G_F \) = original free gas, \( G_A \) = gas currently adsorbed, \( G_R \) = remaining free gas.

By defining the material balance equation for coal bed methane (CBM) in Equation 4.7 and defining the terms in the equation, an equation of a straight line can be obtained with variables \( x \) and \( y \).

\[ G = 1359.7Ah\rho_bG_c \] \hspace{1cm} (4.8)

\[ G_F = 7758Ah\phi(1 - S_w)E_{gi} \] \hspace{1cm} (4.9)

\[ G_A = 1359.7Ah\rho_bV \] \hspace{1cm} (4.10)

\[ G_R = \frac{S_w[1 + c_w(p_i - p)] - \frac{B_w W_p}{7758Ah\phi}}{1 - (p_i - p)c_f} \] \hspace{1cm} (4.11)

\[ G_p = \frac{B_w W_p E_s}{1 - (c_f \Delta P)} = Ah \left[ 1359.7\rho_b \left( G_e - \frac{V_m bp}{1 + bp} \right) + \frac{7758\phi \left[ \Delta P(c_f + S_w c_{wi}) - (1 - S_w) \right] E_s}{1 - (c_f \Delta P)} \right] \] \hspace{1cm} (4.12)

\[ y = G_p = \frac{B_w W_p E_s}{1 - (c_f \Delta P)} \] \hspace{1cm} (4.13)
By using historical production data, a plot of $x$ and $y$ will yield a straight line with a slope and intercept defined respectively as:

$m = Ah$

$a = 7758Ah(1 - S_{wi})E_{gi}$

From these equations, the drainage area $A$ can be obtained and subsequently the original gas in place as:

$OGIP = G + G_F$  .................................................(4.15)

The usefulness of Equation 4.12 is that it can be used to obtain an estimate of the average reservoir pressure, and also to make future reservoir production performance predictions. Ahmed and Roux's (2006) method is applicable to any coal that behaves according to the Langmuir isotherm equation.

### 4.2.5 Moghadam et al., 2011 Method

Moghadam et al., (2011) presented an advanced and more rigorous material balance for gas reservoirs that incorporated many of the modifications by previous authors. Thus, it can account for water influx, expansion of the formation and of residual liquids in over-pressured reservoirs, and gas desorption in coal/shale reservoirs. The modified equation has the same format as the conventional $P/Z$ plot of the material balance equation. According to the authors, one key advantage of the modified material balance is that it can be used to define the total compressibility of the system for analysing fluid flow in unconventional gas reservoirs. They developed a new $Z''$ that is related to $Z^*$ as developed by King (1990) as follows

$$Z'' = Z^* \left( \frac{Z_i}{Z_f} \right) .................................................(4.16)$$

Or

$$Z'' = \frac{p}{\frac{1}{S_{gi}} Z \left( S_{gi} - c_{wp} - c_{ep} - c_{d} \right) + \frac{p_i Z_i}{G_f Z_f - 1} G_f \frac{G}{G_f}}  .................................................(4.17)$$

This new $Z''$ replaces $Z^*$ in the gas material balance equation as:
\[
\frac{P}{Z^*} = \left(1 - \frac{G_p}{G}\right) \frac{P_i}{Z_i^*} \quad \text{(4.18)}
\]

Moghadam et al., (2011) argued that the use of \( \frac{P}{Z} \) normally showed little resemblance to the conventional \( \frac{P}{Z} \) values, but that by using the \( \frac{P}{Z^*} \), the values obtained are more similar to those of \( \frac{P}{Z} \).

### 4.2.6 Firanda Method

Firanda (2011) considered the inclusion of different drive mechanism in the material balance equation that was introduced by King. These drive mechanisms included water expansion, rock compaction, connate water expansion and moisture expansion. By so including these, \( \frac{P}{Z} \) was modified with a new definition of \( Z^* \) (see Equation 4.22) that included these terms. The modified material balance equation as introduced by Firanda (2011) can therefore be used in many aspects of fluid mechanism in a coalbed reservoir. The adsorption term of the modified formula also included the Langmuir isotherm equation. In terms of the methodology for predicting the original gas in place and for making future reservoir performance predictions, Firanda approach is also similar to that of Ahmed and Roux (2006), in that the material balance was expressed as a straight line with \( x \) and \( y \). He proposed two equations for when the coal is in a saturated condition \( (P_{res} \leq P_{critical}) \), Equation 4.20, and when the coal is at under-saturated condition \( (P_{res} \geq P_{critical}) \) Equation 4.21.

The new material balance equation developed by Firanda is defined as follows

\[
U_W = G_{micro} + G_{macro} + W_{macro} + S_{conate} + M_{moisture} + S_{pvshrinkage} + W_{inf influx} \quad \text{(4.19)}
\]

\( U_W \) = underground withdrawal, \( G_{micro} \) = gas expansion in micro pores, \( G_{macro} \) = gas expansion in macro pores, \( W_{macro} \) = water expansion in macro pores, \( S_{conate} \) = connate water expansion, \( M_{moisture} \) = moisture expansion, \( S_{pvshrinkage} \) = pore volume shrinkage, \( W_{inf influx} \) = net water influx.
\[ G_b B = \left( Ah \rho B_m \frac{V_f P_g}{P_f + P_m}(1 - f_m - f_{ash}) - Ah \rho B_m \frac{V_f P_g}{P_f + P_m}(1 - f_m - f_{ash}) \right) B_g + \left( \frac{Ah \phi (1 - S_{m})}{B_m} \right) (B_g - B_m) + \left( \frac{Ah \phi (1 - S_{m} - S_{w})}{B_m} \right) (B_g - B_m) + Ah \phi \Delta P \left( S_{m,c_m} + c_{m,\text{w}} \right) + \left( \frac{Ah \phi B_m \frac{V_f P_g}{P_f + P_m}(1 - f_m - f_{ash})}{1 - f_m} \right) \Delta P \left( f_m c_m + c_{m,\text{w}} \right) \] (4.20)

\[ + (W_e - W_{r,B_m}) \]

\[ G_b B + W_e B_{m} = \left( \frac{Ah \phi (1 - S_{m})}{B_m} \right) (B_g - B_m) + \left( \frac{Ah \phi (1 - S_{m} - S_{w})}{B_m} \right) (B_g - B_m) + Ah \phi \Delta P \left( S_{m,c_m} + c_{m,\text{w}} \right) + W_e \] (4.21)

\[ Z^* = \frac{Z}{(1 - c_{m,\text{w}}) \Delta P \left( 1 - S_{w} \right) + \frac{Z \rho \mu T \phi Z_{m} T_{sc}}{P_f + P_m}(1 - f_m - f_{ash}) - \frac{(1 - S_{m} - S_{w})}{B_m} (B_g - B_m)} \]

\[ - \left( \frac{P_m P_f}{P_f + P_m}(1 - f_m - f_{ash}) \right) \frac{Z T P_{sc}}{\phi Z_{m} T_{sc}(1 - f_m)} \Delta P (f_m c_m + c_{m,\text{w}}) \] (4.22)

### 4.3 New Method – Temperature-Dependent Adsorption Models

Previous modifications of the material balance equation for unconventional gas reservoirs, especially for coal and shale, have included the adsorption capability of these resources. The additional term of gas adsorption has been modelled based on Langmuir isotherm. Langmuir isotherm describes an equilibrium relationship between the free gas and the adsorbed gas under isothermal conditions. Thus, gas adsorption has been expressed only as a function of pressure. Therefore, the use of Langmuir isotherm to account for the adsorption capacity of shale within the material balance equation will be inadequate, since the effects of varying temperature are neglected.

Temperature plays an important role in gas adsorption. Hence any adsorption model should be capable of expressing the adsorption as a function of both pressure and temperature. The majority of gas in shale gas reservoirs is from adsorbed gas, and an ample knowledge of gas adsorption behaviour over a wide range of pressure and temperature is needed. According to Gasparik et al., (2015), sorption isotherms need to be measured over an extended range of pressures greater than 20 MPA and temperatures greater than 100 °C in order for the isotherm to be considered at in-situ reservoir conditions typical of shale gas reservoirs. Langmuir model fails to provide such knowledge, as adsorption can be modelled only at a single temperature.
Since gas adsorption is also a function of temperature, geothermal gradients will contribute substantially to the adsorption capacity of these gases. An example is the black Warrior basin, where there is temperature variation from about 26.85°C to 51.85°C within a 0.3-1.8 km depth range (Charoensuppanimit et al., 2015; Pashin and McIntyre, 2003).

Furthermore, a key assumption of Langmuir isotherm is the homogeneity of the adsorbent. However, this may not be suitable or true for shale gas systems, since different materials such as clay minerals and kerogen may contribute to gas adsorption on shale (Lu et al., 1995).

Over the years, several researchers have modified the classic Langmuir model to include a temperature term that makes it appropriate to describe the adsorption capacity of shale/coal. Lu et al., (1995) proposed the use of bi-Langmuir model to describe the adsorption of gas at several temperatures. One term of the model describes gas adsorption on clay minerals, while the other accounts for gas adsorption on kerogen. The model, therefore, is suitable for non-homogeneous adsorbents, especially in the Devonian shale where two mineral compositions, of clay and kerogen, are said to be mainly responsible for gas storage. Ye et al., (2016) also proposed a variation of the classic Langmuir isotherm equation by introducing an exponential relation that expresses the Langmuir volume \(V_L\) as dependent on temperature. Thus, the constant Langmuir volume \(V_L\) as expressed in the Langmuir equation, is replaced by a \(V_L\) that is a function of temperature.

Based on application of the models to different sets of shale gas data, it has been established that modified Langmuir model with temperature dependency can accurately describe shale gas adsorption under various pressures and temperatures (Fianu et al., 2018; Lu et al., 1995; Ye et al., 2016).

Bi-Langmuir model is expressed as:

\[
V = V_L \left[ \frac{f_1 k_1 T^{-1/2} \exp \left( \frac{-E_1}{RT} \right) p}{1 + k_1 T^{-1/2} \exp \left( \frac{-E_1}{RT} \right) p} + \frac{(1 - f_1) k_2 T^{-1/2} \exp \left( \frac{-E_2}{RT} \right) p}{1 + k_2 T^{-1/2} \exp \left( \frac{-E_2}{RT} \right) p} \right] \quad \text{...............}(4.23)
\]

\[
b_1 = k_1 T^{-1/2} \exp \left( \frac{-E_1}{RT} \right), \quad b_2 = k_2 T^{-1/2} \exp \left( \frac{-E_2}{RT} \right)
\]
All variables with the exception of pressure (P) and temperature (T) are obtained by matching the adsorption data using regression analysis.

Hence,

\[ V = V_i \left[ \frac{f_i b_p}{1 + b_p} + \frac{(1 - f_i)b_p}{1 + b_p} \right] \] ..........................(4.24)

Exponential model for adsorption is given as:

\[ V = V_i \exp(-D_i T) \frac{\beta p}{1 + \beta p} \] ..........................(4.25)

\[ \beta = \frac{1}{c}, \quad c = \frac{\sqrt{T}}{A \exp \left( \frac{B}{T} \right)} \]

The coefficients \( A \) and \( B \) are obtained by matching the adsorption data through regression analysis.

To incorporate Equations 4.23 (Bi-Langmuir model) and 4.25 (Exponential model) into the material balance equation, Ahmed and Roux’s (2006) approach has in this research been used, expressing the material balance as an equation of a straight line with \( x \) and \( y \). This method has the advantage of avoiding the use of an iterative process, as employed by the other methods, in solving the resulting equations. It offers the advantage of minimizing costs associated with obtaining pressure survey data, since the average reservoir pressures can easily be obtained by using the initial reservoir pressure, Langmuir isotherm and cumulative gas production. Table 4.1 summarises the different methods used in the application of MBE in unconventional gas reservoirs including the new methodology developed in this thesis.
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Advantages/Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jensen and Smith Modified Method (1997)</td>
<td>Modified Kings Methodology with a more practical based evaluation of the estimated recovery and remaining reserves. Neglected the effect of water saturation in their solution. Suitable for reservoirs with high adsorption rate.</td>
<td>Use of Langmuir isotherm meant only single temperature could be used for adsorption calculations</td>
</tr>
<tr>
<td>Seidle Method – Modified King Method (1999)</td>
<td>Another modification of Kings methodology but with the assumption of constant water saturation over time instead of average water saturation.</td>
<td>Avoided the iterative solution adopted by King in its calculation. Langmuir isotherm used to account for gas adsorption.</td>
</tr>
<tr>
<td>Ahmed and Roux Method (2006)</td>
<td>Expressed the material balance as an equation of a straight line to enable</td>
<td>Method is applicable to any coal/shale that behaves according to Langmuir.</td>
</tr>
<tr>
<td>Method</td>
<td>Calculations/Approach</td>
<td>Isotherm/Limitation</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Moghadam Method (2009)</td>
<td>similar but more rigorous and advanced form of the material balance proposed by King.</td>
<td>Used to define total compressibility of the system for analysing fluid flow in unconventional gas reservoirs. Adsorption was described by Langmuir isotherm</td>
</tr>
<tr>
<td>Firanda Method (2011)</td>
<td>introduced different drive mechanisms in the material balance equation proposed by King. These included water expansion, rock compaction, connate water expansion and moisture expansion.</td>
<td>Offered similar methodology used by Ahmed and Roux by expressing material balance as a straight line. Adsorption isotherm used is Langmuir isotherm.</td>
</tr>
<tr>
<td>New Approach (This Research)</td>
<td>similar approach adopted by Ahmed and Roux by expressing material balance as a straight line. Average reservoir pressure as well as future performance of the reservoir can be obtained.</td>
<td>Avoids iterative solution of Kings approach. Adopts temperature-dependent gas adsorption model such as Bi-Langmuir and Exponential model in its methodology to account for gas adsorption at several temperatures.</td>
</tr>
</tbody>
</table>
### 4.4 Methodology

From Equation 4.7, the produced gas can be expressed as

\[ G_p = G + G_f - G_A - G_R \] \hspace{1cm} (4.26)

\( G_A \) which is the gas adsorbed can now be expressed as a function of both pressure and temperature. Inserting both the Bi–Langmuir and exponential formulae into \( G_A \) yields the following equations respectively:

\[ G_A = V = V_L \left[ \frac{f_1 b_1 p}{1 + b_1 p} + \frac{1 - f_1}{1 + b_2 p} \right] \] \hspace{1cm} (4.27)

\[ G_A = V = \frac{V_e \exp(-D_e T) \beta p}{1 + \beta p} \] \hspace{1cm} (4.28)

From Equation 4.10, \( V \) can be replaced with either one of the temperature-dependent models. For Bi-Langmuir model, the modified material balance equation can therefore be expressed as:

**Bi-Langmuir model**

\[
G_p + \frac{B_e W_e E_g}{1 - (c_j \Delta P)} = Ah \left[ 1359.7 \rho_b \left( G_e - V_L \left( \frac{f_1 b_1 p}{1 + b_1 p} + \frac{1 - f_1}{1 + b_2 p} \right) \right) \right] + 7758Ah\phi \left( 1 - S_{wi} \right) E_{gi} \] \hspace{1cm} (4.29)

Neglecting rock and fluid compressibility:

\[
G_p + B_e W_e E_g = Ah \left[ 1359.7 \rho_b \left( G_e - V_L \left( \frac{f_1 b_1 p}{1 + b_1 p} + \frac{1 - f_1}{1 + b_2 p} \right) \right) \right] + 7758Ah\phi \left( 1 - S_{wi} \right) E_{gi} \] \hspace{1cm} (4.30)

Equation 4.29 can be expressed as an equation of a straight line, i.e. \( y = mx + c \), where
\[ y = G_p + \frac{B_u W_p E_g}{1 - (c_f \Delta P)} \] ..........................(4.31)

\[ x = 1359.7 \rho_b \left( G_c - V_L \left( \frac{f_i b_p}{1+b_p} + \frac{(1-f_i)b_p}{1+b_p} \right) \right) + \frac{7758\phi\left[\Delta P\left(c_f + S_w c_w\right) - (1-S_w)\right]}{1 - (c_f \Delta P)} E_g \] ..........................(4.32)

Neglecting rock and fluid compressibility:

\[ y = G_p + B_u W_p E_g \] ..........................(4.33)

\[ x = 1359.7 \rho_b \left( G_c - V_L \left( \frac{f_i b_p}{1+b_p} + \frac{(1-f_i)b_p}{1+b_p} \right) \right) + 7758\phi\left[\Delta P\left(c_f + S_w c_w\right) - (1-S_w)\right] E_g \] ..........................(4.34)

When \( x \) is plotted against \( y \), this will yield a straight line with slope \( m \) and intercept \( a \).

\[ a = 7758 Ah \phi \left(1 - S_{wi}\right) E_{gi} \]

\[ m = Ah \]

**Exponential Model**

For the Exponential model, the modified material balance can be expressed as:

\[ G_p + \frac{B_u W_p E_g}{1 - (c_f \Delta P)} = Ah \left[ \frac{1359.7 \rho_b \left( G_c - V_L \exp(-D_f T) \beta p \right)}{1 + \beta p} \right] + 7758\phi\left[\Delta P\left(c_f + S_w c_w\right) - (1-S_w)\right] E_g \] ..........................(4.35)

Neglecting rock and fluid compressibility:

\[ G_p + B_u W_p E_g = Ah \left[ \frac{1359.7 \rho_b \left( G_c - V_L \exp(-D_f T) \beta p \right)}{1 + \beta p} \right] + 7758\phi\left[\Delta P\left(c_f + S_w c_w\right) - (1-S_w)\right] E_g \] ..........................(4.36)

Equation 4.35 Can be expressed as an equation of a straight line i.e. \( y = mx + c \), where

\[ y = G_p + \frac{B_u W_p E_g}{1 - (c_f \Delta P)} \] ..........................(4.37)
\[ x = 1359.7\rho_b \left(G_c - \frac{V \exp(-D_i T) \beta p}{1 + \beta p}\right) + \frac{7758\phi[\Delta P\left(c_f + S_{wi}c_{wi}\right) - (1 - S_{wi})]E_g}{1 - (c_f \Delta P)} \]  

......(4.38)

Neglecting rock and fluid compressibility:

\[ y = G_p + B_wW_pE_g \]  

......(4.39)

\[ x = 1359.7\rho_b \left(G_c - \frac{V \exp(-D_i T) \beta p}{1 + \beta p}\right) + 7758\phi[\Delta P\left(c_f + S_{wi}c_{wi}\right) - (1 - S_{wi})]E_g \]  

......(4.40)

### 4.4.1 Average Reservoir Pressure

Ahmed and Roux's (2006) method of expressing the material balance as an equation of a straight line with variables and can be used in estimating the average reservoir pressure based on historical production data alone. The proposed method by Ahmed and Roux (2006) assumed a single layer reservoir system with a knowledge of the initial reservoir pressure, Langmuir relationship and an initial gas in place.

The material balance equation can be expressed in terms of as:

\[ G_p + W_pE_g = G - \left(1359.7\rho_bAh\right)V_m \frac{bp}{1 + bp} \]  

.............(4.41)

The initial gas in place at the initial reservoir pressure of is given as:

\[ G = \left(1359.7\rho_bAh\right)G_c \]  

.............(4.42)

Where \( G_c = V_m \frac{bp}{1 + bp} \)

Combining Equation 4.41 and Equation 4.42 and rearranging results in:

\[ \left[\frac{p}{p_i}\right]\left(1 + \frac{bp_i}{1 + bp}\right) + \left[\frac{1}{G}\left(G_p + B_wW_pE_p\right)\right] - 1 = 0 \]  

.............(4.43)

Equation 4.23 can be solved iteratively for the average reservoir pressure using Newton Raphson method. By assuming an average reservoir pressure, denoted as , a new pressure can be easily calculated from the expression
\[ p_{\text{new}} = p_{\text{old}} - \frac{f \left( p_{\text{old}} \right)}{f' \left( p_{\text{old}} \right)} \] .................................(4.44)

Where

\[ f \left( p_{\text{old}} \right) = \left( \frac{p}{p_i} \left[ \frac{1 + bp_i}{1 + bp} \right] \right) + \frac{1}{G} \left( G_p + B_w W_p E_p \right) \]
\[ f' \left( p_{\text{old}} \right) = \left( \frac{1}{p_i} \left( \frac{1 + bp_i}{1 + bp_{\text{old}}} \right) - \frac{bp_{\text{old}} \left( 1 + bp_i \right)}{p_i \left( 1 + bp_{\text{old}} \right)^2} \right) + \frac{198.6 B_w W_i}{ZT G} \] .............................(4.46)

\[ E_s = \frac{198.6 \rho}{ZT} \text{ scf/bbl} \] .........................(4.47)

Convergence of the iteration is said to be achieved once \(|p_{\text{old}} - p_{\text{new}}| \leq 10^{-6}\) and a solution is obtained, otherwise the iteration is continued on by setting \(p_{\text{old}}\) to \(p_{\text{new}}\).

The above methodology for obtaining the average reservoir pressure is used only when the adsorption process is represented by Langmuir isotherm. By incorporating a temperature-dependent adsorption model, Equation 4.45 and Equation 4.46 can be modified as follows:

**Bi-Langmuir model:**

\[ f \left( p_{\text{old}} \right) = \left( \frac{f_i b_p}{1 + b_p} + \frac{1}{1 + b_i p_i} \left( \frac{f_i b_p}{1 + b_p} \right) \right) + \frac{1}{G} \left( G_p + \frac{198.6 \rho B_w W_i}{ZT G} \right) \]
\[ f' \left( p_{\text{old}} \right) = \left[ \frac{f_i b_p}{1 + b_p} \left( \frac{1 - f_i b_p}{1 + b_i p_i} \right) + \frac{1}{1 + b_i p_i} \left( \frac{1 - f_i b_p}{1 + b_i p_i} \right) \right] + \frac{198.6 B_w W_i}{GZT} \] .............................(4.49)

**Exponential Model**

\[ f \left( p_{\text{old}} \right) = \left( \frac{p}{p_i} \left[ \frac{1 + \beta p_i}{1 + \beta p} \right] \right) + \frac{1}{G} \left( G_p + B_w W_p E_p \right) \]
\[ f' \left( p_{\text{old}} \right) = \left( \frac{1}{p_i} \left( \frac{1 + \beta p_i}{1 + \beta p_{\text{old}}} \right) - \frac{b_p \left( 1 + \beta p_i \right)}{p_i \left( 1 + \beta p_{\text{old}} \right)^2} \right) + \frac{1}{G} \left( G_p + B_w W_p E_p \right) \] .............................(4.50)
\[ f^\dagger(p_{old}) = \left[ \frac{1}{p_1} \left( \frac{1+\beta p_1}{1+\beta p_{old}} \right) - \frac{bp_{old}(1+\beta p_1)}{p_1(1+\beta p_{old})^2} \right] + \frac{198.6B_w W_p}{ZTG} \] ..................(4.51)

### 4.4.2 Prediction of Reservoir Production Performance

Future reservoir production performance can be predicted with the modified methodology, which includes the temperature-dependent gas adsorption models. A finite difference scheme can be adopted with the modification to predict future reservoir performance. The modified material balance equation can be expressed in the following form, neglecting water and rock compressibility after finite difference approximation.

**Bi-Langmuir model:**

\[ G_p + B_w W_p E_g = G - a_1 \left[ \frac{b_1 p}{1+b_1 p} + \frac{b_2 p}{1+b_2 p} \right] - a_2 \left( E_g-E_g \right) \] ..........................(4.52)

and expressing it in a finite difference scheme after differentiation is:

\[ G_{p}^{n+1} = G_{p}^{n} + \left( B_{w}^{n} W_{p}^{n} E_{g}^{n} - B_{w}^{n+1} W_{p}^{n+1} E_{g}^{n+1} \right) + a_1 \left[ \frac{b_1 \left( p^n - p^{n+1} \right)}{\left( 1+b_1 p^{n+1} \right)^2} + \frac{b_2 \left( p^n - p^{n+1} \right)}{\left( 1+b_2 p^{n+1} \right)^2} \right] + a_2 \left( E_g^n - E_g^{n+1} \right) \] ..........................(4.53)

**Exponential Model**

\[ G_p + B_w W_p E_g = G - a_1 \left[ \frac{\beta p}{1+\beta p} \right] - a_2 \left( E_g-E_g \right) \] ..........................(4.54)

\[ G_{p}^{n+1} = G_{p}^{n} + \left( B_{w}^{n} W_{p}^{n} E_{g}^{n} - B_{w}^{n+1} W_{p}^{n+1} E_{g}^{n+1} \right) + a_1 \left[ \frac{\beta \left( p^n - p^{n+1} \right)}{\left( 1+\beta p^{n+1} \right)^2} \right] + a_2 \left( E_g^n - E_g^{n+1} \right) \] ..........................(4.55)

\[ a_1 = 1359.7Ah \rho_g V_L \quad \text{and} \quad a_2 = 7758\phi Ah \left( 1-S_w \right) \]

The steps needed to carry out a prediction of future reservoir performance are outlined by the algorithm (see Figure 4.1), and the following equations are also useful:

The gas saturation equation is given as
\[ S_{g}^{n+1} = \frac{(1 - S_{wi}) - (p_i - p_{\text{w}g}^{n+1})(c_f + c_w S_{wi})}{1 - (p_i - p_{\text{w}g}^{n+1})c_f} + \frac{B_{\text{p}}^{n+1} W_{p}^{n+1}}{7758 \rho \phi} \]  \hspace{1cm} \text{........................(4.56)}

The relative permeability ratio of \( \frac{k_{rg}}{k_{rw}} \) at the gas saturation \( S_{g}^{n+1} \) can be used to estimate the gas water ratio as

\[ (GWR)^{n+1} = \frac{k_{rg}}{k_{rw}} \left( \frac{\mu_w B_{m}}{\mu_g B_{g}} \right)^{n+1} \]  \hspace{1cm} \text{.................................(4.57)}
Figure 4.1: Algorithm for predicting future production using temperature-dependent models
\[ G_{p}^{n+1} = G_{p}^{n} + \frac{(GWR)^{n+1} + (GWR)^{n}}{2} \left( W_{p}^{n+1} - W_{p}^{n} \right) \]  

Gas and water flow rates are calculated respectively as:

\[ Q_{g}^{n+1} = \frac{0.703hk \left( k_{rg} \right)^{n+1} \left( p_{t}^{n+1} - p_{w} \right)}{T \left( \mu_{g}Z \right)_{avg} \left[ \ln \left( \frac{r_{g}}{r_{w}} \right) - 0.75 + s \right]} \]  

\[ Q_{w}^{n+1} = \left( \frac{k_{nw}}{k_{rg}} \right)^{n+1} \left( \frac{\mu_{w}B_{w}}{\mu_{g}B_{g}} \right)^{n+1} Q_{g}^{n+1} \]

The average gas flow rate as reservoir pressure declines from \( p^{n} \) to \( p^{n+1} \) is

\[ \left( Q_{g} \right)_{avg} = \frac{Q_{g}^{n} + Q_{g}^{n+1}}{2} \]

The incremental time needed for the incremental gas production during the pressure drop is

\[ \Delta t = \frac{\Delta G_{p}}{\left( Q_{g} \right)_{avg}} = \frac{G_{p}^{n+1} - G_{p}^{n}}{\left( Q_{g} \right)_{avg}} \]

4.5 Results and Discussion

To verify the application of the modified method, simulation data provided by King (1990), Ahmed and Roux (2006) and Seidle (1999) have been adopted to confirm the initial gas in place and other historical production data. King (1990) used finite-difference generated data to validate his method as opposed to actual field data. This synthetic data has been used by other researchers in material balance calculations for unconventional gas reservoirs and have also been used throughout this thesis. The reservoir can be described by a 2-D areal model that contains a single coal well. The reservoir is described as being homogeneous with the well-draining a 320-acre coal deposit. Initial water saturation is reported as 0.95 with an initial reservoir pressure of 1500 psia. The estimated initial gas in place is 12.763 Bcf with actual production data given in Appendix 4. The adsorption capacity of this reservoir is expressed by the Langmuir isotherm, with Langmuir parameters given in Appendix 4, Table 4.8.
To obtain the parameters for the adsorption models with temperature dependence, gas adsorption has to be expressed at different temperatures, and a regression analysis performed on the data to obtain the relevant model parameters. Since no data have been provided relating to the experimental adsorption capacity of the coal reservoir at several temperatures, obtaining the model parameters for the temperature-dependent models was a challenge. To obtain the model parameters for the temperature-dependent adsorption model, a similar method to that of Wang (2016) and Yue et al., (2015) was adopted, where unknown independent parameters in Equations 4.24 and 4.25 are determined from Langmuir isotherm curve at provided temperature conditions by nonlinear regression (see Figures 4.2, 4.3 and 4.4). In the case where multiple gas adsorption data at different temperatures are available, temperature-dependent models could easily be applied to obtain model parameters to be used in simulation studies.

Figure 4.2: Regression with Langmuir isotherm parameters (data from Ahmed and Roux, 2006)
Figure 4.3: Shale gas adsorption capacity at selected temperature using Exponential Model (data from Ahmed and Roux, 2006)

Figure 4.4: Shale gas adsorption capacity at selected temperature using Bi-Langmuir Model (data from Ahmed and Roux, 2006)
Tables 4.2 and 4.3 show the model parameters obtained for both Bi-Langmuir and Exponential models.

**Table 4.2: Bi-Langmuir parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_L$ scf/ton</td>
<td>428.49912</td>
</tr>
<tr>
<td>$k_1$ 1/psi</td>
<td>0.0657363</td>
</tr>
<tr>
<td>$k_2$ 1/psi</td>
<td>0.0630964</td>
</tr>
<tr>
<td>$E_1$ cal/mol</td>
<td>-0.036275</td>
</tr>
<tr>
<td>$E_2$ cal/mol</td>
<td>-0.012802</td>
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<td>$f_1$</td>
<td>0.97</td>
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**Table 4.3: Exponential Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$V_s$ scf/ton</td>
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</tr>
<tr>
<td>$D_1$ 1/°F</td>
<td>0.000244</td>
</tr>
<tr>
<td>$A$  °F/psi</td>
<td>0.0655498</td>
</tr>
<tr>
<td>$B$  °F</td>
<td>0.0199987</td>
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</table>
Using the above data, the OGIP has been determined for both temperature-dependent models. By neglecting the formation and water compressibility, Table 4.4 shows the case of Bi-Langmuir model and Exponential model.

**Table 4.4: Expressing MBE as a straight line without compressibility**

<table>
<thead>
<tr>
<th>$p$ psia</th>
<th>Langmuir $V$ scf/ton</th>
<th>$G_p$ MMscf</th>
<th>$W_p$ MMscf</th>
<th>Bi-Langmuir model</th>
<th>Exponential</th>
</tr>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$y$ MMscf</td>
<td>$x$</td>
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<td>345.097</td>
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<td>1021</td>
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<td>1704.033</td>
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<td>111001.7</td>
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<td>2423.4</td>
<td>0.425473</td>
<td>2530.8</td>
<td>155607.3</td>
</tr>
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<td>2992.901</td>
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</tr>
</tbody>
</table>

A plot of $x$ and $y$ will yield a straight line on a Cartesian scale (see Figures 4.5 and 4.6). The slope of the straight line can then be used to determine the drainage area and subsequently the initial gas in place. A slope of 15,946 acre-ft. and 15,933 acre-ft. was obtained for Bi-Langmuir and Exponential models respectively, at the current reservoir temperature. Table 4.5 shows the corresponding drainage area and OGIP.
Figure 4.5: MBE as a straight line for Bi-Langmuir model without compressibility

- New Method: Slope = 15946
- Ahmed and Roux Method: Slope = 15900
Figure 4.6: MBE as a straight line for Exponential model without compressibility

Figure 4.7: MBE as a straight line for Bi-Langmuir model with compressibility
4.5.1 OGIP and Average Pressure

Firstly, by neglecting rock and fluid compressibility, the values of the OGIP obtained for both Bi-Langmuir and Exponential models are 12.757 bscf and 12.742 bscf respectively (See Table 4.5). Compared with Ahmed and Roux’s method, which gave OGIP as 12.72 bscf, the new methodology of incorporating temperature-dependent models into material balance calculation resulted in a much closer estimation of the OGIP obtained from the field data as 12.763 bscf.

However, the inclusion of compressibility calculation resulted in a slight over-prediction of the original gas in place, as shown in Table 4.6. Although using Bi-Langmuir model in the material balance calculation resulted in the correct estimation of the drainage area of 320 acres, the OGIP was slightly higher than actual data reported. Ahmed and Roux’s method under-predicted the OGIP when rock and fluid compressibility were included in the calculation (See Table 4.6).
Furthermore, an estimate for the initial gas in place can be made at different temperatures of the reservoir, something which cannot be done when Langmuir isotherm is used in the calculation of the adsorption potential of the reservoir. Figure 4.9 shows estimated gas in place when both temperature-dependent models are used with decreasing gas in place as the reservoir temperature increases. Thus, it can be concluded that at a much higher reservoir temperature, the original gas in place in a CBM/shale gas reservoir will be much lower than when the reservoir temperature is low. This is because the contribution by gas adsorption will be smaller at higher temperatures, since gas adsorption is exothermic.

Table 4.5: OGIP determination using Bi-Langmuir model and Exponential model without compressibility

<table>
<thead>
<tr>
<th>Method</th>
<th>Slope (acre-ft)</th>
<th>Drainage area (acre)</th>
<th>OGIP (Bscf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
<td></td>
<td>320</td>
<td>12.763</td>
</tr>
<tr>
<td>Ahmed and Roux Method</td>
<td>15900</td>
<td>318</td>
<td>12.72</td>
</tr>
<tr>
<td>Bi-Langmuir</td>
<td>15946</td>
<td>318.92</td>
<td>12.757</td>
</tr>
<tr>
<td>Exponential Model</td>
<td>15933</td>
<td>318.66</td>
<td>12.742</td>
</tr>
</tbody>
</table>

Table 4.6: OGIP determination using Bi-Langmuir model and Exponential model with compressibility

<table>
<thead>
<tr>
<th>Method</th>
<th>Slope (acre-ft)</th>
<th>Drainage area (acre)</th>
<th>OGIP (Bscf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
<td></td>
<td>320</td>
<td>12.763</td>
</tr>
<tr>
<td>Ahmed and Roux Method</td>
<td>15957</td>
<td>319</td>
<td>12.76</td>
</tr>
<tr>
<td>Bi-Langmuir</td>
<td>15946</td>
<td>320</td>
<td>12.800</td>
</tr>
<tr>
<td>Exponential Model</td>
<td>15989</td>
<td>319.78</td>
<td>12.791</td>
</tr>
</tbody>
</table>
Figure 4.9: OGIP at different temperatures using Bi-Langmuir and Exponential model
Using Equations 4.48 and 4.50, the average reservoir pressure for the reservoir can be determined by using only the historical cumulative production values. An excellent pressure match has been obtained for both cases of temperature-dependent models (see Figures 4.10 and 4.11). The pressure match results are in agreement with both the reported data and Ahmed and Roux’s method. This shows that the new methodology is capable of predicting average reservoir pressure using historical production data.

*Figure 4.10: Pressure match for the new method using Bi-Langmuir model*
Figure 4.11: Pressure Match for the new method using Exponential Model
4.5.2 Reservoir performance prediction
Both temperature-dependent models have been used to estimate production performance of the well. The validity of the modified methodology with temperature-dependent models has been tested against the cumulative gas production. The performed simulation in owed for different pressure steps to be used, and it was found that the choice of smaller pressure steps resulted in a much more accurate match to the production data. See Figures 4.12 and 4.13 for a match of the simulated results with those of the cumulative production data. Using Bi-Langmuir model and Exponential model in the methodology showed an excellent match with the reported cumulative gas production when a time step size of 20 psi was chosen. However, using real pressure time steps showed higher total prediction for both models. This result is also in congruence with results reported by Ahmed and Roux (2006).

![Graph showing predicted total production versus reservoir pressure for Bi-Langmuir model](image)

*Figure 4.12: Predicted total production versus reservoir pressure for Bi-Langmuir model*
Figure 4.13: Predicted total production versus reservoir pressure for Exponential model
4.6 Summary

Temperature-dependent models have been introduced into the material balance equation for unconventional gas reservoirs, such as CBM and shale gas reservoirs. These reservoirs have a substantial portion of their gas in place coming from gas adsorption. The limitations of the use of Langmuir isotherm within the material balance equation make it necessary to introduce gas adsorption models that can predict adsorption as a function of both pressure and temperature. Two different temperature-dependent models, namely, Bi-Langmuir model and Exponential model, have been introduced and subsequently incorporated into the material balance equation. By modifying the material balance to include a temperature-dependent gas adsorption model, a new model was developed and applied to available data. The following conclusions are made based on the results of validation of the model:

1. Accurate adsorption potential of the reservoir can be modelled once several gas adsorption data are available at several temperatures. Langmuir isotherm, although useful, fails to model gas adsorption at several temperatures. Results compared with earlier methodologies, like Ahmed and Roux, demonstrated excellent predictions, and in some cases a closer match to reported gas in place.

2. Extrapolation of adsorption capacity can be made at actual reservoir temperature with temperature-dependent gas adsorption models, thereby giving an accurate representation of adsorption capacity that can ultimately improve the estimation of gas in place values.

3. More accurate estimation of reservoir performance can be made with the use of temperature-dependent gas adsorption models in material balance calculations once the adsorption capacity of the reservoir is expressed at different temperatures.
**Nomenclature**

\[ p = \text{pressure} \]

\[ T = \text{temperature} \]

\[ G_p = \text{produced gas} \]

\[ G = \text{gas originally adsorbed} \]

\[ G_f = \text{original free gas} \]

\[ G_A = \text{adsorbed gas currently} \]

\[ G_R = \text{remaining free gas} \]

\[ \phi = \text{porosity} \]

\[ Z = \text{gas compressibility factor} \]

\[ Q_g = \text{gas flow rate} \]

\[ c_f = \text{compressibility of the formation} \]

\[ S_{wi} = \text{initial water saturation} \]

\[ b = \text{Langmuir constant} \]

\[ B_w = \text{water formation volume factor} \]

\[ G_c = \text{gas content at critical desorption pressure} \]

\[ Q_w = \text{water flow rate} \]

\[ V_s = \text{theoretical maximum adsorption capacity} \]

\[ D_f = \text{reduction coefficient} \]

\[ V = \text{gas content at pressure p} \]
\[ A = \text{drainage area} \]

\[ h = \text{average thickness} \]

\[ V_L = \text{Langmuir Volume} \]

\[ R = \text{universal gas constant} \]

\[ E_s = \text{gas expansion factor} \]

\[ E_{gi} = \text{initial gas expansion factor} \]

\[ S_w = \text{water saturation} \]

\[ c_{wi} = \text{water compressibility} \]

\[ W_p = \text{produced water} \]

\[ S_g = \text{gas saturation} \]

\[ GWR = \text{gas water ratio} \]

\[ \rho_B = \text{bulk density} \]

\[ G_i = \text{initial gas in place} \]

\[ k_{rg} = \text{relative permeability of gas} \]

\[ k_{rw} = \text{relative permeability of water} \]

\[ u_g = \text{viscosity of gas} \]

\[ u_w = \text{viscosity of water} \]

\[ (Q_g)_{avg} = \text{average gas rate} \]

\[ B_g = \text{gas formation volume factor} \]
5.1 Introduction
Accurate simulation and modelling of shale gas reservoirs is deemed crucial for efficient exploitation of these resources. Obtaining realistic results for resource estimation and performance predictions has a significant impact on the economics of the operating companies and all interested parties. Integrating all the unique characteristics of shale gas reservoirs within a single reservoir simulator for accurate predictions of future performance is considered a difficult task. For many years now, various researchers have tried to tackle some of these challenges, which include, but are not limited to, how the natural fractures are simplified and represented in a simulator, the transport of gas within the matrix and fractures, adsorption and desorption phenomena within the shale gas system, and how the fractures are propagated within the shale formation upon hydraulic fracturing.

Naturally fractured reservoirs are characterized by the presence of two distinct porous media: the matrix, and fractures. Naturally fractured reservoirs have been referred to as a dual porosity system because of the two porous media that are present (Barenblatt et al., 1960). The matrix feeds fluid locally to the fractures, and the fractures form a continuous system connected to the well.

In the dual porosity model, which was further modified by Warren and Root (1963), the matrix does not contribute directly to the wellbore. The system is seen as an orthogonal set of intersecting fractures and sugar cubic matrix blocks (Figure 5.1) and by using differential equations, analytical solutions could be obtained for well test analysis.
Warren and Root (1963) assumed that flow from the matrix to the fracture occurs under a transfer function with Darcy characteristics, and also that flow occurs under pseudo-steady state conditions in the matrix blocks with a single value assigned to the pressure in the blocks. The pressure differential between the matrix and the fractures, therefore, determines the mass transfer rate of the fluid. Thus, the inter-porosity flow has been described by two main mechanisms, which are the pseudo-steady state and the transient flow. Warren and Root (1963) predicted that on a semi-log plot of the test data, two parallel straight lines will develop. The slope of the parallel lines represents the flow capacities of the formation, whereas the vertical separation of the lines represents the storage capacity of the fractures. This is shown in Figure 5.2.
Odeh (1965) developed a simplified model with mathematical equations that described the unsteady state behavior of fractured reservoirs. He concluded from his studies that there was no difference between fractured reservoirs and homogeneous reservoirs on the basis of drawdown and build-up curves using field-measured data. This, according to Kazemi (1969), contradicted the results of Warren and Root (1963), but with a smaller block dimensions and a higher permeability, their results remains valid. Odeh (1965) used a similar model as Warren and Root (1963), although his results did not show the two parallel straight lines as depicted in Fig. 5.2.

The dual porosity model by Warren and Root (1963) was extended to include transient flow in the matrix block by Kazemi (1969). The main distinction for Kazemi (1969) was the use of transient flow within the matrix, instead of assuming a pseudo-steady state as was done by Warren and Root (1963). Kazemi (1969) also used the slap model (sheets of parallel fracture sets, Figure 5.3) to describe the reservoir. By considering a direct flow to the well, he found that similar results to Warren and Root (1963) were obtainable without affecting the results.
significantly way, except for a smooth transitional zone which occurs due to the non-permanent flow regime of the fluid flow from the matrix to the fractures. Thus deviations will occur in the transitional period when the rock matrix is described by a pseudo-steady state regime.

**Figure 5.3: Dual porosity idealisation (Kazemi, 1969)**

de Swaan (1976) expanded on the dual porosity model by using transient flow as the basis of flow from the matrix to the fractures. He defined his transient model by the intrinsic properties of the matrix and the fractures, as opposed to the bulk properties of the matrix and fractures used by both Warren and Root (1963) and Kazemi (1969). Both a slab matrix shape model and a spherical matrix block solution were also presented in the same study.

Serra et al., (1983) also used the transient model to describe the fluid flow from the matrix to the fractures, and based their model on the use of intrinsic properties rather than bulk properties. Serra et al., (1983) model was very similar to de Swaan (1976), except for the use of a different storativity ratio and inter-porosity coefficient.

Najurieta (1980) showed in a simplified description the pressure behavior of a naturally fractured reservoir based on appropriate solutions of the deSwaan differential equation. In
his study, he deduced equations that described the transitional period, taking into account the unsteady state behavior of the matrix. He also showed that the behavior of a uniformly fractured reservoir can be fully described by four parameters, each of which is a function of two or more of the five basic reservoir parameters (fracture and matrix porosity, fracture and matrix permeability, and fracture spacing).

The method of solving for the system of equations that characterises shale gas reservoirs have been predominately finite difference approximation with several researchers choosing to implement the solution based on popular methods like newton’s method or by specially formulated solutions. Wu et al., (2013) proposed a generalised mathematical model and numerical approach for unconventional gas reservoirs. The model and numerical scheme were based on generalised flow models using unstructured grids. A fully implicit scheme was adopted to solve the discrete nonlinear equations using newton iteration method. They utilised a control volume or integrated finite difference concept to discretise the domain space. Their approach to solving the system of equations that described the shale reservoir was to compute the spatial discretisation, time discretisation and finally using iterative approaches to solve the nonlinear algebraic equations.

Sun et al., (2012) introduced a new technique for the numerical solution of various partial differential equations (PDE) that governs the flow and transport phenomena in porous media. The authors introduced the use of shifting matrices to transfer information between cell-centers and face center and vice versa. Since many programming languages are inefficient when it comes to looping sequences, the technique eliminates the use of loops within the body of the code and therefore reduces the CPU time. Finite difference method was used for the implementation of their study however it was recognised that others like finite volume or finite element may equally be used.

An equation type approach for the numerical solution of partial differential equations that governs transport phenomena in porous media was developed by Sun et al., (2012b). According to the authors, there is no need to reduce the number of governing equations by any mathematical manipulations. In their approach, the physics of the governing equation is separated from the solver and direct solution is obtained without any iterations. They called
this method an equation-type method or experimenting pressure method. One other advantage for using this method is that the boundary conditions are easily implemented.

In this chapter, a review of the concept of dual porosity and dual permeability in shale gas reservoirs is conducted and a mathematical model have been developed to describe this concept with newton iterations implemented to solve the nonlinear PDE. A temperature-dependent gas adsorption model is then incorporated into the simulator to allow for the examination of thermal stimulation as an enhanced gas recovery mechanism in shale gas reservoirs.

5.2 Mathematical Formulation of Isothermal Model in Shale Gas Reservoir

Mathematical formulations are required in order to model the flow of gas through the nanopore networks of shale reservoirs. Several considerations need to be made concerning flow through shale, such as flow due to pressure forces, diffusion, and slippage effect. These need to be included in the mathematical formulation to ensure accurate representation of gas flow through shale. Table 5.2.1 show the flow regimes as a function of Knudsen number. The concept of dual continuum is used in the simulation of shale gas, due to the presence of both matrix and fractures. Free gas exists primarily in the fractures, whereas in the matrix, both free gas and adsorbed gas coexist (See Fig. 5.4). Gas transfer occurs through pressure difference between the matrix and the fractures, and eventually to the wellbore for production (Guo et al., 2015). The following assumptions are made for the purposes of developing the mathematical model for this study. Some of the assumptions will change for the purpose of introducing thermal application in shale gas reservoirs.

1. A single gas component is assumed to be present in our reservoir (methane) and only one phase flow is considered
2. Gravity effect and heterogeneity on the gas flow is ignored
3. The gas present is considered to be ideal, with a gas deviation factor equalled to one
4. Isothermal conditions of flow are assumed throughout the reservoir
5. Formation rocks are considered incompressible and porosity is considered constant throughout the formation
6. Gas viscosity is also considered constant and does not change with pressure depletion
7. Langmuir isotherm is used to describe the gas adsorption and desorption phenomena in the reservoir, with instantaneous equilibrium achieved at any pressure.

![Figure 5.4 Gas storage in shale (Guo et al., 2015)](image)

**Table 5.2.1: flow regimes as a function of Knudsen number (Lee and Kim 2016)**

<table>
<thead>
<tr>
<th>Knudsen Number (Kn)</th>
<th>Flow regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10⁻³</td>
<td>Darcy flow (No slip)</td>
</tr>
<tr>
<td>10⁻³-10⁻¹</td>
<td>Slip Flow</td>
</tr>
<tr>
<td>10⁻¹-10⁻³</td>
<td>Transition flow</td>
</tr>
<tr>
<td>10⁻³-∞</td>
<td>Free –Molecular flow</td>
</tr>
</tbody>
</table>

The continuity equation for every grid block can be expressed in a general format as

\[
\frac{dM}{dt} + \nabla \cdot (\rho u) = Q
\]

………………………………………………………………………… (5.1)

\(M\) = mass accumulation term

\(\rho\) = density

\(u\) = velocity
\[ Q = \text{the source term} \]

\[ t = \text{time.} \]

The fracture–matrix interaction in shale gas reservoirs can be modelled either by using a dual continuum approach or by discrete fracture. A continuum approach, such as dual porosity and dual permeability, has been adopted over the discrete fracture model because it is less rigorous and not as computationally intensive compared to the discrete fracture model. Two mass balance equations can be obtained for both matrix and fracture systems (Warren and Root, 1963, see Figure 5.5).
Figure 5.5: Transport of gas through shale towards production (Modified from Guo et al., 2015)

\[
\left( \frac{dM}{dt} \right)_m + (\nabla \cdot (\rho u))_m = (Q)_m \tag{5.2}
\]
Where subscript \( m \) and \( f \) refers to the matrix and fracture respectively.

### 5.2.1 Mass Accumulation Term

The mass accumulation term can be expressed in a general form as

\[
M = \phi \sum S_g \rho_g 
\]

\[ \text{……………………………………………………………………………………………………………………………………………… (5.4)} \]

For a gas reservoir, \( S_g = 1 \), which refers to the fraction of pore volume occupied by the gas phase and subscript \( g \) refers to gas phase.

Considering the matrix system of shale gas reservoirs, the mass accumulation can be written for both free gas and adsorbed gas as follows:

\[
M_{\text{free}} = \phi \sum S_g \rho_g 
\]

\[ \text{……………………………………………………………………………………………………………………………………………… (5.5)} \]

\[
M_{\text{ads}} = \sum (1-\phi) q_{\text{ads}} 
\]

\[ \text{……………………………………………………………………………………………………………………………………………… (5.6)} \]

\[ \text{Where } q_{\text{ads}} \text{ is gas adsorption volume per unit bulk volume; this can be represented by the use of Langmuir isotherm.} \]

\[
q_a = \frac{\rho_s M_g V_{\text{std}}}{V_L P_L + P_m} 
\]

\[ \text{……………………………………………………………………………………………………………………………………………… (5.7)} \]

\[ \text{\( V_{\text{std}} \) = mole volume under standard conditions} \]

\[ \text{\( P_L \) = Langmuir pressure} \]

\[ \text{\( V_L \) = Langmuir volume} \]

\[ \text{\( \rho_s \) = density of shale} \]
\( p_m \) = pressure for the matrix

Combining the above equations, the mass accumulation for the matrix can be represented as

\[
M = \sum \left( \phi p_g + (1-\phi) q_{ads} \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.8)
\]

With the corresponding partial differential form given as

\[
\frac{dM}{dt} = \frac{\partial \left( \rho_g \phi \right)}{\partial t} + \frac{\partial \left[ (1-\phi) q_{ads} \right]}{\partial t} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.9)
\]

Using the equation of state (EOS), the density of the gas can be expressed as

\[
\rho_g = \frac{m}{V} = \frac{pM}{ZRT} = \frac{\gamma}{Z} p \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.10)
\]

For an ideal gas,

\[
\rho_g = \gamma p \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.11)
\]

\[
\frac{\partial q_{ads}}{\partial t} = \frac{\partial q_{ads}}{\partial p_m} \cdot \frac{\partial p_m}{\partial t} = -\frac{\partial}{\partial p_m} \left( \frac{\rho_g M}{V_{std}} V_L P_m \right) \cdot \frac{\partial p_m}{\partial t} = \frac{MP_L V_L \rho_s}{V_{std} (P_L + P_m)^2} \frac{\partial p_m}{\partial t} \quad \ldots \ldots \ldots (5.12)
\]

Therefore, the accumulation term for the matrix can be expressed as

\[
\left( \frac{dM}{dt} \right)_m = -\frac{\partial}{\partial p_m} \left( \frac{\rho_g M}{V_{std}} V_L P_m \right) \cdot \frac{\partial p_m}{\partial t} = \left[ \gamma \phi_m + \frac{(1-\phi_m)MP_L V_L \rho_s}{V_{std} (P_L + P_m)^2} \right] \frac{\partial p_m}{\partial t} \quad \ldots \ldots \ldots (5.13)
\]

Due to the presence of only free gas within the fracture system, the mass accumulation can be expressed as

\[
\left( \frac{dM}{dt} \right)_f = \frac{\partial (\rho_g \phi)}{\partial t} = \left[ \gamma \phi_f \right] \frac{\partial p_L}{\partial t} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.14)
\]

### 5.2.2 Flow Vector Term

Gas flow in shale gas reservoirs is distinguished by flowing media such as the matrix and fracture system (Guo et al., 2015). The flow occurs from the matrix to the fractures and then subsequently to the wellbore for production (see fig 5.5).
Assuming the gravity term is ignored in a gas system due to low density of the fluid, Darcy’s law can be written without the gravity term

\[ u = -\frac{1}{\mu} K. (\nabla p) \] .......................... (5.15)

\( K \) = permeability tensor.

\[ \nabla (\rho u) = -\nabla \left( \rho \left( \frac{1}{\mu} K \nabla p \right) \right) \] .................................(5.16)

However, due to the nanopores network in shale, conventional Darcy law cannot be used to represent the flow process in the matrix. Gas transport in nanopores includes mechanisms such as Knudsen diffusion, viscous flow and slip flow (see Fig. 5.6)

\( \text{Figure 5.6: Gas flow mechanism in a nano pore. Red dots are Knudsen diffusion while blue dots are viscous flow. (Guo et al, 2015)} \)

When the Knudsen number is less than one, flow is normally described as viscous flow that is that the mean free path of the gas is smaller compared to the pore diameter. The viscous flow caused by pressure gradient can be described by Darcy law (Kast and Hohenthanner, 2000).

Knudsen diffusion is more likely to occur when the pore diameter is small enough so that the mean free path of the gas is close to the pore diameter, that is, that the Knudsen number will be greater than 1. In such circumstances, the collision between the gas molecules and the
wall surfaces dominates. The gas mass flow can be expressed by the Knudsen diffusion (Kast and Hohenthanner, 2000).

However, slip flow occurs in low permeability formations or under very low-pressure conditions. It is therefore important to take into account the Klinkenberg effect (Klinkenberg, 1941; Sakhaee-Pour and Bryant, 2012)

The apparent permeability is expressed as

\[ k_m = k_{mi} \left( 1 + \frac{b_m}{P_m} \right) \] ..........................(5.17)

\[ b_m = \frac{16 \mu}{3 r_f^2} \left( \frac{8 RT}{\pi M} \right)^{0.5} + \left( \frac{8 \pi RT}{M} \right) \frac{\mu}{r} \left( 2 - \alpha \right) \] ..........................(5.18)

Therefore, the flow vector term for the matrix can now be expressed as

\[ \nabla (\rho u) = -\nabla \left( \rho \frac{k_m}{\mu} \nabla P_m \right) = -\nabla \left( \gamma P_m \left( \frac{k_m}{\mu} \nabla P_m \right) \right) \] ..........................(5.19)

Viscous flow and Knudsen diffusion occurs in the fracture and hence has been included by Guo et al., (2015). Considering these two flow terms, the mass flux can be represented by the summation of these mechanisms.

\[ J_f = J_{fi} + J_{kf} = -\frac{\rho_f}{\mu} \frac{k_f}{\mu} \nabla P_f - \frac{\rho_f D_{sf}}{p_f} \nabla P_f \] ..........................(5.20)

\[ J_f = -\frac{k_{sf} \rho_f}{\mu} \left( 1 + \frac{b_{sf}}{p_f} \right) \nabla P_f \] ..........................(5.21)

Expressing Equation 4.1.21 in the form of the conventional Darcy flow equation, the fracture apparent permeability can be expressed as

\[ k_f = k_{sf} \left( 1 + \frac{b_{sf}}{p_f} \right) \] ..........................(5.22)

\[ b_f = \frac{D_{sf} \mu}{k_{sf}} \] ..........................(5.23)

\[ D_{sf} = \frac{4k_f}{2.8284} \sqrt{\frac{\pi RT}{k_f \phi_f}} \] ............................(5.24)

\( p_j \) = fracture pressure

\( k_{fi} \) = initial fracture permeability

\( k_f \) = apparent fracture permeability

\( b_f \) = Klinkenberg coefficient for the fracture system

\( D_{sf} \) = Knudsen diffusion coefficient for the fracture system

\( \phi_f \) = fracture porosity

Finally, combining all the above equations results in the flow vector term being defined for the fracture as

\[ \nabla \cdot (\rho u) = -\nabla \cdot \left( \rho_f \left( \frac{k_f}{\mu} \nabla p_f \right) \right) = -\nabla \cdot \left( \gamma p_f \left( \frac{k_f}{\mu} \nabla p_f \right) \right) \] .............................(5.25)

### 5.2.3 Source and Sink Term

In shale gas reservoirs, the dominating factor that ensures the production of shale gas is the fracture system. The matrix system also plays an important role in production, as fluids are transferred from the matrix and consequently into the fracture for production. It is therefore critical that the interaction between the matrix and fracture system is well modelled in the case of a dual porosity continuum system. Kazemi et al., (1976) and Warren and Root (1963) proposed a method to help calculate the cross-flux that results between the matrix and the fracture by assuming that flow occurs in a pseudo-steady state with a confined boundary. The transfer of gas between the matrix and the fracture is therefore represented as

\[ T = \frac{k_i \rho \sigma (p_m - p_f)}{\mu} \] .................................(5.26)
\[ \sigma = 4 \left( \frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right) \] .........................................................(5.27)

The fracture spacing in the \( x \), \( y \) and \( z \) directions are represented by \( L_x, L_y, L_z \) respectively.

\( \sigma \) is the crossflow coefficient

Since fluid will be flowing out from the matrix into the fractures, the sink term for the matrix can be described as

\[ Q_m = -T \] .................................................................(5.28)

By producing from a vertical well in the fracture system, the model developed by Aronofsky and Jenkins (1954) is

\[ q_p = \frac{k_f \rho_f}{\mu} \frac{\theta}{\ln \left( \frac{r_x}{r_w} \right) + s + D_q} \left( p_f - p_{wf} \right) \] ................................(5.29)

For a well located at the corner, \( \theta = \pi / 2 \), and for a production well located in the centre, \( \theta = 2\pi \).

The drainage radius can be defined where \( k_x = k_y \) as

\[ r_x = 0.14 \sqrt{2 \left[ (\Delta x)^2 + (\Delta y)^2 \right]} \] ......................................................... (5.30)

\( \Delta x, \Delta y \) refers to the length of the grid.

The source/sink term for the fracture system can therefore be expressed as

\[ Q_f = T - q_q \] ................................................................. (5.31)

Finally, to characterise gas flow through shale gas reservoirs, the partial differential equation model can be expressed as:

For a matrix system:
\[
\left[ \gamma \phi_m + \frac{(1-\phi_m)MPV_c\rho_L}{V_{m0} (P_L + P_m)^2} \right] \frac{\partial p_m}{\partial t} - \nabla \left( \gamma \left( \frac{k_m}{\mu} \nabla p_m \right) \right) = -T \quad \text{.......................... (5.32)}
\]

Or

\[
\left[ \gamma \phi_m + \frac{(1-\phi_m)MPV_c\rho_L}{V_{m0} (P_L + P_m)^2} \right] \frac{\partial p_m}{\partial t} - \nabla \left( \gamma \left( \frac{k_m(p_m + b_m)}{\mu} \nabla p_m \right) \right) = -T \quad \text{..........................(5.33)}
\]

For a fracture system:

\[
\left[ \gamma \phi_f \right] \frac{\partial p_f}{\partial t} - \nabla \left( \gamma p_f \left( \frac{k_f}{\mu} \nabla p_f \right) \right) = T - q_f \quad \text{..........................(5.34)}
\]

or

\[
\left[ \gamma \phi_f \right] \frac{\partial p_f}{\partial t} - \nabla \left( \gamma p_f \left( \frac{k_f (p_f + b_f)}{\mu} \nabla p_f \right) \right) = T - q_f \quad \text{..........................(5.35)}
\]

The boundary conditions considered for this study are:

Initial conditions: \( p_m(x, y, t)|_{t=0} = p_f(x, y, t)|_{t=0} = p_i \quad \text{..........................(5.36)} \)

Boundary conditions for matrix: \( F_m, n \mid_{r=1} = 0 \left( \frac{\partial p}{\partial n} \right) \mid_{r=1} = 0 \quad \text{..........................(5.37)} \)

Boundary conditions for fracture: \( F_f, n \mid_{r=2} = 0 \left( \frac{\partial p}{\partial n} \right) \mid_{r=2} = 0 \), \( p_f(x, y, t) \mid_{r=2} = p_w \quad \text{..........................(5.38)} \)
5.3 Discretization and Implementation

In reservoir simulation, the finite difference approach is the most widely adopted numerical technique used. Other numerical techniques include the finite element and finite volume method. The Finite difference approach offers great flexibility when handling a nonlinear partial differential equation. The set of governing equations can be converted into both a spatial and time discrete form. 1-D finite difference method have been applied on the system of equations in this chapter for the purpose of showing the formulation and derivation of the final discretised equations, however the actual simulation was achieved with a 2-D formulation as shown in Appendix 5. The Central difference scheme is used for spatial discretization of both the first and second order derivative terms, as follows:

\[
\frac{\partial p}{\partial x} = \frac{p_{i+1} - p_{i-1}}{2\Delta x} \quad \text{..................}(5.39)
\]

\[
\frac{\partial^2 p}{\partial x^2} = \frac{p_{i+1} - 2p_i + p_{i-1}}{\Delta x^2} \quad \text{..................}(5.40)
\]

For the time derivative, a backward difference scheme is adopted, which gives rise to an implicit backward difference method.

\[
\frac{\partial p}{\partial t} = \frac{p_{i}^{n+1} - p_{i}^{n}}{\Delta t} \quad \text{..................} \quad (5.41)
\]

Applying the above difference schemes to the systems of equations 5.33 - 5.38 results in the following approximation:

Matrix system:

\[
\left[ \gamma \phi_m + \frac{(1-\phi_m)M_P V_f \rho_f}{V_{sat} (P_L + P_m)^2} \right] \frac{\partial p_m}{\partial t} - \nabla \left( \gamma \left( \frac{k_m (p_m + b_m)}{\mu} \nabla p_m \right) \right) = -\frac{k_m \rho_s \sigma (p_m - p_f)}{\mu_k}
\]
\[ f = \left[ C + \frac{B}{(P_L + U_i^{n+1})^2} \right] \left( \frac{U_i^{n+1} - U_i^n}{\Delta t} \right) - A \left[ \frac{U_i^{n+1} - U_i^{n-1}}{(2\Delta x)} \right]^2 - AU_i^{n+1} \left[ \frac{U_i^{(n+1)} + U_i^{(n-1)} - 2U_i^{(n)}}{\Delta x^2} \right] \]
\[ -E \left[ \frac{U_i^{(n+1)} + U_i^{(n-1)} - 2U_i^{(n)}}{\Delta x^2} \right] + DU_i^{n+1} \left( U_i^{n+1} - V_i^{n+1} \right) = 0 \]

\[ \text{Where } p_m = U, \ p_f = V, \ \gamma \phi_f = C, \ \frac{(1-\phi_m)MP_iV_i}{V_{std}} = B, \ \gamma \frac{k_m}{\mu} = A, \ p_m = U, \ p_f = V, \]
\[ \frac{k_m\gamma}{\mu_g} = D, \ A_b = E \]

Fracture system:
\[ \left[ \gamma_f \right] \frac{\partial p_f}{\partial t} - \nabla \left( \gamma \left( \frac{k_f(p_f + b_f)}{\mu} \nabla p_f \right) \right) = \frac{k_m\gamma}{\mu_g} \left( p_m - p_f \right) - q_q, \ \text{\\ } \text{\\ } \text{\\ } \text{\\ } \text{\\ } \text{(5.43)} \]
\[ f_i = K \left( \frac{V_i^{n+1} - V_i^n}{\Delta t} \right) - A^i \left( \frac{V_i^{n+1} - V_i^{n+1}}{2\Delta x} \right)^2 - AV_i^{(n+1)} \left( \frac{V_i^{n+1} + V_i^{n+1} - 2V_i^{n+1}}{(\Delta x)^2} \right) - F \left( \frac{V_i^{n+1} + V_i^{n+1} - 2V_i^{n+1}}{(\Delta x)^2} \right) \]
\[ -DV_i^{n+1} \left( U_i^{n+1} - V_i^{n+1} \right) = 0 \]

\[ \text{Where } p_m = U, \ p_f = V, \ \gamma \phi_f = K, \ \gamma \frac{k_m}{\mu} = A^i, \ p_m = U, \ p_f = V, \ \frac{k_m\gamma}{\mu_g} = D, \ q_q = 0 \]
\[ A^ib_f = F, \]

5.3.1 Newton Method
The newton iterative method is used to solve systems of equation involving nonlinear partial differential equations. The Newton Method is known to give second order convergence or quadratic convergence. The idea of a quadratic convergence means fewer iterations may be required, compared to other methods that might have much lower convergence rate before a solution is reached. This method is thus less complicated when compared with other methods, and it can also be easily applied to a variety of other problems. However, one key
problem associated with the Newton method has to do with the fact that convergence might not always be achieved, and it is highly sensitive to the initial guess used.

For a system of nonlinear equations with \( N \) unknowns, they can be represented by a multidimensional function as

\[
\begin{align*}
 f_1 (\phi_1, \phi_2, \ldots, \phi_N) &= 0 \\
 f_2 (\phi_1, \phi_2, \ldots, \phi_N) &= 0 \\
 \vdots & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots
\end{align*}
\]

By denoting the unknowns as \( [\phi] \) and giving an initial solution guess to be \( [\phi^{(0)}] \), the Taylor series for the system of equation can be written

\[
\begin{align*}
 f_1 (\phi_1, \phi_2, \ldots, \phi_N) &= f_1 (\phi_1^{(0)}, \phi_2^{(0)}, \ldots, \phi_N^{(0)}) + \left. \frac{\partial f_1}{\partial \phi_1} \right|^{(0)} \Delta \phi_1 \\
 &+ \left. \frac{\partial f_1}{\partial \phi_2} \right|^{(0)} \Delta \phi_2 + \ldots + \left. \frac{\partial f_1}{\partial \phi_N} \right|^{(0)} \Delta \phi_N + \ldots = 0 \\
 \vdots & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots
\end{align*}
\]

\[
\begin{align*}
 f_2 (\phi_1, \phi_2, \ldots, \phi_N) &= f_2 (\phi_1^{(0)}, \phi_2^{(0)}, \ldots, \phi_N^{(0)}) + \left. \frac{\partial f_2}{\partial \phi_1} \right|^{(0)} \Delta \phi_1 \\
 &+ \left. \frac{\partial f_2}{\partial \phi_2} \right|^{(0)} \Delta \phi_2 + \ldots + \left. \frac{\partial f_2}{\partial \phi_N} \right|^{(0)} \Delta \phi_N + \ldots = 0 \\
 \vdots & \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots
\end{align*}
\]

\[
\begin{align*}
 f_3 (\phi_1, \phi_2, \ldots, \phi_N) &= f_3 (\phi_1^{(0)}, \phi_2^{(0)}, \ldots, \phi_N^{(0)}) + \left. \frac{\partial f_3}{\partial \phi_1} \right|^{(0)} \Delta \phi_1 \\
 &+ \left. \frac{\partial f_3}{\partial \phi_2} \right|^{(0)} \Delta \phi_2 + \ldots + \left. \frac{\partial f_3}{\partial \phi_N} \right|^{(0)} \Delta \phi_N + \ldots = 0 \quad \text{............... (5.46)}
\end{align*}
\]
The matrix form of Equation 5.46 can be written as

\[
\begin{bmatrix}
\frac{\partial f_1}{\partial \phi_1} |^{(0)} & \frac{\partial f_1}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_1}{\partial \phi_N} |^{(0)} \\
\frac{\partial f_2}{\partial \phi_1} |^{(0)} & \frac{\partial f_2}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_2}{\partial \phi_N} |^{(0)} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial f_N}{\partial \phi_1} |^{(0)} & \frac{\partial f_N}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_N}{\partial \phi_N} |^{(0)} \\
\end{bmatrix}
\begin{bmatrix}
\Delta \phi_1 \\
\Delta \phi_2 \\
\vdots \\
\Delta \phi_N \\
\end{bmatrix}
= 
\begin{bmatrix}
-f_1(\phi_1, \phi_2, \ldots, \phi_N) \\
-f_2(\phi_1, \phi_2, \ldots, \phi_N) \\
\vdots \\
-f_N(\phi_1, \phi_2, \ldots, \phi_N) \\
\end{bmatrix}
\]

\[
\Delta \phi_i = \phi_i - \phi_i^{(0)} \quad \text{Represents the change in the solution from one iteration to the next.}
\]

\[
[J] \quad \text{is the Jacobean matrix for the Newton method containing the partial derivatives from Equation 5.45 above.}
\]

\[
\begin{bmatrix}
\frac{\partial f_1}{\partial \phi_1} |^{(0)} & \frac{\partial f_1}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_1}{\partial \phi_N} |^{(0)} \\
\frac{\partial f_2}{\partial \phi_1} |^{(0)} & \frac{\partial f_2}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_2}{\partial \phi_N} |^{(0)} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial f_N}{\partial \phi_1} |^{(0)} & \frac{\partial f_N}{\partial \phi_2} |^{(0)} & \cdots & \frac{\partial f_N}{\partial \phi_N} |^{(0)} \\
\end{bmatrix}
\]

Hence the updated formula for Newton’s method is as follows

\[
[J]^{(n)} [\Delta \phi]^{(n)} = -[J]^{(n)} \quad \text{........................................(5.49)}
\]

Where \([\Delta \phi]^{(n)} = [\Delta \phi]^{(n+1)} - [\Delta \phi]^{(n)}\)

Finally, the algorithm for the implementation of Newton’s method for a system of nonlinear equations can be represented in the following steps.
Step 1: Guess an initial root: \( \phi = [\phi]^{(0)} \)

Step 2: Determine the Jacobian matrix for the system of equations: \( [J] \)

Step 3: Solve \( [J]^{(n)} [\Delta \phi]^{(n)} = -[J]^{(n)} \) ideally iterative solver must be used with convergence checks implemented within this step

Step 4: Update results by introducing a relaxation factor \( \omega \):

\[
[\phi]^{(n+1)} = [\phi]^{(n)} + (\omega [\phi]^{(n+1)} - [\phi]^{(n)})
\]

Step 5: Repeat Steps 3 and 4 until convergence.

Computing the Jacobian for the Matrix results in

\[
\frac{\partial f}{\partial U_i} = -\frac{2B(U_{i+1}^{n+1} - U_i^n)}{\Delta t (P_L + U_{i+1}^{n+1})^2} + \frac{C + B}{\Delta t} - A \left( \frac{U_{i+1}^{n+1} + U_{i+1}^{n+1} - 2U_i^{n+1}}{(\Delta x)^2} \right) + \frac{2A}{(\Delta x)^2} U_i^{n+1} + \frac{2E}{(\Delta x)^2} \quad \text{-Diagonal} \quad \text{(5.50)}
\]

\[
\frac{\partial f}{\partial U_{i+1}} = -\frac{1}{2} A \left( \frac{U_{i+1}^{n+1} - U_{i+1}^{n+1}}{(\Delta x)^2} \right) - A \left( \frac{U_{i+1}^{n+1}}{(\Delta x)^2} \right) - E \quad \text{-Upper diagonal} \quad \text{(5.51)}
\]

\[
\frac{\partial f}{\partial U_{i-1}} = \frac{1}{2} A \left( \frac{U_{i+1}^{n+1} - U_{i+1}^{n+1}}{(\Delta x)^2} \right) - A \left( \frac{U_{i+1}^{n+1}}{(\Delta x)^2} \right) - E \quad \text{-Lower diagonal} \quad \text{(5.52)}
\]

Computing the Jacobian for the Fractures results in

\[
\frac{\partial f_i}{\partial V_i} = \frac{K}{\Delta t} - A^i \left( \frac{V_{i+1}^{n+1} + V_{i-1}^{n+1} - 2V_i^{n+1}}{(\Delta x)^2} \right) + \frac{2A^i}{(\Delta x)^2} V_i^{(n+1)} + \frac{2F}{(\Delta x)^2} - D(U_i^{n+1} - V_i^{n+1}) \quad \text{-Diagonal} \quad \text{(5.53)}
\]

\[
\frac{\partial f_i}{\partial V_{i+1}} = \frac{1}{2} A^i \left( \frac{V_{i+1}^{n+1} - V_{i+1}^{n+1}}{(\Delta x)^2} \right) - A^i \left( \frac{V_{i+1}^{n+1}}{(\Delta x)^2} \right) - \frac{F}{(\Delta x)^2} \quad \text{-Upper diagonal} \quad \text{(5.54)}
\]
\[
\frac{\partial f_i}{\partial V_{i+1}} = \frac{1}{2} \frac{A^1}{(\Delta x)^2} (V_{i+1} - V_{i+1}^\prime) - \frac{A^1}{(\Delta x)^2} V_i^{n+1} - \frac{F}{(\Delta x)^2} \quad \text{Lower diagonal .......... (5.55)}
\]

The above-noted Jacobean for the shale matrix and fracture PDE can now be used to set up Jacobean matrices in Equation 5.48.

### 5.3.2 Solution Method of Coupled Nonlinear PDE

There are two main approaches to solving a set of coupled partial differential equations (PDEs): the segregated solution approach and the coupled solution approach (Mazumder, 2016). The segregated solution approach has been adopted for the solution of the two nonlinear PDEs involving the matrix and fracture of the shale rock. This method involves solving each individual PDE sequentially and in isolation. To address the coupling between the two PDEs, the sequence of the solution is normally enclosed within an outer loop. Each inner iteration is continued until the PDEs have attained partial convergence. The main advantage of using this method over the coupled solution approach is its modularity (Mazumder, 2016). That is, the code written for the solution of the two PDEs can easily be extended to include other PDEs. For instance, the isothermal code written for the two nonlinear PDEs can be extended to include heat transfer. Fig. 5.7 shows the schematic representation of the segregated solution approach.
5.3.3 Validation of Numerical Method with Analytical method

Engineering predictions and decisions are sometimes based on computational models that are deemed robust and have also been validated. Computational models’ results are sometimes checked for reliability and consistency by validating the results with either a physical model or actual field data. This allows for decisions related to engineering processes to be made with confidence.

Guo et al., (2015) noted that there are no real field data that are similar to the theoretical case developed above for the governing mathematical equations; it is expected that the analytical results can be compared with the numerical simulation to verify the accuracy of the results. Guo et al., (2015) adopted the approach of validating the numerical method by simplifying Equation 5.42 into a one dimensional, linear, horizontal and steady state flow condition (See Equation 5.56). The results obtained can be compared with the analytical solution derived by Wu et al., (1998) for a 1D steady state gas transport. Thus, in this research, similar approach to Guo et al., (2015) have been adopted to validate the numerical method.
\[
\frac{\partial}{\partial x} \left( \frac{k_\beta (P + b) \partial P}{\mu} \right) = 0 \quad \text{(5.56)}
\]

The boundary conditions given for the solution of the steady-state gas transport are:

A constant mass injection rate \( q_m \) per unit cross-sectional area is imposed at the inlet \( (x = 0) \), and

Gas pressure is kept constant at the outlet \( (x = L) \). The analytical solution is given by Wu et al., (1998) as

\[
p(x) = -b + \sqrt{b^2 + \left( p(L)^2 + 2b[p(L)] + \frac{2q_m u_s (L - x)}{k_\beta} \right)} \quad \text{............... (5.57)}
\]

The results from numerical simulation of Equation 5.56 (See Figure 5.8) show a clear and exact match to the analytical solution developed by Wu et al. (1998), implying that the model is capable of representing the flow conditions in a shale gas reservoir.
Figure 5.8: Comparison of numerical and analytical solutions for steady state gas flow in a finite linear system.
5.4 Results and Discussion

5.4.1 Simulation Study I

Bustin et al., (2008) and Guo et al., (2015) presented numerical data that could be used for numerical examples involving the flow of gas in shale gas reservoirs. Table 5.1 provides the rock properties and fluid properties used in the simulation. Gas production is considered from the fracture systems due to the higher permeability compared with the matrix systems. A single well is drilled in the middle of the domain, as illustrated in Fig 5.9, to be a producer well. A 2-D reservoir model with dimensions of 160ft x 160ft has been discretized into 51 x 51 uniform grids. It is assumed that only a single gas (methane) phase is present and that the gas adsorption and desorption obey the Langmuir isotherm with constant temperature. The duration of the numerical simulation has been set to 2.7 years (1000 days). All the simulation in chapter 5 and 6 have been conducted using high level programming language MATLAB. MATLAB is an efficient programming tool for solving numerical problems especially non-linear partial differential equations compared to other programming language. No commercial simulator has been used throughout this study.

![Figure 5.9: Schematics of numerical experiment with single well production](image)

Figure 5.9: Schematics of numerical experiment with single well production
Table 5.1: Parameters used in the simulation model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir depth</td>
<td>5463 ft</td>
</tr>
<tr>
<td>Pressure gradient</td>
<td>0.54 psi/ft</td>
</tr>
<tr>
<td>Temperature</td>
<td>579.6 °R</td>
</tr>
<tr>
<td>Matrix initial permeability</td>
<td>0.04 mD</td>
</tr>
<tr>
<td>Fracture initial permeability</td>
<td>10 mD</td>
</tr>
<tr>
<td>Matrix porosity</td>
<td>0.05</td>
</tr>
<tr>
<td>Fracture porosity</td>
<td>0.001</td>
</tr>
<tr>
<td>Initial reservoir pressure</td>
<td>1508 psia</td>
</tr>
<tr>
<td>Bottomhole pressure</td>
<td>500 psia</td>
</tr>
<tr>
<td>Molecular Weight (CH4)</td>
<td>0.016 lb/lb mole</td>
</tr>
<tr>
<td>Standard gas volume</td>
<td>0.7910 scf/mol</td>
</tr>
<tr>
<td>Langmuir pressure</td>
<td>300 psia</td>
</tr>
<tr>
<td>Langmuir volume</td>
<td>0.0448 gmol/lb</td>
</tr>
<tr>
<td>Shale rock density</td>
<td>159.19 lb/scf</td>
</tr>
<tr>
<td>Initial gas viscosity</td>
<td>0.0102 cp</td>
</tr>
<tr>
<td>Wellbore radius</td>
<td>0.328 ft</td>
</tr>
<tr>
<td>Fracture spacing</td>
<td>0.656 ft</td>
</tr>
</tbody>
</table>

Figs. 5.10 and 5.11 show the pressure distribution in the matrix and fractures after a period of 1000 days of production. It can be observed that pressures in both cases have reached the value of bottomhole pressure. The pressure distribution shows a slight decrease towards the centre of the domain where the well is located (see Figs. 5.10-5.11). Production rate and eventual cumulative production over the period of simulation are shown in Figs. 5.12 and 5.13.
Figure 5.10: Fracture pressure at the end of simulation (2.7 years)
The gas production rate results show an initially high production followed by a gradual decline in production with time, over the life of the field (see Fig. 5.12). The effect of several reservoir parameters has been evaluated to show how they impact on gas production in shale gas reservoirs. These include the effect of matrix and fracture porosity and permeability.
Figure 5.12: Gas production rate for a shale gas model

Figure 5.13: Cumulative production of gas for a shale gas model

5.4.2 Effect of Gas Adsorption
To illustrate the effect of gas adsorption on production rate and cumulative production, simulation studies were conducted, first by considering only the free gas present in the system. Thus, the total gas in place was considered to be made up of only the free gas. The
second simulation was conducted by incorporating an adsorption term defined by Langmuir
isotherm. This meant that the total gas in place was now a combination of both free gas and
adsorbed gas. Simulation results in Figs. 5.14 and 5.15 show the effect of considering the
production rate and cumulative production in the system with and without adsorption. It can
be observed that with the inclusion of gas adsorption defined by Langmuir isotherm, the
production rate increases significantly, whereas without the adsorption term, production
could be underestimated. Thus it can be concluded that gas adsorption in shale gas reservoirs
will have a great effect on overall production from the reservoir. It is important to note that
there was a significant contribution from desorption at the early stage of production from
Figure 5.14 due to the choice of a much lower bottomhole pressure. The lower bottomhole
pressure meant more gas could be desorbed and consequently produced compared in a real
case where bottomhole pressure might be higher and may take considerable time to drop to
the economic shut in pressure. In such instance, the influence of gas desorption will be felt at
later stages of production. A higher pressure value might have resulted in a solution closer to
the actual case, however due to the numerical set up of this study and the fact that newton’s
method requires a selection of an initial guess closer to the actual solution, it meant that
choosing any other pressure value may have resulted in convergence issues causing the
simulation not to reach full convergence.
Figure 5.14: Gas production rate with and without adsorption

Figure 5.15: Cumulative production rate with and without adsorption
5.4.3 Effect of Matrix and Fracture Porosity
To study the effect of porosity on production from shale gas reservoirs, different porosity values have been chosen for both the matrix and fracture porosity. Porosity defines the amount of gas that can be stored in the reservoir. For shale gas reservoirs, the matrix porosity has a greater influence on production than the fracture porosity. Figs. 5.16 and 5.17 shows that an increase in porosity leads to increase in production rate, and Figs. 5.16-5.19 show that matrix porosity has a significant effect on shale gas production, compared with fracture porosity. This difference confirms the idea of the dual porosity model being incorporated into the shale gas model where the matrix system is the main storage space for the gas.

![Figure 5.16: Effect of matrix porosity on gas production rate](image)

*Figure 5.16: Effect of matrix porosity on gas production rate*
Figure 5.17: Effect of matrix porosity on cumulative production

Figure 5.18: Effect of fracture porosity on gas production rate
5.4.4 Effect of Matrix and Fracture Permeability

In shale gas reservoirs, permeability has a great influence on production results. The effect of matrix permeability is different from the effect of fracture permeability. Matrix permeability is usually very small and hence will have the least effect on production results, whereas in shale gas reservoirs, fracture permeability contributes greatly to production from the reservoirs. Figs. 5.20-5.23 show that as the fracture and matrix permeability increases, production results also increase. The results from Figs. 5.20-5.23 also show that the main contributing channel towards production is from the fracture system.
Figure 5.20: Effect of matrix permeability on production rate

Figure 5.21: Effect of matrix permeability on cumulative production
Figure 5.22: Effect of fracture permeability on gas production

Figure 5.23: Effect of fracture permeability on cumulative gas production
5.5 Heat Transfer through a Porous Media

By the first law of thermodynamics, the total energy of a system is conserved; that is, the energy stored in a volume is equal to the energy that enters the volume, minus the amount of energy that leaves the volume. The internal energy of a system is therefore conserved and is equal to the sensible component of the thermal energy. The change in thermal energy can be described as the summation of the transport of energy by flow, change of energy by conduction and heat sources and the surroundings. The mathematical form of the above description can be seen as

\[ \phi \frac{d}{dt} \int_{\Omega} e dx - \phi \int_{\partial \Omega} q_{\text{adv}} nds - \phi \int_{\partial \Omega} q_{\text{cond}} nds + \int_{\Omega} Q_T dx \] .......................................................... (5.58)

\( e \) is the internal thermal energy density

\( n \) is the outward unit normal vector

\( Q_T \) is the energy production term in J/ (s.m3)

\( Q_T = \phi Q_{\text{source}} + Q_{\text{conv}} \) .......................................................... (5.59)

\( Q_{\text{conv}} = ah(T_m - T) \)

\( a \) is the specific surface area

\( h \) is the heat transfer coefficient

\( Q_{\text{conv}} \) is the rate of energy transfer per volume of the exchange from the solid to the fluid

Applying the divergence theorem on the surface integral, the volume integral can be expressed as

\[ \int_{\Omega} \left( \phi \frac{de}{dt} + \phi \nabla \cdot q_{\text{adv}} + \phi \nabla \cdot q_{\text{cond}} - Q_T \right) dx = 0 \] .......................................................... (5.60)

\[ \phi \frac{de}{dt} + \phi \nabla \cdot q_{\text{adv}} + \phi \nabla \cdot q_{\text{cond}} - Q_T = 0 \] .......................................................... (5.61)
By inserting the heat flux expressions:

\[
\frac{d\phi}{dt} + \phi \nabla (e V) - \phi \nabla (k T V) - Q_T = 0 \quad \text{.......................... (5.62)}
\]

\[
q_{\text{cond}} = -k_T \nabla T \quad \text{........................................ (5.63)}
\]

\[
q_{\text{adv}} = e V \quad \text{.................................................. (5.64)}
\]

\( V \) Intrinsic volume flux

\( k_T \) is thermal conductivity

The change in thermal energy density can be expressed as

\[
\Delta e = \rho c_p \Delta T \quad \text{.................................................... (5.65)}
\]

This is similar to the definition of the specific heat capacity, where the thermal energy required to raise the temperature of a volume with mass \( M \) by \( \Delta T \) degrees (Lampe, 2013) is given as

\[
\Delta U = M \rho c_p \Delta T \quad \text{..................................................... (5.66)}
\]

\( c_p \) is the specific heat capacity.

By replacing \( e \) in Equation 5.62 with Equation 5.65, and using the velocity term \( v \), the following expression can be obtained:

\[
\phi \rho c_p \frac{\partial T}{\partial t} + \rho c_p v \nabla T + \rho c_p T \Delta v - \phi \nabla (k_T \nabla T) - Q_T = 0 \quad \text{.......................... (5.67)}
\]

\( v \), actual velocity is related to the intrinsic velocity by the expression

\[
v = \phi V \quad \text{.................................................................(5.68)}
\]

Rearranging and applying the continuity equation results in the expression

\[
\phi \rho c_p \frac{\partial T}{\partial t} + \rho c_p v \nabla T = \phi \nabla (k_T \nabla T) - Q_T \quad \text{.......................... (5.69)}
\]
Equation 5.69 can therefore be assumed to be the energy equation for the gas phase. Similar derivation can be obtained for the matrix system except that no advective term is applied and the scale factor is now \((1 - \phi)\).

The two energy equations can therefore be written explicitly as

For matrix:

\[
(1 - \phi) \rho_m c_{p,m} \frac{\partial T_m}{\partial t} = (1 - \phi) \nabla \cdot (k_{T,m} \nabla T_m) + (1 - \phi) q^\cdot_m + ah(T_m - T_g) \tag{5.70}
\]

For the gas:

\[
(\phi) \rho_g c_{p,g} \frac{\partial T_g}{\partial t} + (\phi) \nabla \cdot (-k_{T,g} \nabla T_g) + \rho_g c_{p,g} \nabla T_g q^\cdot_g = \phi q^\cdot_g + ah(T_m - T_g) \tag{5.71}
\]

Where

\(q^\cdot_g\) is the velocity vector of the gas phase.

\(q^\cdot\) is the heat source term.

By assuming a local thermal equilibrium, the energy equation can easily be simplified at the walls of the pores by setting the relation \(T_m = T_g = T\), and by summing Equations 5.70 and 5.71, the following expression is obtained:

\[
(\rho c_p)_{\text{final}} \frac{\partial T}{\partial t} + \nabla \cdot (-K_{\text{final}} \nabla T) + \rho_c c_{p,g} q_g \nabla T = Q^\cdot \tag{5.72}
\]

Where

\[(\rho c_p)_{\text{final}} = (1 - \phi) \rho_m c_{p,m} + \phi \rho_g c_{p,g} \tag{5.73}\]

\[K_{\text{final}} = (1 - \phi) k_{T,m} + \phi k_{T,g} \tag{5.74}\]

\[Q^\cdot = (1 - \phi) q^\cdot_m + \phi q^\cdot_g \tag{5.75}\]

Equation 5.73 is similar to the volumetric heat capacity at constant pressure, Equation 5.74 is equivalent to thermal conductivity, and Equation 5.75, is the overall heat source.
According to Wang (2016), the heat capacity of most formations is at least 100 times larger than that of the gas phase, and since formation porosity of a shale formation is normally less than 3%, Equations 5.73-5.75 are dominated by the terms \((1-\phi)\rho_m c_{p,m}\), \((1-\phi)k_{T,m}\) and \((1-\phi)q_m^*\) respectively. Also, since the flow rate of the gas is limited by the low permeability of shale formation, and considering that the gas has low density, the term \(\rho_g c_{p,g} q_g \nabla T\) can be neglected in Equation 5.72.

Therefore, we can simplify equation 5.72 as the following:

\[
\left(\rho_m c_{p,m}\right)\frac{\partial T}{\partial t} + \nabla \cdot (-k_{T,m} \nabla T) = Q^* \quad \text{(5.76)}
\]

Equations 5.42, 5.43 and 5.76 can therefore be combined and with appropriate initial and boundary conditions, a complete description of the system coupled with heat can be achieved.

\[
\left[\gamma \phi_m + \frac{(1-\phi_m) MP_V \rho_s}{V_{slg} (P_L + p_m)^2}\right] \frac{\partial p_m}{\partial t} - \nabla \cdot \left[\gamma \left(\frac{k_m (p_m + b_m)}{\mu} \nabla p_m\right)\right] = -T \quad \text{(5.77)}
\]

\[
\left[\gamma \phi_f \right] \frac{\partial p_f}{\partial t} - \nabla \cdot \left[\gamma p_f \left(\frac{k_f (p_f + b_f)}{\mu} \nabla p_f\right)\right] = T - q_q \quad \text{(5.78)}
\]

\[
\left(\rho_m c_{p,m}\right)\frac{\partial T}{\partial t} + \nabla \cdot (-k_{T,m} \nabla T) = Q^* \quad \text{(5.79)}
\]

Note: Assumptions have been made to simplify the gas properties and flow equations. In general, gas flow in deep pressurized reservoirs does not follow the ideal gas law, and the variations of pressure around gas production wells are too large to use constant properties.
5.5.1 Fully Implicit Method for the Heat Equation

Since the heat equation introduced in this chapter is a linear PDE, use can be made of the fully implicit discretization method to solve for the temperature distributions within the reservoir.

The discretized form of the heat equation can be written as:

\[ \frac{T_{i,j}^{n+1} - T_{i,j}^n}{\Delta t} = k \left( \frac{T_{i+1,j}^{n+1} - 2T_{i,j}^{n+1} + T_{i-1,j}^{n+1}}{\Delta x^2} + \frac{T_{i,j+1}^{n+1} - 2T_{i,j}^{n+1} + T_{i,j-1}^{n+1}}{\Delta y^2} \right) + \frac{Q_{i,j}^n}{\rho m c_p} \] .......(5.80)

\[ S_x = \frac{k \Delta t}{\Delta x^2}, \text{ and } S_y = \frac{k \Delta t}{\Delta y^2} \]

Rearranging terms will result in

\[ -S_x T_{i+1,j}^{n+1} - S_y T_{i,j+1}^{n+1} = (1 + 2S_x + 2S_y)T_{i,j}^n + \frac{Q_{i,j}^n}{\rho m c_p} \] .......(5.81)

And finally, temperature distribution can be estimated as

\[ \frac{T_{i,j}^{n+1} + \frac{Q_{i,j}^n \Delta t}{\rho m c_p} + S_x T_{i+1,j}^{n+1} + S_y T_{i,j+1}^{n+1} + S_y T_{i,j-1}^{n+1} + S_x T_{i-1,j}^{n+1}}{\rho m c_p (1 + 2S_x + 2S_y)} \] .......(5.82)

5.5.2 Temperature – Dependent Variables

The introduction of temperature-dependent variables is needed in order to investigate the process of thermal stimulation applications in shale gas reservoirs. Thus, several temperature-dependent variables would have to be defined to enable the coupling of the previous governing equations for both the matrix and fracture systems with the heat equation. The key variables to be explored include the gas adsorption capacity and the viscosity of the gas, both of which are temperature dependent.

The most widely used adsorption model is the Langmuir isotherm. This model is able to describe the relationship between pressure and the adsorbed gas content as a function of pressure. The key disadvantage of this model is that it does not account for the effect of temperature on the adsorption of gas onto the shale matrix. To account for the effect of
temperature, several modifications of the Langmuir isotherm have been adopted and used in the coupling process.

The modified Langmuir model can be expressed as follows:

\[ V = \frac{\rho M_g}{V_{std}} \left( V_L \frac{bp}{1+bp} \right) \quad (5.83) \]

Where \( b = b_0 \exp\left(-\Delta H/RT\right) \)

Freundlich isotherm has been combined with Langmuir isotherm to account for the heterogeneity of the adsorbent (Fianu et al., 2018; Helminen et al., 2000). The variable \( n \) describes the degree of heterogeneity of the adsorbent. A value of \( n \) greater than one represents a highly heterogeneous adsorbent. The combined Langmuir-Freundlich model is:

\[ V = \frac{\rho M_g}{V_{std}} \left( V_L \frac{bp^n}{1+bp^n} \right) \quad (5.84) \]

Finally, to account for temperature dependency of the Langmuir volume \( V_L \), Ye et al., (2016) proposed an exponential model. The exponential model is expressed as:

\[ V = \frac{\rho M_g}{V_{std}} \left( V_s \frac{\exp\left(-D_T T\right) p}{p + \sqrt{T}} \right) \quad (5.85) \]

Where \( V_s \), \( D_T \), \( A \) and \( B \) are parameters to be determined by fitting the experimental adsorption data.

5.5.3 Gas Viscosity

Well established correlations have been used to derive gas viscosity. One of the most popular and comprehensive studies on the viscosities of natural gases was carried out by Lee et al., (1966). Their correlation can be used to calculate gas viscosities at pressures from 0.69 to 55.16MPa and temperatures from 310 to 455 K. This correlation is given below as:

\[ u_g = K \exp\left(X \rho^y\right) \quad (5.86) \]
Where

\[
K = \frac{(7.77 + 0.0063M)T^{1.5}}{122.4 + 12.9M + T}
\]

\[
X = 2.57 + \frac{1914.5}{T} + 0.0095M
\]

\[
Y = 1.11 + 0.04X
\]

**5.5.4 Z Factor Correlation**

There are several equations of states that can be solved to obtain the Z-factor or correlations. In this study, Hall and Yarborough’s correlation has been used to obtain the Z-factor.

\[
t = \frac{1}{T_{pr}}
\]

\[
A = 0.06125te^{-1.2(1-t)^2}
\]

\[
B = 14.76t - 9.76t^2 + 4.58t^2
\]

\[
C = 90.7t - 242.2t^2 + 42.4t^2
\]

\[
D = 2.18 + 2.82t
\]

\[-AP_{pr} + \frac{y + y^2 + y^3 - y^4}{(1-y)^3} - By^2 + Cy^3 = 0 \quad \text{..........................}(5.87)\]

\[
T_{pr} = \frac{T}{T_{pc}}
\]

\[
P_{pr} = \frac{P}{P_{pc}}
\]

\[z = \frac{AP_{pr}}{y}\]
5.6 Simulation Study II

With the introduction of temperature dependent variables, it is now possible to investigate the application of thermal stimulation in simulation study I. However, to do this, certain assumptions that were made for simulation study I would have to be altered. In particular, the model changes from an isothermal condition to a non-isothermal condition. Several temperature-dependent forms of the Langmuir isotherm are considered, and temperature effects on density and viscosity are also considered. Temperature effects increase the complexities in reservoir modelling and simulation because changes in the formation temperature have multiple effects on adsorption capacities and real gas properties, and can also induce thermal stress (Wang, 2016). The thermal properties used for the simulation of study II are shown in Table 5.2.

<table>
<thead>
<tr>
<th>Thermal Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Stimulation temperature</td>
<td>700°R</td>
</tr>
<tr>
<td>Formation-heat capacity</td>
<td>1000 J/K/Kg</td>
</tr>
<tr>
<td>Formation-heat conductivity</td>
<td>4 W/m/K</td>
</tr>
</tbody>
</table>

Under simulation study II, two different scenarios have been considered. Firstly, the adsorption/desorption relationship has been modelled using modified Langmuir model with temperature-dependent parameters to compare simulations with and without thermal stimulation. Secondary, different temperature-dependent gas adsorption models have been compared to understand their application in predicting future gas productions. An exponential model with temperature-dependent Langmuir volume and the Langmuir-Freundlich model have been considered. The simulation run has been conducted for 1000 days.

The reason for the choice of these two models stems from earlier studies in chapter 3, where several temperature-dependent adsorption models were applied to a wide range of shale gas datasets. In those studies, it was observed that Exponential model and Langmuir-Freundlich
model proved most accurate for a variety of the shale data, thus, including both models in the shale gas model to evaluate the thermal stimulation.

In scenario 1, Figs. 5.24 and 5.25 show the temperature distribution within the formation after 10 days and 1000 days of production. It can be observed that the heat propagation has increased from the initial temperature throughout the reservoir over the course of the production period. The gas production rate increased in the case of thermal stimulation, compared with when no thermal stimulation was applied. As has been mentioned earlier, the modified Langmuir model with a temperature-dependent gas adsorption model have been used in the simulation studies to represent the adsorption potential as a function of both pressure and temperature. The rate of propagation is, however, dependent on the thermal properties of the rock and the stimulation temperature that is used. A higher stimulation temperature will no doubt improve the temperature propagation throughout the formation. A much higher thermal conductivity will also imply an increase in the rate of heat propagation in the formation.

Figure 5.24: Temperature profile after 10 days of heating
Figure 5.25: Temperature profile after 1000 days of heating

Figure 5.26: effect of thermal stimulation on production rate
Figure 5.27 Effect of thermal stimulation on cumulative production

In scenario 2, the production profile from Figs. 5.28-5.29 shows the different production results using different temperature-dependent gas adsorption models. The results show that the choice of temperature-dependent model used in the simulation studies results in a different production recovery profile. This is because different temperature dependent models would extrapolate different adsorption capacities at different temperatures, as can be seen in Fig. 5.30. Temperatures have been extrapolated to 700°R, and from Fig. 5.30 it can be seen that the Exponential model predicted a much higher gas adsorption rate than the temperature-dependent forms of the Langmuir model and Freundlich model. The predictions of different gas adsorption at different temperatures affect the overall gas production from the system. As can be observed from Figs. 5.29 and 5.30, overall gas production rate and cumulative production over 1000 days was higher for the Exponential model compared with the temperature-dependent forms of Langmuir model and Langmuir-Freundlich model. There was a percentage decrease of about 0.008 % in the cumulative production of Langmuir model when compared with the Exponential model. Exponential model showed an increase of 0.032% in cumulative production compared with Bi-Langmuir model. Langmuir Model showed a 0.024% increase in overall cumulative production, compared with Bi-Langmuir
model. From Figure 5.30, it can be observed that exponential model predicted higher adsorption rate even at temperature of 700°R, compared with modified Langmuir and Langmuir–Freundlich models. This higher rate in gas adsorption at that temperature meant that more gas could be produced at the end of simulation. The fact that different models predicted different gas production at the end of simulation study suggests that care must be taken when choosing the model to use in reservoir simulation studies. Validation of models with multiple temperature as well as validation of extrapolated temperature for gas adsorption is needed before choosing a particular model to be used in predicting future gas production in shale gas reservoirs.

Figure 5.28: Gas adsorption at extrapolated temperature from 579.8°R to 700°R
Table 5.3: Best fitted parameters for Temperature dependent models at 700°R (Based on AAD%)

<table>
<thead>
<tr>
<th></th>
<th>Exponential Model</th>
<th>Langmuir-Freundlich Model</th>
<th>Langmuir Model(Temperature Dependent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Value</td>
<td>Parameters</td>
<td>Value</td>
</tr>
<tr>
<td>$V_s$ gmol/lb</td>
<td>0.05</td>
<td>$V_L$ gmol/lb</td>
<td>0.044811876</td>
</tr>
<tr>
<td>$D_i$</td>
<td>0.00004</td>
<td>$b_o$ 1/psi</td>
<td>7.42932E-05</td>
</tr>
<tr>
<td>$A$</td>
<td>7.75E-02</td>
<td>$\Delta H$ KJ/mol</td>
<td>-23667.6696</td>
</tr>
<tr>
<td>$B$</td>
<td>20.39</td>
<td>$n$</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_L$ gmol/lb</td>
<td>0.044799994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b_o$ 1/psi</td>
<td>0.000536127</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\Delta H$ KJ/mol</td>
<td>-11706.5652</td>
</tr>
</tbody>
</table>

Figure 5.29: Prediction of production rate by different temperature-dependent adsorption models
5.7 Summary

In this chapter, a mathematical model for simulation of shale gas reservoirs is developed. The model includes non-Darcy flow that occurs within the matrix of the shale. Two simulation studies were conducted, first to evaluate the effect of including adsorption in numerical simulation of shale gas reservoirs, and second to introduce the concept of temperature-dependent adsorption models in mathematical models for shale gas reservoirs. The results from simulation study I showed the following:

- Gas production increased as a result of simulation with adsorption rather than without adsorption. This showed that gas adsorption can affect the rate of gas production.
- Matrix porosity and fracture permeability have considerable influence in gas production. Thus, an increase in these two factors will cause an overall increase in gas production.
- Fracture porosity and matrix permeability had minimal influence on gas production in shale gas reservoirs. Any considerable increase will result in increase in the overall gas production.
In simulation study II, temperature-dependent gas adsorption models have been used in mathematical formulation to account for thermal stimulation in shale gas reservoirs. Different temperature-dependent gas adsorption models, including modified Langmuir temperature-dependent model, Exponential model with temperature-dependent Langmuir volume and combined Langmuir – Freundlich model, were included in the simulation studies to investigate future gas production. The results showed that:

- Thermal stimulation has the advantage of increasing cumulative gas production at the end of simulation window, compared with when no thermal stimulation was employed
- Different temperature dependent gas adsorption models predicted different cumulative gas production over the course of simulation
- There was a 0.032% increase in cumulative production using Exponential model compared with Bi-Langmuir model, and a decrease of 0.008% in cumulative production of Langmuir model when compared with the Exponential model. Langmuir model showed a 0.024% increase in cumulative production, compared with Bi-Langmuir model
- Validation of all the models with published data at multiple temperatures is necessary to ensure the most accurate model is used in simulation studies.
Nomenclature
M = mass accumulation term
\( \rho \) = density
\( u \) = velocity
\( Q \) = source term
\( t \) = time.
\( m \) = matrix
\( f \) = fracture
\( S_g \) = fraction of pore volume occupied by the gas phase
\( q_{ads} \) = gas adsorption volume per unit bulk volume
\( V_{std} \) = mole volume under standard conditions
\( P_L \) = Langmuir pressure
\( V_L \) = Langmuir volume
\( \rho_s \) = density of shale
\( p_m \) = pressure for the matrix
\( K \) = the permeability tensor
\( p_f \) = fracture pressure
\( k_p \) = initial fracture permeability
\( k_f \) = apparent fracture permeability
\( b_f \) = Klinkenberg coefficient for the fracture system
\( D_{lf} \) = Knudsen diffusion coefficient for the fracture system

\( \phi_f \) = fracture porosity

\( \sigma \) = crossflow coefficient

\( b \) = Klinkenberg factor

\( p(L) \) = gas pressure at the outlet

\( L \) = length from the inlet to the outlet

\( x \) = task location along the gas transport path

\( k_c \) = intrinsic permeability

\( \beta \) = compressibility factor

\( q_m \) = air injection rate

\( u_g \) = dynamic viscosity

\( e \) = internal thermal energy density

\( n \) = outward unit normal vector

\( Q_T \) = energy production term in J/(s.m3)

\( a \) = specific surface area

\( h \) = heat transfer coefficient

\( Q_{\text{conv}} \) = rate of energy transfer per volume of the exchange from the solid to the fluid

\( V \) = intrinsic volume flux

\( k_T \) = thermal conductivity

\( c_p \) = specific heat capacity
\( q \) = velocity vector of the gas phase.

\( \rho' \) = heat source term.
Chapter 6
Thermal Stimulation of Shale Gas Reservoirs Using Microwave Heating

6.1 Introduction
Thermal stimulation strategies have been used by several researchers as a way of improving oil recovery by increasing formation temperature. They have grown in prominence especially in unconventional reservoirs, such as heavy oil and shale oil. Recently, thermal stimulation has also been applied to coal bed methane reservoirs. The different kinds of thermal stimulation that are currently being used in unconventional reservoirs include cyclic steam injection, in-situ combustion and steam assisted gravity drainage (SAGD). Thermal stimulation as a means of enhanced oil recovery can account for about 60% of oil production in our world today (Chekhonin et al., 2012).

Though several studies have been conducted on how to improve heavy oil or shale oil recovery by elevating the formation temperature, very few have considered the implementation of similar thermal techniques as a way of enhancing gas recoveries (Lin et al., 2015).

In recent years, there have been developments in the use of coupled electromagnetic-thermal modelling to quantify and visualize microwave heating; however, these developments have been focused primarily on food, wood and minerals, with few applications in shale and coal (Li et al., 2017; Pitchai et al., 2016).

Wang (2016) demonstrated that the efficiency of thermal stimulation largely depends on the gas adsorption and rock properties of the formation. Thus by altering the gas adsorption/desorption behaviour through thermal stimulation, more gas could be recovered from hydraulically fractured shale gas reservoirs. Wang et al., (2015) also used similar techniques in coal bed methane reservoirs, by investigating the application of thermal stimulation of hydraulically fractured coalbed methane reservoir. Altering the gas adsorption and desorption behaviour through thermal stimulation in coal bed methane (CBM) has also resulted in increased gas recoveries. Studies conducted by Salmachi and Haghhighi (2012)
showed that as the formation temperature increased through a process of hot water injection for a period of 2 years, the gas adsorption/desorption process was altered. This led to an increase in methane production by 58% in 12 years of production. They argued that thermal treatment in CBM results in the breakdown of bonds between the gas molecules and surfaces, which ultimately alters the adsorption/desorption properties of the coal.

In-situ combustion has also been studied (Chapiro and Bruining, 2015) as a means of improving the permeability of shale gas reservoirs. Permeability is a key factor in improving the production from tight/shale gas reservoirs. An increase in permeability would cause the natural gas to flow more easily to the surface and hence recoveries would improve. The authors argued that the combination of hydraulic fracturing and horizontal drilling allowed more gas to be easily extracted from shale; however, the impact of this combination on the environment suggests that alternative techniques needs to be explored. Similar studies have also suggested that thermal stimulation of shale gas reservoirs can result in permeability improvements, just as with oil shales (Busch and Amann-Hildenbrand, 2013; Sanmiguel et al., 2002). According to Jamaluddin et al., (2000), thermal treatments in tight gas reservoirs enhance the permeability of the formation by vaporizing the capillary blocked water, dehydrating the clay bound water and creating thermally induced micro-fractures. Their studies demonstrated increase in permeability of 50% or more for core samples that were exposed to heat treatments.

In order to study shale gas interactions during microwave heating, a fully coupled electromagnetic-thermal model has been developed for this research. The development of such a coupled electromagnetic-thermal model enables the understanding of microwave heating with the mechanical model of shale gas considering non-Darcy effects. The effect of microwave frequency on temperature evolution and also on production have been studied. Free gas evolution during microwave heating, and also overall production with and without microwave heating, has been investigated.
6.2 Microwave Heating

There are three main kinds of electrical heating that are most used in the oil and gas industry as a stimulation strategy for improved production. These are low frequency electric heating, inductive heating where an alternating current is used, and high frequency heating in the form of microwaves (Sahni et al., 2000). Microwaves are electromagnetic waves that have frequency range between 300 MHz and 300 GHz with wavelength of 1 mm to 1m (Denny, 2007). The applications of microwave technology are varied, ranging from food processing and pharmaceuticals to wood processing and ceramics. In the petroleum industry, it is often seen as an enhanced recovery method targeting mostly unconventional resources such as heavy oil and tar sands. Microwave application is preferred where the medium is made up of polar molecules rather than non-polar molecules, which cannot absorb the microwave energy. Water content in the formation plays a key role in microwave heating since the high frequency waves act on the water molecules, causing them to heat up (through dipole rotation or molecular rotation causing friction as a result of the rotation); the heat is transmitted towards the surrounding formation. The microwave antenna can be placed either downhole (see Figure 6.1) or an electromagnetic wave generator is placed at the surface and transmitted downhole into the formation.

![Figure 6.1: Schematics of microwave heating in a shale reservoir](image)

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Microwave heating is sometimes referred to as dielectric heating. Dielectric heating refers mainly to heating by electric field due to the presence of dipoles in polar molecules. The heating process is mainly influenced by the dielectric properties of the medium, which in turn depend on the electrical properties of the medium. Other factors that control the temperature distribution within the medium are the heat capacity and thermal conductivity of the material.

Conventional heating methods such as conduction, convection and radiation are the main heating sources for both the internal and external medium, but usually at much slower heating speeds compared with heating by microwave. Instead of heat transfer like most conventional heating, the energy is converted from electromagnetic energy to thermal energy (Sun et al., 2016).

The use of microwave heating in oil and gas reservoirs is mostly limited to heavy oil production, with limited application to or studies about gas production in shale gas reservoirs (Mutyala et al., 2010). According to Mutyala et al., (2010), commercial application of microwave heating is lacking due to high initial setup costs and the uncertainty surrounding its potential. However, they went further to argue that if it could be demonstrated that the potential of microwave heating significantly increases production and ultimately profits, then microwave heating could be a useful application in the future for the petroleum industry.

Applications of microwave heating began in the 1970’s (Eskandari et al., 2014) with different researchers mainly involved in researching the effect of field specification on the performance of microwave heating. Numerical modelling studies of microwave heating involve highly coupled nonlinear problems that combine several fields of physics and material science (Sun et al., 2016). An attempt is often made to replace the conventional heat source with a microwave source. Rybakov et al., (2013) argue that where such a replacement can be justified economically, the microwave technology can replace the conventional heat source either fully or partially.

For increasing the formation temperature, microwaves can be generated either at the surface or downhole (See Figure 6.1). The surface microwaves are directed to the formation via waveguides similar to optical fibres, whereas for downhole microwave generation, electricity
is sent downhole with the help of electric cables and the microwaves propagated through the formation (Kamal et al., 2011).

Thermal stimulation is particularly useful with heavy oil and bitumen, where the temperature of the formation is raised to the point where the viscosity of the fluid is drastically reduced. In most of these unconventional resources where thermal stimulation has been applied, the most common techniques are steam injection, steam assisted gravity drainage (SAGD), THAI and THAI – CAPRI, with very few applications of electrical heating. The use of electric heating is particularly useful where steam cannot be used because of the formation depth or excessive heat losses, and in cases where there exist thief zones (Sierra et al., 2001).

Microwave technology has recently been applied to shale oil (Hascakir and Akin, 2009), but as yet, no application in shale gas reservoirs has been reported in a full field demonstration. The purpose of this chapter is to develop a microwave heating model as a source of thermal stimulation by coupling with the fluid flow equations developed in the previous chapter.

The application of microwave heating in the petroleum industry is often targeted at specific problems, such as reducing oil viscosity in heavy oil reservoirs. Early applications of electrical heating employed in heavy oil have been summarised by Sierra et al., (2001) and are summarised in the table below.

<table>
<thead>
<tr>
<th>Date</th>
<th>Test Site</th>
<th>Project description</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>Ardmore, Oklahoma</td>
<td>Very viscous oil6-15 API. Several temperature observation wells were drilled within 4-15’ of test well. Electrode energized by 50 KVA Power Unit</td>
<td>Starting with 18-20°C the temperature within 3 feet rose to greater than 105°C within 40 days of heating</td>
</tr>
<tr>
<td>1988</td>
<td>Frog Lake 11D-15-56-3 W4M</td>
<td>Low frequency Resistive heating using avg. 30KW</td>
<td>2-3 times production increase</td>
</tr>
<tr>
<td>1989</td>
<td>Schoonebeck 280</td>
<td>Low frequency Resistive heating using avg. 60KW</td>
<td>Production increase 13 to 31 m3/day</td>
</tr>
<tr>
<td>91-88</td>
<td>Lashburn A1-11-48-25-W3M</td>
<td>Mix of resistive heating and tubing heating application power: 30-50 KW</td>
<td>Peak simulation ratio of 3.75 while tubing heating yielded marginal improvement</td>
</tr>
<tr>
<td>Year</td>
<td>Field</td>
<td>Heating Method</td>
<td>Result</td>
</tr>
<tr>
<td>------</td>
<td>----------------</td>
<td>---------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>1997</td>
<td>St. Paul, Alberta</td>
<td>Induction heating avg. power 10KW</td>
<td>Production increase by 1.5 times</td>
</tr>
<tr>
<td>1998</td>
<td>Jenner Field, Alberta</td>
<td>Induction heating avg. power 30KW</td>
<td>Marginal decrease in water cut</td>
</tr>
<tr>
<td>1998-99</td>
<td>pelican</td>
<td>Strap well induction heating</td>
<td>Not successful</td>
</tr>
<tr>
<td>1998</td>
<td>Elk Point</td>
<td>Induction heating avg. power 20KW</td>
<td>Marginal success</td>
</tr>
<tr>
<td>1998-2001</td>
<td>Bahrain Oilfield</td>
<td>Induction heating with power 5-8 KW</td>
<td>Tripling of the production is reported</td>
</tr>
</tbody>
</table>

Microwave heating has been shown to be effective in increasing the overall gas production when compared with primary depletion mechanisms in highly viscous and low permeability reservoirs. By conducting simulation studies, Sahni et al., (2000) modelled the application of electromagnetic heating in two different reservoirs of thin sand zones separated by shale layers and a low permeability reservoir with moderate viscous oil. They showed that in some cases, electromagnetic heating could be a substitute for steam injection, or could be used in combination with steam to improve oil production. For example, it could be used as a pre-heating mechanism to create preferential pathways before steam is injected, especially in tar sand. This, according to Sahni et al., (2000), can reduce heat loses during steam injection and improve its performance. The results of Sahni et al., (2000) showed an 80% increase in cumulative production over primary depletion when two 60 Kw microwave sources were placed around the antenna within a year, with temperature rising by 300°F.

A numerical simulation study was conducted by Pizarro and Trevisan (1990) to simulate electric heating in heavy oils, with the aim of improving recovery. The results were then validated with analytical solutions and a comparison made with the field test that was conducted. Results from the simulation studies point to electrical heating as a well stimulation process, since the heating effect observed was concentrated on the near well region. A reasonable match with the numerical simulation was also observed for the field test data from Rio Panon in Brazil. The field test showed an increase in production from 1.2 Bbls/day to 10 Bbls/day after applying 300 Kw of power for 70 days in a viscous oil.
Kasevich et al., (1994) concluded from several field tests they conducted that high frequency waves in the form of radio frequency heating performs as is expected from theoretical applications. In one such test, temperature rose to about 220 °F around a borehole of formation temperature of 90°F after stimulating the formation with radio frequency for 40 hours. Thus, they demonstrated through both low and high-power tests that the use of radio frequency as a thermal stimulation is a viable alternative to conventional heating methods.

Ovalles et al., (2018) carried out simulation studies to investigate the impact of dielectric heating in a heavy oil reservoir using a shaped dipole antenna. The results from simulation showed an increase in oil production when dielectric heating is applied in a heavy oil reservoir. They also demonstrated that peak production is increased when the radio frequency heating is started before the start of production.

Besides the use of microwave heating in heavy oil production, it has also been used in removing moisture in the near wellbore area. Water blockage during drilling, completion and stimulation can seriously affect gas well deliverability if not treated. For instance, moisture invasion can result in a decrease in permeability, thereby inhibiting the wells from producing to their maximum capacity. Studies conducted by Wang et al., (2015) demonstrated the effectiveness of using microwave heating to increase gas relative permeability as well as decreasing water saturation through the heated zone in the reservoir. This resulted in an increase in gas well productivity.

Denny (2007), Jamaluddin et al., (1995) and Li et al., (2006) conducted experiments using microwave heating as a way of reducing water blockage caused by fluid invasion during drilling in a sandstone gas reservoir. The aim of their studies was to investigate the feasibility of microwave heating for removing excess water. The results from the experiment conducted by using MW heating (2450 MHz, 600 W, 40 minutes) showed the composition of the samples remained the same, while water saturation decreased rapidly. Kamal et al., (2011) also demonstrated the use of microwave heating in addressing the problem of liquid loading in gas reservoirs. The target of the experiment was to use dielectric heating to reduce the fluid density, thereby allowing the gas to flow naturally to the surface. The result of the experiment showed that fluid density decreased and gas and vapour flow occurred naturally to the surface.
Several advantages can be obtained from the use of microwave heating over conventional electric heating as well as other thermal stimulation methods. Some of the challenges of thermal stimulation using fluid injection, like steam, can be easily overcome by the use of microwave heating. These include low initial fluid injection, steam override, and difficulty in establishing communication paths between wells. Hiebert et al., (1986) argue that these problems hardly occur in microwave heating. They argue, for instance, that since no fluid is involved in microwave heating, the problem of low initial fluid injection can be easily avoided; also, the penetration depth of microwaves normally occurs around the near wellbore and deeper into the formation, allowing for a larger portion of the reservoir to be stimulated. Finally, production can easily be obtained during or immediately after the microwave is injected, provided sufficient formation pressure is available.

Other advantages of microwave heating over conventional heating methods include quicker start-up and stopping, non-contact, speed and volumetric features, a higher level of safety and automation, and energy conversion instead of heat transfer; also, it is environmentally friendly (Farag et al., 2012; Ge et al., 2013; Li et al., 2017)

Even though at present there are no commercial applications of microwave heating in shale gas reservoirs, different energy transfer methods from the source to the formation mean that microwave energy is more beneficial than other conventional thermal processes (Mutyala et al., 2010). According to Mutyala et al., (2010), conventional issues, such as long heating periods coupled with energy loss, can be easily minimised when microwave heating is used.

Microwave application can have several drawbacks. Over exposure of electromagnetic waves can cause damage to personnel and hence proper insulation is required for all the tubing, casing and wellhead. The use of microwave heating can also be more costly than the same amount of steam energy (Hiebert et al., 1986).

One major drawback of using microwave heating is the problem of high temperature localisation around the microwave antenna. This can easily cause damage, especially to the encasing material, resulting in poor energy distribution, with the heat being conducted instead of being electromagnetically transported as a wave (Bientinesi et al., 2013; Muhammad, 2017). Bientinesi et al., (2013), however, showed that the presence of shale quartz can limit the increase in temperature around the antenna, by investigating
temperature distribution, oil displacement and the effectiveness of “low lossy” quartz sand in reducing temperature around the casing.

### 6.3 Modelling microwave heating

The heating process using microwaves can be modelled either analytically or numerically. Analytical solutions to microwave heat transfer has been performed by Hossan and Dutta (2011) and Pincombe and Smyth (1991). However, due to the complexities associated with Maxwell’s equation, almost all of the microwave heating process is solved using numerical techniques. Several researchers have modelled the process of microwave heating using numerical techniques such as the finite difference time domain method (FDTD) that was proposed by Yee (1966).

Microwave heating can be solved by coupling the heat and mass transfer equation with a source term. Rather than solving Maxwell’s equation for the electromagnetic field, Lambert’s law, expressing power as an exponential decay, could also be used to describe the source term (Campañone and Zaritzky, 2005; Zhou et al., 1995) with the expression

\[ P = P_o e^{-\alpha d} \]  

\[ P_o = \text{surface power} \]

\[ d = \text{maximum distance measured from the surface} \]

\[ \alpha = \text{attenuation factor, which is a function of the dielectric constant of the material.} \]

Where Maxwell’s equation is used, the source term is determined by the electromagnetic (EM) power that is dissipated in the material due to its dielectric losses. This can be expressed (Torres and Jecko, 1997; Zhao et al., 2011) by

\[ P = \frac{1}{2} \left( \vec{E} \cdot \frac{\partial \vec{D}}{\partial t} - \vec{D} \cdot \frac{\partial \vec{E}}{\partial t} \right) \]  

And for the case of steady state time harmonic EM fields, this may yield
\[ P = \frac{1}{2} \omega \varepsilon_0 \varepsilon'' E^2 \] .................................(6.3)

\( P \) is the absorbed power per unit volume (W/m\(^3\))

Where \( \omega \) is the angular frequency, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon'' \) refers to the imaginary part of the materials permittivity, \( E \) is the amplitude of \( \vec{E} \). The microwave power absorbed can also be represented as a function of the electric field (Chaiyo and Rattanadecho, 2013; Klayborworn et al., 2013):

\[ P = 2\pi f \varepsilon_0 \varepsilon_r \left( \tan \delta \right) E^2 \] .................................(6.4)

Where \( \varepsilon_r \) represents relative dielectric constant, \( \varepsilon_0 \) is the permittivity of free space and \( \tan \delta \) is the tangential loss coefficient.

Farag et al., (2012) describe the equation given by Lambert’s law as representing the local value of the power at a certain distance from the surface of the heated material, while Equation 6.3 represents generated power.

### 6.3.1 Maxwell equations

There are basically four of governing equations that can be used to characterised electromagnetism, known collectively as the Maxwell equation. These four equations are derived from the work of other researchers, but were combined together to describe electromagnetism by Maxwell in 1873. They include Gauss’s law, Faraday’s law and Ampere’s law. Maxwell’s equations are expressed in terms of vector components of electric and magnetic field together with their source quantities \( J \) and \( \rho \). The differential form of Maxwell’s equation can be expressed as follows:

\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \] .................................(6.5)
Equation 6.5 is known as Faraday’s law and it states that a circulating electric field induces a time varying magnetic field, whilst a time varying magnetic field induces a circulating electric field.

\[ \nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}, \]  

\[ \text{...........................................(6.6)} \]

According to Ampère's law (Equation 6.6), a circulating magnetic field will induce current and a time varying electric field.

Gauss’s law is defined by Equation 6.7, which shows that an electric field will diverge on positive charges and converge on negative charges, whilst Equation 6.8 shows that the net magnetic flux out of a region is zero. Thus, the magnetic field will always form loops.

\[ \nabla \cdot \vec{D} = \rho \]  

\[ \text{..................................................(6.7)} \]

\[ \nabla \cdot \vec{B} = 0, \]  

\[ \text{..................................................(6.8)} \]

\[ \vec{E} = \vec{E}(x,y,z,t) \] refers to the Electric filed, \[ \vec{H} = \vec{H}(x,y,z,t) \] is the magnetic field, \[ \vec{D} = \vec{D}(x,y,z,t) \] is the electric flux density, \[ \vec{B} = \vec{B}(x,y,z,t) \] is the magnetic flux density, \[ \vec{J} = \vec{J}(x,y,z,t) \] is the electric current density, \[ \rho = \rho(x,y,z,t) \] electric charge density.

### 6.3.2 Dielectric properties and constitutive relations

One key factor that controls the interaction between the material and electric field is the dielectric properties of the material. The dielectric constant is the measure of how the electric fields interact with the material. It can also be defined as the permittivity relative to the permittivity of free space. The permittivity \( \varepsilon \) measures how well the material stores electric energy, whereas the permeability \( \mu \) refers to how well the material stores magnetic energy.

\[ \varepsilon = \varepsilon_0 \varepsilon_r, \]  

\[ \text{.............................................(6.9)} \]

\[ \mu = \mu_0 \mu_r, \]  

\[ \text{.............................................(6.10)} \]
\[ \varepsilon_r = 8.854187817 \times 10^{-12} \text{ F/m} \quad \mu_r = 1.256637061 \times 10^{-6} \text{ H/m} \]

\( \varepsilon_r \) = relative permittivity

\( \mu_r \) = relative permeability.

A constitutive relationship can be established between the electric field and the electric flux density and the dielectric constant as

\[ \vec{D}(t) = \varepsilon \vec{E} \] .................................(6.11)

\[ \vec{B}(t) = \mu \vec{H} \] .................................(6.12)

For linear, isotropic and dispersive material

\[ \vec{D}(t) = \varepsilon(t)^* \vec{E}(t) \] .................................(6.13)

The relative permittivity is made up of two parts, real and imaginary parts. The real part refers to the dielectric constant \( \varepsilon' \), whereas the imaginary part refers to dielectric loss factor \( \varepsilon'' \).

\[ \varepsilon_r = \varepsilon'_r - j\varepsilon''_r \] .................................(6.14)

Where the dielectric properties of a porous material is a function of temperature, this can be further defined as  (Klayborworn et al., 2013)

\[ \varepsilon'_r (T) = \phi \varepsilon''_r (T) + (1 - \phi) \varepsilon''_r \] .................................(6.15)

\[ \varepsilon'_r (T) = \phi \varepsilon''_r (T) + (1 - \phi) \varepsilon''_r \] .................................(6.16)

The loss tangent coefficient can be written as

\[ \tan \delta = \frac{\varepsilon''_r (T)}{\varepsilon'_r (T)} \] .................................(6.17)

By assuming no charges or current, the Maxwell equations for linear and isotropic material can be written as
\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \]  
\[ \text{......................................................................}(6.18) \]

\[ \nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} \]  
\[ \text{......................................................................}(6.19) \]

\[ \nabla \cdot \vec{D} = 0 \]  
\[ \text{......................................................................}(6.20) \]

\[ \nabla \cdot \vec{B} = 0 \]  
\[ \text{......................................................................}(6.21) \]

Where \( \vec{D}(t) = \varepsilon \vec{E} \), \( \vec{B}(t) = \mu \vec{H} \)

To solve Equations 6.18-6.21, Yee (1966) proposed a method called finite difference time domain (FDTD) as a three dimensional solution to Maxwell’s equations. By substituting the constitutive relations into Maxwell’s equations, we can obtain the following final set of equations:

\[ \nabla \times \vec{E} = -\mu \frac{\partial \vec{H}}{\partial t} \]  
\[ \text{......................................................................}(6.22) \]

\[ \nabla \times \vec{H} = \varepsilon \frac{\partial \vec{E}}{\partial t} \]  
\[ \text{......................................................................}(6.23) \]

\[ \nabla \left( \mu \vec{H} \right) = 0 \]  
\[ \text{......................................................................}(6.24) \]

\[ \nabla \left( \varepsilon \vec{H} \right) = 0 \]  
\[ \text{......................................................................}(6.26) \]
6.3.3 Transverse Electromagnetism (TEM), Transverse Electric (TE) and Transverse Magnetic (TM)

There are three categories of electromagnetic waves according to the longitudinal components of the electric field ($E_z$) and the magnetic field ($H_z$). These three categories are known as the transverse electromagnetic, transverse electric and transverse magnetic (Figure 6.2). Where the $E_z = 0$ and $H_z = 0$, both $E$ and $H$ are said to be transverse to the direction of propagation. When this happens, the electromagnetic wave is normally referred to as a TEM wave. In the transverse magnetic mode, $E_z \neq 0$ and $H_z = 0$. The magnetic field is transverse to the direction of propagation. In transverse electric mode, $E_z = 0$ while $H_z \neq 0$. The electric field is transverse to the direction of propagation. TE mode have been chosen as the mode of propagation for this work.

![Figure 6.2: TEM, TE and TM](image)

6.4 Finite Difference Time Domain (FDTD) Method

The finite difference time domain method has been widely used in solving most electromagnetic problems due to its simplicity. It was first proposed by Yee (1966) but has subsequently been improved by other researchers. It has been successfully applied in a variety of problematic situations, such as antennas, electromagnetic absorption in the human body exposed to radiation, and microchip circuits (Akram and Jasmy, 2012; Rathi et al., 2012; Toroğlu and Sevgi, 2014). Since the exact solution of Maxwell’s equations is impossible,
numerical methods such as FDTD can be applied. For the time-dependent Maxwell’s equations, discretization is achieved using central difference approximations to space and time, with resulting finite difference equations solved using a leapfrog approach. The curl equations are written in FDTD form on a Yee cell, as shown in Figure 6.3. The electric and magnetic fields are staggered in time so that the electric field will exist at integer time steps of $0, \Delta t, 2\Delta t, \ldots$ and the magnetic field at half time steps of $\Delta t/2, t+\Delta t/2, 2t+\Delta t/2, \ldots$.

*Figure 6.3: The Yee cell*

In the main loop of the FDTD equation, an update equation is derived and the resulting equations are solved using the finite difference equations for the future time values of each field. The curl equations are defined in Equations 6.27 and 6.28.

\[
C_x^{E,i,j,k} = \frac{\tilde{E}_z|_{i,j+1,k} - \tilde{E}_z|_{i,j,k}}{\Delta y} - \frac{\tilde{E}_y|_{i,j+1,k} - \tilde{E}_y|_{i,j,k}}{\Delta z}
\]
\[
C_y^{E,i,j,k} = \frac{\tilde{E}_z|_{i+1,j,k} - \tilde{E}_z|_{i,j,k}}{\Delta z} - \frac{\tilde{E}_x|_{i+1,j,k} - \tilde{E}_x|_{i,j,k}}{\Delta z}
\]
\[
C_z^{E,i,j,k} = \frac{\tilde{E}_y|_{i+1,j,k} - \tilde{E}_y|_{i,j,k}}{\Delta x} - \frac{\tilde{E}_x|_{i,j+1,k} - \tilde{E}_x|_{i,j,k}}{\Delta y}
\]

And also
6.4.1 Courant stability criterion

For numerical stability, the appropriate time step needs to be chosen according to stability conditions. In general, the Courant condition is given as

\[ \Delta t \leq \frac{\Delta x}{c_o \sqrt{d}} \]  \hspace{1cm} \text{(6.29)}

\( \Delta x \) is the grid size, with \( d = 1, 2 \) or 3 for one, two- and three-dimensional problems respectively. The time step \( \Delta t \) is however normally chosen as

\[ \Delta t = \frac{\Delta x}{2c_o} \]  \hspace{1cm} \text{(Sullivan, 2000)}

6.4.2 Update Equations

Update equations can now be written for solving the future time values of the fields associated with \( E_z \) and \( H_z \) modes. (See appendix 6 for derivation of update equations)

\[
C^H_{x_{l+\Delta t/2}} \frac{\psi_{l,j,k}}{\Delta y} = \frac{H_z \psi_{l,j,k}^{l+\Delta t/2} - H_z \psi_{l,j,k}^{l-\Delta t/2}}{\Delta y} - \frac{H_y \psi_{l,j,k}^{l+\Delta t/2} - H_y \psi_{l,j,k}^{l-\Delta t/2}}{\Delta z}
\]

\[
C^H_{y_{l+\Delta t/2}} \frac{\psi_{l,j,k}}{\Delta z} = \frac{H_x \psi_{l,j,k}^{l+\Delta t/2} - H_x \psi_{l,j,k}^{l-\Delta t/2}}{\Delta z} - \frac{H_x \psi_{l,j,k}^{l+\Delta t/2} - H_x \psi_{l,j,k}^{l-\Delta t/2}}{\Delta x}
\]

\[
C^H_{z_{l+\Delta t/2}} \frac{\psi_{l,j,k}}{\Delta x} = \frac{H_y \psi_{l,j,k}^{l+\Delta t/2} - H_y \psi_{l,j,k}^{l-\Delta t/2}}{\Delta x} - \frac{H_x \psi_{l,j,k}^{l+\Delta t/2} - H_x \psi_{l,j,k}^{l-\Delta t/2}}{\Delta y}
\]

\[ \text{…………………………………..(6.28)} \]

Likewise, \( H_z \) mode is derived from the following update equations:
6.4.3 Microwave penetration depth

In microwave heating, an efficient energy process is highly dependent on the penetration depth of the sample. According to Sun et al., (2016), the penetration depth remains a useful parameter to quantify the heating efficiency and uniformity within a sample heated by microwave. This can normally be observed in very low efficiency of heating in samples that have large size but shallow penetration depth. The penetration depth, \( d \), is normally defined as the distance from the surface to the place at which the wave power or magnitude of the field strength drops to \( e^{-1} \) (=0.37) of its value at the surface (See Figure 6.4), whereas power penetration depth, \( D_p \), is half the value of the field penetration depth (Peng et al., 2010; Sun et al., 2016). There is a negative correlation between the frequency and the penetration depth. That is, when the frequency is increased, the penetration depth also decreases. This implies that materials with a high capability to convert microwave energy to heat will have a very low penetration depth. In microwave heating, a sample dimension needs to be approximately equal to the penetration depth, since any penetration depth smaller than the sample dimension will imply very limited microwave energy, and hence only a small portion of the sample could end up being heated.

The penetration depth can be expressed (Peng et al., 2012, 2010; Sun et al., 2016) as

\[
d = 2 \times D_p = \frac{\sqrt{2c}}{c_0 \sqrt{\epsilon_r \mu_r}} \left[ \left( 1 + \tan^2 \delta_x \tan^2 \delta_y + \tan^2 \delta_x + \tan^2 \delta_y \right)^{1/2} + \tan^2 \delta_x \tan^2 \delta_y - 1 \right]^{1/2}
\]

...(6.32)
Since shale is highly non-magnetic, we can ignore the magnetic effects, and hence the penetration depth of the microwave can be expressed as

\[
d = \frac{\sqrt{2c}}{\omega \left[ \varepsilon \left( \sqrt{1 + (\tan \delta)^2} \right) - 1 \right]^{1/2}}
\]

...............(6.33)

Where \( c \) is the velocity of light, \( \tan \delta \) is the loss tangent.

![Diagram showing energy deposition in a lossy formation.](image)

**Figure 6.4: Energy deposition in a lossy formation. (Liu et al., 2018)**

Figure 6.5 shows the penetration depth of three different recommended industrial frequencies, of 0.915 GHz, 2.45 GHz and 5.8 GHz. It can be observed that a higher frequency of 5.8 GHz resulted in the lowest power penetration depth of the sample. According to Sun et al., (2016), once the frequency is set, any material with a high capability of converting microwave energy to heat tends to have a low penetration depth, while low-loss materials have a high penetration depth.
Figure 6.5: Effect of microwave frequency of 0.915, 2.45 and 5.8 GHz on power penetration depth

6.5 Numerical Modelling of a 2D Reservoir
In order to investigate the application of microwave technology in shale gas reservoirs, a 2D reservoir model was simplified with a waveguide in Transverse Electric (TE) mode. A microwave waveguide is located at the centre of the model. The microwave frequency is set at 2.45 GHz. The initial temperature of the reservoir is 579.6 °R. The reservoir is divided into a 21 x 21 matrix block with dimensions of 50 ft. x 50 ft. A summary of all computational parameters is taken from literature, experimental data or from our estimations, and is given in Table 6.2.
Table 6.2: Parameters used in simulation study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave frequency</td>
<td>2.45 GHz</td>
<td>(Abdulrahman and Meribout, 2014)</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>3</td>
<td>(Josh et al., 2012)</td>
</tr>
<tr>
<td>Lost Factor</td>
<td>0.2</td>
<td>(Al-Harahsheh et al., 2009)</td>
</tr>
<tr>
<td>Heat capacity of shale (J/K/kg)</td>
<td>1000</td>
<td>(Wang et al., 2017)</td>
</tr>
<tr>
<td>Thermal Conductivity (W/M/K)</td>
<td>4</td>
<td>(Wang et al., 2017)</td>
</tr>
<tr>
<td>Initial reservoir Pressure (psia)</td>
<td>1508.39</td>
<td>(Guo et al., 2015)</td>
</tr>
<tr>
<td>Initial reservoir temperature(°R)</td>
<td>579.6</td>
<td>Assumption</td>
</tr>
<tr>
<td>Bottom hole pressure (psia)</td>
<td>500</td>
<td>Assumption</td>
</tr>
</tbody>
</table>

To solve for the gas production associated with microwave heating in shale gas reservoirs, a coupled electromagnetic–thermal model has been developed for a shale gas reservoir. The process of coupling all of the equations is described using Figure 6.6.

1. Firstly, the electric field from Maxwell’s equation is solved using finite difference time domain (FDTD) and a transverse electric (TE) formulation
2. The power dissipated is calculated from the solution of Maxwell’s equation in step 1
3. Temperature computations within the reservoir are calculated using power obtained from Maxwell’s equation as a heat source
4. The pressure field of matrix and fracture is determined from shale gas equations
5. Production from the reservoir is calculated.
Figure 6.6: Combined electromagnetic, thermal and production algorithm for a shale gas reservoir
Figure 6.7: Finite difference time domain (FDTD) algorithm for solving electric field with a perfectly matched layer (PML) as boundary condition
6.6 Results and Discussion

6.6.1 Effect of microwave heating on gas production
The effect of microwave heating on production rate and cumulative production can be observed in Figures 6.8 and 6.9. From Figure 6.8, production rate increases considerably where microwave heating is applied, compared with no microwave heating. This is because the application of microwave heating ensures an increase in temperature of the formation, which consequently increases desorption of the adsorbed gas. The contribution from the adsorbed gas therefore enhances the production rate from the reservoir. After 360 days, microwave heating contributes to an increase of 25% in overall cumulative production.

Figure 6.8: Cumulative production with and without microwave heating
6.6.2 Temperature distribution

Figure 6.10a-6.10c shows temperature distributions in the reservoir following microwave heating at different heating time periods: 90 days, 180 days and 360 days. Temperature is highest at the centre where the microwave radiation is emitted and gradually decreases at surrounding nodes. As the heating time increases and reaches 360 days, it can be observed that the central node where the microwave pulse is excited has the highest temperature. Also, the average temperature throughout the reservoir rises as the microwave heating continues around the central node where the waveguide is located.
Figure 6.10a: Temperature distribution after 90 days of microwave heating

Figure 6.10b: Temperature distribution after 180 days of microwave heating
6.6.3 Effect of microwave frequency

Frequency ranges that are normally suggested for industrial microwave processing include 915 MHz, 2450 MHz and 5800 MHz (Li et al., 2017; Peng et al., 2011). Different frequency ranges used in microwave heating can affect the temperature differential within the material or, as in this case, the reservoir formation. The choice of different frequencies also has a significant effect on production in shale gas reservoirs. In order to demonstrate the effect of microwave heating, three frequency ranges of 915 MHz, 2450 MHz and 5800 MHz have been chosen, and this resulted in different temperature profiles, as shown in Figures 6.11-6.13. Critical observation of Figures 6.11-6.13 shows that higher microwave frequency results in relatively higher temperature profile. However, the increase in temperature for higher microwave frequency is only observed at the surface of the material, whereas for lower frequencies, temperature rises more than the higher frequencies at the inner section of the sample. This is because the penetration depth for high microwave frequency is much lower than the penetration depth of lower microwave frequency (Peng et al., 2011). The penetration depth is, however, strongly dependent on the dielectric properties of the material, which is also heavily dependent on microwave frequency and temperature. Thus, there would be poor heating efficiency at the higher frequency range of 5800 MHz and 2450 MHz compared with 915 MHz, since energy would be easily lost to the surroundings. The
greater energy efficiency at the lower frequency range of 915 MHz would lead to an increase in production and ultimately higher cumulative production, compared with a high frequency of 2450 MHz, as seen in Figures 6.14 and 6.15. Production rate is highest when frequency is lowest at 915 MHz, and lowest at the high frequency of 5800 MHz as seen from Figure 6.14. In Figure 6.14, overall cumulative production is highest at a frequency of 915 MHz, compared with 2450 MHz and 5800 MHz.

![Temperature Distribution at 5800 MHz](image)

**Figure 6.11: Temperature distribution at 5800 MHz at time 360 days**
Figure 6.12: Temperature distribution at 2450 MHz at time 360 days
Figure 6.13: Temperature distribution at 915 MHz at time 360 days

Figure 6.14: Production rate at frequency of 915, 2450 and 5800 MHz
6.6.4 Effect of microwave heating on free gas content

According to Mariotte’s law, free gas content can be predicted (Liu et al., 2012, Li et al., 2017) by

\[ V_g = \frac{\phi PT_s}{P_T \rho_s} \]  \hspace{1cm} (6.34)
Where $V_g$ is the free gas content, $P$ is the gas pressure, $T$ is the reservoir temperature, $\rho_s$ is the density of shale, $T_s$ and $P_s$ represents the temperature and pressure at standard conditions. From Figures 6.16 and 6.17, we can observe the evolution of the gas content with and without microwave heating. Reliance on normal pressure depletion mechanisms, without any heating, shows very small changes in the gas content. We can observe that gas content around the location of the wellbore is lower than that further away from the wellbore. However, after a period of 360 days of microwave heating, there is a considerable drop in the gas content around the wellbore and waveguide. Also, the gas drainage is much higher further away from the wellbore with microwave heating, compared with the case of no microwave heating. This is because the areas affected by the microwave heating result in desorption of the gas. Therefore, as the temperature rises, there is a consequent decrease in the gas content.

**Figure 6.16: Free gas content evolution with microwave heating at 360 days**
6.7 Conclusion:
Thermal stimulation in shale gas reservoirs could be invaluable in increasing gas production. The idea behind thermal stimulation is to accelerate desorption of the adsorbed gas by altering the desorption behaviour through a rise in formation temperature. To do this, a fully coupled electromagnetic–thermal reservoir model has been developed to investigate the impact of thermal stimulation on shale gas recovery, and several factors have been investigated to assess their impact on the effectiveness of thermal stimulation. Microwave heating has been particular chosen as the heat source. In order to couple the heat source from the microwave to the shale system, Maxwell equations that describe electromagnetism have been solved using a finite difference time domain method (FDTD). This methodology involved solving for the electric field using a leapfrog approach. A transverse electric (TE) mode has been chosen as the propagating mode. Several conclusions can be deduced from the results of the simulation undertaken in this chapter:
Firstly, the coupled electromagnetic–thermal model for shale gas reservoirs predicted a more production, compared with a scenario where no microwave heating was used. Cumulative production increased by 25% at the end of 360 days when microwave heating was used. The simulation results show that thermal stimulation by microwave can indeed promote shale gas recovery.

Secondly, the temperature profile at the location of the waveguide showed the highest heat distribution compared with surroundings further away from the heat source. The choice of microwave frequency also had an effect on the overall production and heat distribution in the formation. The highest temperature was observed for frequencies of 2450 MHz and 5800 MHz, compared with 915 MHz. However, penetration depth was low for frequency ranges of 2450 and 5800 MHz, compared with 915 MHz. Low penetration depth meant only a small portion of the formation was heated and consequently, production rate was low for high frequency ranges, compared with a frequency of 915 MHz.

Finally, simulation results showed decreasing free gas content in the matrix block when microwave heating was applied, compared with no microwave heating. This can be attributed to the rise in temperature at the surrounding waveguide, which causes desorption of the adsorbed gas around the thermally stimulated areas.
**Nomenclature**

\( P_o = \) surface power

\( d = \) maximum distance measured from the surface

\( \alpha = \) attenuation factor

\( P = \) absorbed power per unit volume \((W/m^3)\)

\( \omega = \) angular frequency,

\( \mathcal{E}_o = \) vacuum permittivity,

\( \mathcal{E}^* = \) imaginary part of the materials permittivity,

\( E = \) amplitude of \( \vec{E} \)

\( \varepsilon_r = \) relative dielectric constant

\( \varepsilon_o = \) permittivity of free space

\( \tan \delta = \) tangential loss coefficient

\( \varepsilon_r = \) relative permittivity

\( \mu_r = \) relative permeability

\( c = \) velocity of light

\( \vec{E} = \) refers to the Electric field

\( \vec{H} = \) is the magnetic field

\( \vec{D} = \) is the electric flux density

\( \vec{B} = \) is the magnetic flux density

\( \vec{J} = \) is the electric current density

\( \rho = \) electric charge density

\( V_g = \) free gas content
\( T \) is the reservoir temperature

\( \rho_s \) is the density of shale

\( T_s \) = temperature at standard conditions

\( P_s \) = pressure at standard conditions
Chapter 7

Summary, Conclusion and Future Work

7.1 Conclusion:
This thesis presents novel coupled electromagnetic –thermal model with microwave heating taking into consideration the non-Darcy flow within the shale matrix and fractures while also developing new methodology for the inclusion of temperature dependent gas adsorption models in material balance calculations. The main results are summarised as:

1. A statistically robust method of sum of normalised error approach have been adopted when selecting error function to use in gas adsorption modelling. This ensures optimal selection of adsorption model
2. Several variation of temperature dependent adsorption models have been developed using isosteric heat of adsorption and applied to shale gas data
3. Designing new methodology for the inclusion of temperature dependent adsorption models in material balance calculations for unconventional gas reservoirs
4. Evaluating thermal stimulation strategy as enhance gas recovery using microwave heating as the main heat source to improve overall cumulative production.

Based on the achievements outlined above, a detailed summary is provided in the following section.

7.1.1 Review and Modelling in Shale Gas Reservoirs (Chapter 2)
Several single- and multi- component shale gas adsorption models commonly used in estimating gas adsorption were reviewed, and applied to both shale and activated carbon to evaluate their accuracy and effectiveness in predicting gas adsorption:

1. Langmuir isotherm is the most common single adsorption model applied in most commercial simulators, despite its limitations.
2. Vacancy solution model proved to be more successful in predicting single gas adsorption when applied to the New Albany shale dataset.
3. Due to very limited studies on multi-component adsorption in shales, activated carbon is commonly used as an adsorbent for binary gas adsorption in shale gas.
4. Vacancy solution model was most successful in predicting binary gas adsorption, compared to ideal adsorbed solution and extended Langmuir model.

5. A statistically robust method of analysing error functions such as sum of normalised error (SNE) have been used adsorption modelling. This has enabled the selection of adsorption models with the most accurate representation of gas adsorption phenomenon in shale gas reservoirs.

7.1.2 Temperature Dependent Gas Adsorption Modelling in Shale gas Reservoirs (Chapter 3)
This thesis introduced several modified version of Langmuir models to account for temperature variation in the shale gas reservoir. Both temperature-dependent Langmuir volume and non-temperature-dependent Langmuir volume have been included in modelling to evaluate their accuracy in modelling shale gas reservoirs:

1. Data from several literature sources have been collected and for the first time, temperature-dependent gas adsorption models have been used to evaluate their accuracy in predicting shale gas adsorption.
2. Exponential model showed the most accuracy for all the data sets analysed, followed by Langmuir-Freundlich model 2.
3. Very little difference was observed between models that have temperature-dependent Langmuir volume and those with non-temperature-dependent Langmuir volume.
4. Introduction of temperature-dependent models enables the extrapolation of temperatures for which data about gas adsorption is unavailable.
5. Validation and extrapolation showed different predictions for all three-key temperature-dependent adsorption models in the form of Bi-Langmuir, Exponential and Langmuir-Freundlich models.
6. Due to differences in gas adsorption prediction upon extrapolating to higher temperatures, caution is advised when choosing a particular temperature-dependent adsorption model to be used in numerical simulation studies involving thermal stimulation.
7.1.3 Material Balance Calculations for Unconventional Gas Reservoirs Using Temperature Dependent Gas Adsorption Models (Chapter 4)

New analytical methodology has been developed, similar to that of Ahmed and Roux, to be used in material balance analysis for unconventional gas reservoirs. The methodology has been validated using data from available literature sources:

1. Temperature-dependent gas adsorption models can be used in place of Langmuir isotherm to evaluate gas in place calculations.
2. Accurate reservoir performance analysis can be done with temperature-dependent models. Gas in place calculations, pressure predictions and future productions can be accurately obtained using this method.
3. Comparison of the results of Ahmed and Roux with the new methodology in predicting reservoir performance showed slight variations, but overall, both models showed a good match with actual reservoir data.
4. The new methodology developed in this study has the added advantage of predicting gas adsorption at several temperatures where adsorption data is unavailable.

7.1.4 Numerical Simulation of Gas adsorption in Shale Gas Reservoirs (Chapter 5)

A mathematical model for shale gas reservoirs has been developed including dual porosity and dual permeability concept. The mathematical model accounts for non-Darcy flow in the shale matrix. Simulation studies with and without gas adsorption have been evaluated. Finally, the heat equation is coupled with the shale gas model to evaluate thermal stimulation.

1. Including gas adsorption in reservoir simulation studies shows an increase in gas production, compared with simulation studies in which no adsorption model is used.
2. Matrix porosity and fracture permeability have the greatest influence on production in shale gas reservoirs, compared with matrix permeability and fracture porosity.
3. Gas production increased with a thermally enhanced gas recovery process, compared with when no thermal stimulation is applied to the reservoir.
4. The choice of adsorption model used in thermal stimulation studies can result in different production profiles, since extrapolation at higher temperatures results in different adsorption capacity predictions.
5. Validation of adsorption models with actual data at multiple temperatures is necessary to ensure accurate simulation.

7.1.5 Thermal stimulation of shale Gas Reservoirs using Microwave Heating (Chapter 6)
Thermal stimulation of shale gas reservoirs using microwave heating involves solving Maxwell’s equation. The finite difference time domain method has been used to obtain the electric field needed to calculate the power source. This is then coupled to the heat equation as a source term to obtain the temperature distributions in the reservoirs.

1. Gas production involving microwave heating resulted in an increase of about 25% in total production at the end of one year.
2. A higher temperature profile could be observed at the centre of the reservoir where the microwave waveguide is located. Further away from the waveguide, lower temperature distributions were obtained.
3. A lower frequency range resulted in much higher penetration depth and consequently a higher production profile, compared with a higher frequency range, which resulted in a much higher temperature distribution but lower penetration depth.
4. A higher temperature profile near the waveguide showed much greater drainage of free gas content than when no microwave heating was employed.

7.2 Future Work
Considerable amount of work was made in this study to evaluate the contribution of gas adsorption in shale gas reservoirs; however, further attempts could be made to improve the overall understanding of modelling and simulation of shale gas reservoirs some of which are recommended below as future work:

1. Use of artificial neural networks in predicting gas adsorption could help to improve on the adsorption predictions in shale gas reservoirs. Neural networks have been applied in many areas of the petroleum industry and they have proven to be very accurate in use. The use of artificial neural networks to predict gas adsorption of single component, multi-component and temperature dependency of the adsorbent could prove invaluable in obtaining accurate estimates in modelling shale gas reservoirs. To achieve this, a database of gas adsorption in shale gas reservoirs is essential, because
training the network to be able to predict accurately the adsorption capacities relies heavily on having available data. The main challenge will be with obtaining reliable shale gas multi-component adsorption data for such training and prediction by the network.

2. The coupled electromagnetic–thermal model developed for this thesis only assumed a single phase; however, most shale gas reservoirs have more than a single-phase fluid present. Hence developing a two-phase model with both gas and water could help to improve the understanding of reservoir simulation when predicting gas recovery. Also, since the gas present in shale gas is mostly multi-component gas, the temperature-dependent adsorption model used in simulation could be replaced with a multi-component model.

3. The effect of heterogeneity should also be investigated. Throughout this thesis, the reservoir is assumed to be homogeneous. This is not necessarily true in a shale gas reservoir, and as such, using a heterogeneous model to understand the thermal stimulation application could be useful.

4. A Temperature-dependent form of permittivity should be used in microwave heating of shale gas reservoirs. It is well established that the permittivity of a substance is a function of temperature. Hence to improve any simulation involving microwave heating, the temperature-dependent form of permittivity should be used instead of a constant value. However, the functional form of this dependency is not readily available unless experiments are carried out to determine this.

5. Finally, consideration of hydraulic fracturing within the shale gas reservoir will move this conceptual study a step closer to actual representation of shale gas production. Hydraulic fracturing in shale gas reservoir is essential for gas production and hence further studies should incorporate this concept to simulate potential production from shale gas reservoirs.
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doi:10.1021/ie0507427
## Appendix 2

### Table 2.8: Excess adsorption data of Methane and Nitrogen in Albany Shale (Chareonsuppanimit et al., 2012)

<table>
<thead>
<tr>
<th>Methane</th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>Excess adsorption (mmol/g)</td>
<td>Pressure (MPa)</td>
</tr>
<tr>
<td>1.45</td>
<td>0.0138</td>
<td>1.47</td>
</tr>
<tr>
<td>2.85</td>
<td>0.0253</td>
<td>2.86</td>
</tr>
<tr>
<td>4.23</td>
<td>0.0316</td>
<td>4.23</td>
</tr>
<tr>
<td>5.63</td>
<td>0.0352</td>
<td>5.62</td>
</tr>
<tr>
<td>6.99</td>
<td>0.0374</td>
<td>6.99</td>
</tr>
<tr>
<td>8.36</td>
<td>0.0386</td>
<td>8.37</td>
</tr>
<tr>
<td>9.76</td>
<td>0.0395</td>
<td>9.77</td>
</tr>
<tr>
<td>11.12</td>
<td>0.0397</td>
<td>11.14</td>
</tr>
<tr>
<td>12.52</td>
<td>0.0412</td>
<td>12.56</td>
</tr>
</tbody>
</table>

### Table 2.9: single component Adsorption data for Methane and Ethane on Activated Carbon (Valenzuela and Myers 1989)

<table>
<thead>
<tr>
<th>Ethane</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(Kpa)</td>
<td>n(mmol/g)</td>
</tr>
<tr>
<td>0.56</td>
<td>0.2432</td>
</tr>
<tr>
<td>2.3465</td>
<td>0.547</td>
</tr>
<tr>
<td>2.5331</td>
<td>0.485</td>
</tr>
<tr>
<td>4.5729</td>
<td>0.8049</td>
</tr>
<tr>
<td>4.7329</td>
<td>0.8018</td>
</tr>
<tr>
<td>7.706</td>
<td>1.0642</td>
</tr>
<tr>
<td>9.5325</td>
<td>1.169</td>
</tr>
<tr>
<td>11.7723</td>
<td>1.3238</td>
</tr>
<tr>
<td>15.1987</td>
<td>1.4979</td>
</tr>
<tr>
<td>17.2385</td>
<td>1.6063</td>
</tr>
<tr>
<td>24.3446</td>
<td>1.8785</td>
</tr>
<tr>
<td>28.4642</td>
<td>1.9802</td>
</tr>
<tr>
<td>32.0373</td>
<td>2.1167</td>
</tr>
<tr>
<td>37.0635</td>
<td>2.2399</td>
</tr>
<tr>
<td>43.9563</td>
<td>2.4108</td>
</tr>
<tr>
<td>50.0624</td>
<td>2.5402</td>
</tr>
<tr>
<td>60.4615</td>
<td>2.72</td>
</tr>
</tbody>
</table>
Table 2.10: Binary gas Mixture of Ethane and Methane on activated carbon at temperature of 293.15K (Valenzuela and Myers 1989)

<table>
<thead>
<tr>
<th>P(Kpa)</th>
<th>y1 (Ethane)</th>
<th>x1 (Ethane)</th>
<th>n(mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101.191</td>
<td>0.066</td>
<td>0.605</td>
<td>1.3456</td>
</tr>
<tr>
<td>99.7249</td>
<td>0.083</td>
<td>0.658</td>
<td>1.4116</td>
</tr>
<tr>
<td>102.485</td>
<td>0.245</td>
<td>0.852</td>
<td>2.0652</td>
</tr>
<tr>
<td>99.7249</td>
<td>0.251</td>
<td>0.859</td>
<td>2.054</td>
</tr>
<tr>
<td>99.7249</td>
<td>0.489</td>
<td>0.941</td>
<td>2.6255</td>
</tr>
<tr>
<td>102.538</td>
<td>0.519</td>
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<td>2.7692</td>
</tr>
<tr>
<td>99.7515</td>
<td>0.731</td>
<td>0.975</td>
<td>2.9887</td>
</tr>
</tbody>
</table>

Example calculation of Sum of normalised error

1. Select an isotherm model. Example langmuir isotherm
2. Select an error function to use. example is SSE
3. Using excel solver, the parameters for SSE are

\[
\begin{align*}
V_l &= 0.052580101 \\
b &= 0.319189112
\end{align*}
\]

4. Using these parameters, we can obtain the error values for the rest of the other error functions

<table>
<thead>
<tr>
<th>Function</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSE</td>
<td>1.5951E-05</td>
</tr>
<tr>
<td>ARE</td>
<td>4.444640058</td>
</tr>
<tr>
<td>SAE</td>
<td>0.009828207</td>
</tr>
<tr>
<td>MPSD</td>
<td>15.11924434</td>
</tr>
<tr>
<td>Hybrid</td>
<td>0.011474011</td>
</tr>
</tbody>
</table>

5. Now find the parameters for the other error functions

<table>
<thead>
<tr>
<th>Function</th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_l</td>
<td>0.052580101</td>
<td>0.051587</td>
<td>0.045547</td>
<td>0.052739</td>
<td>0.05</td>
</tr>
<tr>
<td>b</td>
<td>0.319189112</td>
<td>0.337697</td>
<td>0.610559</td>
<td>0.305701</td>
<td>0.4</td>
</tr>
</tbody>
</table>
6. Complete a table using the parameters for a specific error function to compute the rest of the other error functions

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>Hybrid</th>
<th>MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSE</td>
<td>1.5951E-05</td>
<td>1.65E-05</td>
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<td>1.73E-05</td>
<td>2.48E-05</td>
<td>7.39E-05</td>
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<tr>
<td>ARE</td>
<td>4.444640058</td>
<td>4.367862</td>
<td>8.846628</td>
<td>4.590383</td>
<td>5.226215</td>
<td>8.846628</td>
</tr>
<tr>
<td>SAE</td>
<td>0.009828207</td>
<td>0.009114</td>
<td>0.014963</td>
<td>0.010677</td>
<td>0.009225</td>
<td>0.014963</td>
</tr>
<tr>
<td>MPSD</td>
<td>15.11924434</td>
<td>14.85807</td>
<td>30.0934</td>
<td>15.61501</td>
<td>17.77791</td>
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<tr>
<td>Hybrid</td>
<td>0.011474011</td>
<td>0.012915</td>
<td>0.068296</td>
<td>0.010742</td>
<td>0.023323</td>
<td>0.068296</td>
</tr>
</tbody>
</table>

7. Find the maximum error value for each individual row

<table>
<thead>
<tr>
<th></th>
<th>MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSE</td>
<td>7.39E-05</td>
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<tr>
<td>ARE</td>
<td>8.846628</td>
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<td>SAE</td>
<td>0.014963</td>
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<tr>
<td>MPSD</td>
<td>30.0934</td>
</tr>
<tr>
<td>Hybrid</td>
<td>0.068296</td>
</tr>
</tbody>
</table>

8. Compute the ratio of each column using the maximum values

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
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</thead>
<tbody>
<tr>
<td>SSE</td>
<td>0.215958065</td>
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<td>0.335855</td>
</tr>
<tr>
<td>ARE</td>
<td>0.502410632</td>
<td>0.493732</td>
<td>1</td>
<td>0.518885</td>
<td>0.590758</td>
</tr>
<tr>
<td>SAE</td>
<td>0.656839031</td>
<td>0.609083</td>
<td>1</td>
<td>0.713589</td>
<td>0.616516</td>
</tr>
<tr>
<td>MPSD</td>
<td>0.502410632</td>
<td>0.493732</td>
<td>1</td>
<td>0.518885</td>
<td>0.590758</td>
</tr>
<tr>
<td>Hybrid</td>
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<td>0.189107</td>
<td>1</td>
<td>0.15728</td>
<td>0.341501</td>
</tr>
</tbody>
</table>

9. Add all the values from each column. This becomes the SNE for the individual error function

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
<th>MPSD</th>
<th>HYBRID</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNE</td>
<td>2.045622464</td>
<td>2.008392</td>
<td>5</td>
<td>2.142759</td>
<td>2.475388</td>
</tr>
</tbody>
</table>

10. The minimum value becomes the optimal error function (Bold) to use in calculations

<table>
<thead>
<tr>
<th></th>
<th>SSE</th>
<th>ARE</th>
<th>SAE</th>
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### Table 2.11: Non-linear Langmuir isotherm parameters

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### Table 2.12: Non-linear BET isotherm parameters

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### Table 2.13: Non-linear Dubinin –Astakhov isotherm parameters

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<td><strong>CO(_2)</strong></td>
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<td>( W_o )</td>
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<td>( m )</td>
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Table 2.14: Non-linear Vacancy Solution Model isotherm parameters

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Table 2.15: Langmuir isotherm parameters and for methane and ethane adsorption

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<td>$V_L$</td>
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Table 2.16: Vacancy Solution Model isotherm parameters for methane and ethane adsorption

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<td>( n_1^n )</td>
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<tr>
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<td>0.9440</td>
<td>1.0706</td>
<td>1.6863</td>
<td>1.7015</td>
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<td>( n_1^n )</td>
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### Appendix 3

Table 3.5: Best fitted parameters for the Langmuir 1 model on the studied samples

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<th>Sample</th>
<th>Reference</th>
<th>$a_1$ m$^3$/kg</th>
<th>$a_2$ K.m$^3$/kg</th>
<th>$b_0$ 1/Pa</th>
<th>$-\Delta H$ KJ/mol</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>2.53E-02</td>
<td>4.28E-04</td>
<td>3.44E-04</td>
<td>15.61E+03</td>
<td>0.99</td>
</tr>
<tr>
<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
<td>3.44E-04</td>
<td>4.28E-04</td>
<td>8.10E-04</td>
<td>14.4E+03</td>
<td>0.99</td>
</tr>
<tr>
<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>4.43E-02</td>
<td>4.27E-04</td>
<td>8.99E-03</td>
<td>8.29E+03</td>
<td>0.99</td>
</tr>
<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>5.69E-02</td>
<td>4.28E-04</td>
<td>2.92418E-05</td>
<td>23.7E+03</td>
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<td>Ji et al 2014</td>
<td>2.46E-03</td>
<td>1.09E+00</td>
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<td>27.5E+03</td>
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<td>Guo 2014</td>
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<td>4.43E-04</td>
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<td>$b_0$ 1/Pa</td>
<td>$-\Delta H$ KJ/mol</td>
<td>$R^2$</td>
</tr>
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<td>CSW2</td>
<td>Lu et al 1995</td>
<td>1.69E-03</td>
<td>8.25E-04</td>
<td>2.66E-04</td>
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<td>Antrim-7</td>
<td>Lu et al 1995</td>
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Table 3.6: Best fitted parameters for Langmuir 2 model on the studied samples

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<th>Reference</th>
<th>$q_{so}$ m$^3$/kg</th>
<th>$-q_1$ K</th>
<th>$b_0$ 1/Pa</th>
<th>$-\Delta H$ KJ/mol</th>
<th>$R^2$</th>
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<tr>
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<td>Zhang et al 2012</td>
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<td>1.33</td>
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<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
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<td>Zhang et al 2012</td>
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<td>0.96</td>
<td>9.01E-03</td>
<td>8.28E+03</td>
<td>0.99</td>
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<td>Zhang et al 2012</td>
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<td>1.20</td>
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<td>23.7E+03</td>
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<td>Ji et al 2014</td>
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<td>1.36743E-06</td>
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<td>Ordos Basin B</td>
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<td>30.0E+03</td>
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Table 3.7: Best fitted parameters for the Langmuir-Freundlich 1 model on the studied samples

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<th>Sample</th>
<th>Reference</th>
<th>$a_1$ m$^3$/kg</th>
<th>$a_2$ K. m$^3$/kg</th>
<th>$b_0$ 1/Pa</th>
<th>$\Delta H$ KJ/mol</th>
<th>$n$</th>
<th>$R^2$</th>
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<td>Zhang et al 2012</td>
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<tr>
<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>0.041</td>
<td>0.30</td>
<td>7.79E-03</td>
<td>8.70E+03</td>
<td>1.04</td>
<td>0.99</td>
</tr>
<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>0.022</td>
<td>129.57</td>
<td>9.05E-04</td>
<td>9.36E+03</td>
<td>0.50</td>
<td>0.68</td>
</tr>
<tr>
<td>Ordos Basin YY33-2</td>
<td>Ji et al 2014</td>
<td>0.002</td>
<td>1.36</td>
<td>1.08495E-05</td>
<td>27.5E+03</td>
<td>0.73</td>
<td>0.97</td>
</tr>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>0.002</td>
<td>3.91</td>
<td>2.86225E-05</td>
<td>22.2E+03</td>
<td>0.42</td>
<td>0.94</td>
</tr>
<tr>
<td>Sample</td>
<td>Reference</td>
<td>so</td>
<td>q</td>
<td>m</td>
<td>3</td>
<td>kg</td>
<td>soq</td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>---</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>0.004</td>
<td>4.20</td>
<td>8.54037E-05</td>
<td>18.0E+03</td>
<td>0.28</td>
<td>0.94</td>
</tr>
<tr>
<td>Ordos Basin B</td>
<td>Guo 2014</td>
<td>0.006</td>
<td>19.62</td>
<td>6.1835E-05</td>
<td>15.5E+03</td>
<td>0.47</td>
<td>0.95</td>
</tr>
<tr>
<td>Ordos Basin C</td>
<td>Guo 2014</td>
<td>0.006</td>
<td>20.13</td>
<td>6.48377E-05</td>
<td>15.6E+03</td>
<td>0.42</td>
<td>0.91</td>
</tr>
<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.006</td>
<td>24.48</td>
<td>8.41994E-05</td>
<td>9.20E+03</td>
<td>0.63</td>
<td>0.98</td>
</tr>
<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.012</td>
<td>94.71</td>
<td>3.85E-04</td>
<td>5.59E+03</td>
<td>0.54</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 3.8: Best fitted parameters for the Langmuir-Freundlich 2 model on the studied samples
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>$V_s$ std m$^3$/kg</th>
<th>$D_1$ 1/K</th>
<th>$A$ K$^{1/2}$/Mpa</th>
<th>$B$ K</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>0.0028</td>
<td>243.54</td>
<td>4.07482E-07</td>
<td>35.6E+03</td>
<td>0.85</td>
</tr>
<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>0.0092</td>
<td>2.99</td>
<td>3.56432E-05</td>
<td>22.1E+03</td>
<td>0.30</td>
</tr>
<tr>
<td>Ordos Basin B</td>
<td>Guo 2014</td>
<td>0.0345</td>
<td>3.29</td>
<td>3.61044E-05</td>
<td>18.7E+03</td>
<td>0.49</td>
</tr>
<tr>
<td>Ordos Basin C</td>
<td>Guo 2014</td>
<td>0.0996</td>
<td>3.21</td>
<td>1.78E-04</td>
<td>11.8E+03</td>
<td>0.42</td>
</tr>
<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.0049</td>
<td>2.57</td>
<td>1.38E-03</td>
<td>9.31E+03</td>
<td>0.71</td>
</tr>
<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.0075</td>
<td>2.57</td>
<td>1.69E-03</td>
<td>11.7E+03</td>
<td>0.74</td>
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Table 3.9: Best fitted parameters for the Exponential model on the studied samples
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>$N_m$ m$^3$/kg</th>
<th>std</th>
<th>$k_1$ 1/Mpa</th>
<th>$k_2$ 1/Mpa</th>
<th>$-E_1$ J/mol</th>
<th>$-E_2$ J/mol</th>
<th>$f_1$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>0.0284</td>
<td>3.00E-04</td>
<td>2.06E+00</td>
<td>6.20E-07</td>
<td>3.04E-03</td>
<td>0.10</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
<td>0.0315</td>
<td>3.00E-04</td>
<td>2.92E+00</td>
<td>6.18E-07</td>
<td>3.04E-03</td>
<td>0.13</td>
<td>0.96</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.10: Best fitted parameters for the Bi- Langmuir model on the studied samples
Table 3.11: Best fitted parameters for the Langmuir 3 model on the studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>$q_{iso}$ m$^3$/kg</th>
<th>$b_0$ 1/Pa</th>
<th>$-\Delta H$ KJ/mol</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>0.0511</td>
<td>3.00E-04</td>
<td>3.42E+00</td>
<td>6.31E-07</td>
</tr>
<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>0.0413</td>
<td>1.39E-03</td>
<td>1.08E+01</td>
<td>2.29E+04</td>
</tr>
<tr>
<td>Ordos Basin YY33-2</td>
<td>Ji et al 2014</td>
<td>0.0061</td>
<td>3.00E-04</td>
<td>9.09E+00</td>
<td>8.12E-07</td>
</tr>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>0.0058</td>
<td>2.75E-03</td>
<td>1.15E-05</td>
<td>2.44E+03</td>
</tr>
<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>0.0023</td>
<td>2.65E-03</td>
<td>2.28E-07</td>
<td>2.37E+03</td>
</tr>
<tr>
<td>Ordos Basin B</td>
<td>Guo 2014</td>
<td>0.0047</td>
<td>2.65E-03</td>
<td>8.07E-07</td>
<td>2.37E+03</td>
</tr>
<tr>
<td>Ordos Basin C</td>
<td>Guo 2014</td>
<td>0.0046</td>
<td>3.00E-04</td>
<td>6.48E+00</td>
<td>8.21E-07</td>
</tr>
<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.0140</td>
<td>1.50E-03</td>
<td>4.17E-04</td>
<td>1.08E+04</td>
</tr>
<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.0249</td>
<td>4.58E-03</td>
<td>1.10E-03</td>
<td>8.65E+03</td>
</tr>
</tbody>
</table>

Table 3.11: Best fitted parameters for the Langmuir 3 model on the studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>$q_{iso}$ m$^3$/kg</th>
<th>$b_0$ 1/Pa</th>
<th>$-\Delta H$ KJ/mol</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>0.025</td>
<td>1.20E-04</td>
<td>18.3E+03</td>
<td>0.98</td>
</tr>
</tbody>
</table>

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<p>| Formation          | Reference       | θ  | ρSAT  | κ  | S |
|-------------------|-----------------|----|-------|----|---|---|
| Woodford Shale    | Zhang et al 2012| 0.026 | 8.10E-04 | 14.4E+03 | 0.99 |
| Barnett Shale Tarrant A3 | Zhang et al 2012 | 0.044 | 8.86E-03 | 8.33E+03 | 0.99 |
| Barnett Shale Blakeley 1 | Zhang et al 2012 | 0.056 | 2.96E-05 | 2.37E+03 | 0.64 |
| Ordos Basin YY33-2 | Ji et al 2014  | 0.005 | 1.22E-07 | 40.0E+03 | 0.97 |
| Ordos Basin YY34-1 | Ji et al 2014  | 0.005 | 1.12E-09 | 52.0E+03 | 0.93 |
| Ordos Basin A     | Guo 2014       | 0.002 | 5.81E-06 | 31.7E+03 | 0.75 |
| Ordos Basin B     | Guo 2014       | 0.005 | 3.90E-05 | 23.2E+03 | 0.87 |
| Ordos Basin C     | Guo 2014       | 0.004 | 3.94E-05 | 25.0E+03 | 0.95 |
| CSW2              | Lu et al 1995  | 0.001 | 3.20E-04 | 15.8E+03 | 0.98 |
| Antrim-7          | Lu et al 1995  | 0.004 | 3.22E-04 | 17.4E+03 | 0.99 |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reference</th>
<th>$q_{sw}$ m$^3$/kg</th>
<th>$b_0$ 1/Pa</th>
<th>$-\Delta H$ KJ/mol</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green River Formation</td>
<td>Zhang et al 2012</td>
<td>0.024</td>
<td>2.56E-04</td>
<td>16.4E+03</td>
<td>1.04</td>
<td>0.99</td>
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<tr>
<td>Woodford Shale</td>
<td>Zhang et al 2012</td>
<td>0.025</td>
<td>5.69E-04</td>
<td>15.4E+03</td>
<td>1.04</td>
<td>0.99</td>
</tr>
<tr>
<td>Barnett Shale Tarrant A3</td>
<td>Zhang et al 2012</td>
<td>0.042</td>
<td>5.84E-03</td>
<td>9.48E+03</td>
<td>1.06</td>
<td>0.99</td>
</tr>
<tr>
<td>Barnett Shale Blakeley 1</td>
<td>Zhang et al 2012</td>
<td>3.051</td>
<td>4.82E-05</td>
<td>11.9E+03</td>
<td>0.48</td>
<td>0.68</td>
</tr>
<tr>
<td>Ordos Basin YY33-2</td>
<td>Ji et al 2014</td>
<td>0.006</td>
<td>1.25E-06</td>
<td>33.6E+03</td>
<td>0.83</td>
<td>0.98</td>
</tr>
<tr>
<td>Ordos Basin YY34-1</td>
<td>Ji et al 2014</td>
<td>0.006</td>
<td>8.41E-07</td>
<td>33.7E+03</td>
<td>0.83</td>
<td>0.93</td>
</tr>
<tr>
<td>Ordos Basin A</td>
<td>Guo 2014</td>
<td>0.011</td>
<td>3.78E-05</td>
<td>21.5E+03</td>
<td>0.29</td>
<td>0.94</td>
</tr>
<tr>
<td>Ordos Basin B</td>
<td>Guo 2014</td>
<td>0.035</td>
<td>3.51E-05</td>
<td>18.7E+03</td>
<td>0.49</td>
<td>0.95</td>
</tr>
<tr>
<td>Ordos Basin C</td>
<td>Guo 2014</td>
<td>0.103</td>
<td>1.69E-04</td>
<td>11.8E+03</td>
<td>0.42</td>
<td>0.96</td>
</tr>
<tr>
<td>CSW2</td>
<td>Lu et al 1995</td>
<td>0.007</td>
<td>6.50E-04</td>
<td>10.0E+03</td>
<td>0.68</td>
<td>0.98</td>
</tr>
<tr>
<td>Antrim-7</td>
<td>Lu et al 1995</td>
<td>0.005</td>
<td>9.48E-04</td>
<td>14.0E+03</td>
<td>0.84</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Appendix 4

Table 4.7: production data (Ahmed and Roux, 2006)

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>$G_p$ (MMscf)</th>
<th>$W_p$ (MMscf)</th>
<th>$P$ (psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1500</td>
</tr>
<tr>
<td>730</td>
<td>265.086</td>
<td>0.15749</td>
<td>1315</td>
</tr>
<tr>
<td>1460</td>
<td>968.41</td>
<td>0.290238</td>
<td>1021</td>
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<tr>
<td>2190</td>
<td>1704.033</td>
<td>0.368292</td>
<td>814.4</td>
</tr>
<tr>
<td>2920</td>
<td>2423.4</td>
<td>0.425473</td>
<td>664.9</td>
</tr>
<tr>
<td>3650</td>
<td>2992.901</td>
<td>0.464361</td>
<td>571.1</td>
</tr>
</tbody>
</table>

Table 4.8: Coal properties (Ahmed and Roux, 2006)

<table>
<thead>
<tr>
<th>Language</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir’s pressure constant</td>
<td>$b = 0.00276 \text{ psi}^{-1}$</td>
</tr>
<tr>
<td>Langmuir volume constant</td>
<td>$V_L = 428.5 \text{ scf/ton}$</td>
</tr>
<tr>
<td>Average bulk density</td>
<td>$\rho_B = 1.70 \text{ g/cm}^3$</td>
</tr>
<tr>
<td>Average thickness</td>
<td>$h = 50 \text{ ft}$</td>
</tr>
<tr>
<td>Initial water saturation</td>
<td>$S_{wi} = 0.95$</td>
</tr>
<tr>
<td>Drainage area</td>
<td>$A = 320 \text{ acres}$</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>$p_i = 1500 \text{ psia}$</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>$p_d = 1500 \text{ psia}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T = 105^\circ \text{ F}$</td>
</tr>
<tr>
<td>Initial gas content</td>
<td>$G_i = 345.1 \text{ scf/ton}$</td>
</tr>
<tr>
<td>Formation volume factor</td>
<td>$B_w = 1.00 \text{ bbl/STB}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\phi = 0.01$</td>
</tr>
<tr>
<td>Water compressibility</td>
<td>$c_w = 3\times10^{-6} \text{ psi}^{-1}$</td>
</tr>
<tr>
<td>Formation compressibility</td>
<td>$c_f = 6\times10^{-6} \text{ psi}^{-1}$</td>
</tr>
</tbody>
</table>
Appendix 5

Reda (1987) carried out an experimental study of the welded tuff at Yucca Mountain, with the following properties used in the verification of the analytical model given below:

$\hat{h}$ (Klinkenberg factor) = $7.6 \times 10^5$ Pa

$p(L)$ is the gas pressure at the outlet = $1.0 \times 10^{-5}$ Pa.s

$L$ is the length from the inlet to the outlet = 10 m

$x$ is the task location along the gas transport path

$k_e$ is the intrinsic permeability = $5.0 \times 10^{-19}$ m$^2$

$\beta$ is the compressibility factor = $1.8 \times 10^{-5}$ Pa$^{-1}$m$^{-1}$

$q_m$ is the air injection rate = $1.0 \times 10^{-6}$ kg/s

$\mu_g$ is the dynamic viscosity = $1.84 \times 10^{-5}$ Pa.s
Discretizing the systems of equations using finite difference method

Matrix:

\[
\begin{bmatrix}
\gamma \phi_m + \left(1 - \phi_m \right) \frac{MP_L V_L \rho_s}{V_{std} (P_L + p_m)^2} \frac{\partial p_m}{\partial t} - \nabla \left( \gamma \left( \frac{k_{mi}}{\mu} \frac{p_m + b_m}{\mu} \right) \nabla p_m \right) & = & - \frac{k_m \rho_s \sigma}{\mu} (p_m - p_f)
\end{bmatrix}
\]

\[
\begin{bmatrix}
\gamma \phi_m + \left(1 - \phi_m \right) \frac{MP_L V_L \rho_s}{V_{std} (P_L + p_m)^2} \frac{\partial p_m}{\partial t} - \frac{1}{\mu} \frac{\partial p_m}{\partial x} \left( \gamma \left( \frac{k_{mi}}{\mu} \frac{p_m + b_m}{\mu} \frac{\partial p_m}{\partial x} + \gamma \frac{k_{mi} b_m}{\mu} \frac{\partial p_m}{\partial x} \right) \right) & = & - \frac{k_m \gamma}{\mu} \frac{p_m \sigma}{\mu} (p_m - p_f)
\end{bmatrix}
\]

\[
\gamma \phi_m = C, \quad \left(1 - \phi_m \right) \frac{MP_L V_L \rho_s}{V_{std}} = B, \quad \gamma \frac{k_{mi}}{\mu} = A, \quad p_m = U, \quad p_f = V, \quad \frac{k_{mi} \sigma}{u_g} = D, \quad \lambda \rho_s = E
\]

\[
\begin{bmatrix}
C + \frac{B}{(P_L + U)^2} \frac{\partial U}{\partial t} - \frac{1}{\mu} \frac{\partial U}{\partial x} \left[ A U \frac{\partial U}{\partial x} + E \frac{\partial U}{\partial x} \right] & = & -DU (U - V)
\end{bmatrix}
\]

\[
\begin{bmatrix}
C + \frac{B}{(P_L + U)^2} \frac{\partial U}{\partial t} - A \left( \frac{\partial U}{\partial x} \right)^2 - A U \frac{\partial^2 U}{\partial x^2} - E \frac{\partial^2 U}{\partial x^2} & = & -D(U - V)
\end{bmatrix}
\]
Now to compute the Jacobian (Partial derivative for the Jacobian Matrix)

\[
\begin{align*}
f &= C + \frac{B}{(P_L + U_{i,j})^2} \left( \frac{U_{i,j}^{n+1} - U_{i,j}^n}{\Delta t} \right) - \left( \frac{U_{i+1,j}^{n+1} - U_{i,j}^{n+1}}{2\Delta x} \right)^2 - A \left[ \frac{U_{i+1,j}^{n+1} - U_{i,j}^{n+1}}{(2\Delta y)} \right]^2 - A \left[ \frac{U_{i,j+1}^{n+1} - U_{i,j}^{n+1}}{2U_{i,j}^{n+1}} \right] - A \left[ \frac{U_{i,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta y)^2} \right] - A \left[ \frac{U_{i,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta x)^2} \right] \\
&= -\left[ \frac{U_{i+1,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta x)^2} \right] - E \left[ \frac{U_{i,j+1}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta y)^2} \right] + DU_{i,j}^{n+1} \left( U_{i,j}^{n+1} - V_{i,j}^{n+1} \right)
\end{align*}
\]

\[
\frac{\partial f}{\partial U_{i,j}} = -\frac{2B\left(U_{i,j}^{n+1} - U_{i,j}^n\right)}{\Delta t(P_L + U_{i,j})^3} - \frac{C+B}{\Delta t} - A\left(\frac{U_{i+1,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(2\Delta x)^2}\right) - A\left(\frac{U_{i,j+1}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(2\Delta y)^2}\right) + 2A\left(\frac{U_{i,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta x)^2}\right) + 2A\left(\frac{U_{i,j}^{n+1} + U_{i,j}^{n+1} - 2U_{i,j}^{n+1}}{(\Delta y)^2}\right)
\]

\[
\frac{\partial f}{\partial U_{i+1,j}} = \frac{1}{2}A\left(\frac{U_{i+1,j}^{n+1} - U_{i,j}^{n+1}}{(\Delta x)^2}\right) - A\left(\frac{U_{i+2,j}^{n+1} - U_{i+1,j}^{n+1}}{(\Delta x)^2}\right) - E \left(\frac{U_{i+1,j}^{n+1} - V_{i+1,j}^{n+1}}{(\Delta x)^2}\right)
\]

\[
\frac{\partial f}{\partial U_{i,j+1}} = \frac{1}{2}A\left(\frac{U_{i,j+1}^{n+1} - U_{i,j}^{n+1}}{(\Delta y)^2}\right) - A\left(\frac{U_{i,j+2}^{n+1} - U_{i,j+1}^{n+1}}{(\Delta y)^2}\right) - E \left(\frac{U_{i,j+1}^{n+1} - V_{i,j+1}^{n+1}}{(\Delta y)^2}\right)
\]

\[
\frac{\partial f}{\partial U_{i-1,j}} = \frac{1}{2}A\left(\frac{U_{i-1,j}^{n+1} - U_{i,j}^{n+1}}{(\Delta x)^2}\right) - A\left(\frac{U_{i-2,j}^{n+1} - U_{i-1,j}^{n+1}}{(\Delta x)^2}\right) - E \left(\frac{U_{i-1,j}^{n+1} - V_{i-1,j}^{n+1}}{(\Delta x)^2}\right)
\]

\[
\frac{\partial f}{\partial U_{i,j-1}} = \frac{1}{2}A\left(\frac{U_{i,j-1}^{n+1} - U_{i,j}^{n+1}}{(\Delta y)^2}\right) - A\left(\frac{U_{i,j-2}^{n+1} - U_{i,j-1}^{n+1}}{(\Delta y)^2}\right) - E \left(\frac{U_{i,j-1}^{n+1} - V_{i,j-1}^{n+1}}{(\Delta y)^2}\right)
\]

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FRACTURE:

\[
\gamma \phi_f \frac{\partial p_f}{\partial t} - \nabla \left( \gamma \left( \frac{k_f (p_f + b_f)}{\mu} \nabla p_f \right) \right) = \frac{k_m \rho_s \sigma (p_m - p_f)}{\mu_s} - q_a
\]

\[
\gamma \phi_f = K, \quad \frac{k_f}{\mu} = A^1, \quad p_m = U, \quad p_f = V, \quad \frac{k_m \gamma \sigma}{u_s} = D, \quad q_a = 0
\]

\[
K \frac{\partial V}{\partial t} - \frac{\partial}{\partial x} \left( A^1 (V + b_f) \frac{\partial V}{\partial x} \right) = DU (U - V)
\]

\[
K \frac{\partial V}{\partial t} - A \left( \frac{\partial V}{\partial x} \right)^2 - AV \frac{\partial^2 V}{\partial x^2} - Ab_f \frac{\partial^3 V}{\partial x^3} - DU (U - V) = 0
\]

\[
A^1 b_f = F
\]

\[
K \frac{\partial V}{\partial t} - A \left( \frac{\partial V}{\partial x} \right)^2 - AV \frac{\partial^2 V}{\partial x^2} - F \frac{\partial^3 V}{\partial x^3} - DU (U - V) = 0
\]

Discretization:
\[ K \left( \frac{V_{i,j}^{n+1} - V_{i,j}^n}{\Delta t} \right) - A \left( \frac{V_{i+1,j}^{n+1} - V_{i,j}^{n+1}}{2\Delta x} \right) - A \left( \frac{V_{i,j+1}^{n+1} - V_{i,j}^{n+1}}{2\Delta y} \right) - AV_{i,j}^{(n+1)} \left( \frac{V_{i+1,j}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - AV_{i,j}^{(n+1)} \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) \]

\[-F \left( \frac{V_{i+1,j}^{n+1} + V_{i-1,j}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - F \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) - DV_{i,j}^{n+1} (U_{i,j}^{n+1} - V_{i,j}^{n+1}) = 0 \]

\[ f_{i,j} = K \left( \frac{V_{i,j}^{n+1} - V_{i,j}^n}{\Delta t} \right) - A \left( \frac{V_{i+1,j}^{n+1} - V_{i,j}^{n+1}}{2\Delta x} \right) - A \left( \frac{V_{i,j+1}^{n+1} - V_{i,j}^{n+1}}{2\Delta y} \right) - AV_{i,j}^{(n+1)} \left( \frac{V_{i+1,j}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - AV_{i,j}^{(n+1)} \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) \]

\[-F \left( \frac{V_{i+1,j}^{n+1} + V_{i-1,j}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - F \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) - DV_{i,j}^{n+1} (U_{i,j}^{n+1} - V_{i,j}^{n+1}) \]

Now to compute the Jacobian (Partial derivative for the Jacobian Matrix)

\[ \frac{\partial f}{\partial V_{i,j}} = K \Delta t - A \left( \frac{V_{i+1,j}^{n+1} + V_{i-1,j}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - A \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) - A \left( \frac{V_{i+1,j}^{n+1} + V_{i-1,j}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta x)^2} \right) - A \left( \frac{V_{i,j+1}^{n+1} + V_{i,j-1}^{n+1} - 2V_{i,j}^{n+1}}{(\Delta y)^2} \right) + \frac{2A^1}{(\Delta x)^2} V_{i,j}^{(n+1)} + \frac{2A^1}{(\Delta y)^2} V_{i,j}^{(n+1)} + \frac{2F}{(\Delta x)^2} + \frac{2F}{(\Delta y)^2} - D(U_{i,j}^{n+1} - V_{i,j}^{n+1}) + DV_{i,j}^{n+1} \]

**Diagonal**

\[ \frac{\partial f}{\partial V_{i+1,j}} = -\frac{1}{2} \frac{A^1}{(\Delta x)^2} (V_{i+1,j}^{n+1} - V_{i-1,j}^{n+1}) - \frac{A^1}{(\Delta y)^2} V_{i,j}^{n+1} - \frac{F}{(\Delta x)^2} \]

**Upper diagonal (South)**

**North**

\[ \frac{\partial f}{\partial V_{i,j+1}} = -\frac{1}{2} \frac{A^1}{(\Delta x)^2} (V_{i,j+1}^{n+1} - V_{i,j-1}^{n+1}) - \frac{A^1}{(\Delta y)^2} V_{i,j}^{n+1} - \frac{F}{(\Delta y)^2} \]
\[
\frac{\partial f}{\partial V_{i+1,j}} = \frac{1}{2} \frac{A_i}{(\Delta x)^2} (V_{i+1,j}^{n+1} - V_{i-1,j}^{n+1}) - \frac{A_i}{(\Delta x)^2} V_{i,j}^{n+1} - \frac{F}{(\Delta x)^2}
\]
\[
\text{Lower diagonal}
\]
\[
\frac{\partial f}{\partial V_{i,j-1}} = \frac{1}{2} \frac{A_i}{(\Delta y)^2} (V_{i,j-1}^{n+1} - V_{i,j-1}^{n+1}) - \frac{A_i}{(\Delta y)^2} V_{i,j}^{n+1} - \frac{F}{(\Delta y)^2}
\]
\[
\text{(South)}
\]
Appendix 6

Solving the Maxwell Equations using FDTD

By assuming no charges or current, the Maxwell equations for linear, isotropic, on-dispersive material can be written as

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]

\[ \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} \]

\[ \nabla \cdot \mathbf{D} = 0 \]

\[ \nabla \cdot \mathbf{B} = 0 \]

Where

\[ \mathbf{D}(t) = \varepsilon \mathbf{E} \]

\[ \mathbf{B}(t) = \mu \mathbf{H} \]

To solve these equation, Yee et al proposed a method called finite difference time domain (FDTD) as a three dimensional solution to Maxwell’s equations.

By substituting the constitutive relations into the Maxwell’s equations we can obtain the following set of Maxwell’s equation

\[ \nabla \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t} \]

\[ \nabla \times \mathbf{H} = \varepsilon \frac{\partial \mathbf{E}}{\partial t} \]

\[ \nabla \cdot \left( \mu \mathbf{H} \right) = 0 \]

\[ \nabla \cdot \left( \varepsilon \mathbf{H} \right) = 0 \]
Since the exact solutions of Maxwell's equations is impossible, numerical methods such as FDTD can be applied. For the time dependent Maxwell's equations, discretization is achieved using central difference approximations to space and time with resulting finite difference equations solved using a leapfrog approach. The curl equations are written in FDTD form on a yee cell as shown below. The electric and magnetic field are staggered in time so that the electric field will exist at integer time steps of $t, t+\Delta t, 2t, \ldots$ and the magnetic field at half time steps of $\frac{t+\Delta t}{2}, t+\Delta t/2, 2t+\Delta t/2, \ldots$

\[
C_{x}^{E_{i,j,k}} = \frac{E_{z_{i,j,k}} - E_{z_{i,j,k+1}}}{\Delta y} - \frac{E_{y_{i,j+1,k}} - E_{y_{i,j,k}}}{\Delta z}
\]

\[
C_{y}^{E_{i,j,k}} = \frac{E_{x_{i+1,j,k}} - E_{x_{i,j,k}}}{\Delta z} - \frac{E_{z_{i,j,k}} - E_{z_{i,j,k+1}}}{\Delta x}
\]

\[
C_{z}^{E_{i,j,k}} = \frac{E_{y_{i,j+1,k}} - E_{y_{i,j,k}}}{\Delta x} - \frac{E_{x_{i,j,k}} - E_{x_{i+1,j,k}}}{\Delta y}
\]

And now

\[
C_{x}^{H_{i,j,k}} = -\frac{\mu_{x} H_{x_{i,j,k}}}{c_{o}} \frac{H_{x_{i+1,j,k}} - H_{x_{i,j,k}}}{\Delta t}
\]

\[
C_{y}^{H_{i,j,k}} = -\frac{\mu_{y} H_{y_{i,j,k}}}{c_{o}} \frac{H_{y_{i,j+1,k}} - H_{y_{i,j,k}}}{\Delta t}
\]

\[
C_{z}^{H_{i,j,k}} = -\frac{\mu_{z} H_{z_{i,j,k}}}{c_{o}} \frac{H_{z_{i,j+1,k}} - H_{z_{i,j,k}}}{\Delta t}
\]

\[
C_{x}^{H_{i,j+k/2}} = \frac{H_{x_{i+1,j,k/2}} - H_{x_{i,j,k}}}{\Delta y} - \frac{H_{y_{i,j,k+1/2}} - H_{y_{i,j,k}}}{\Delta z}
\]

\[
C_{y}^{H_{i,j+k/2}} = \frac{H_{y_{i,j+1,k/2}} - H_{y_{i,j,k}}}{\Delta z} - \frac{H_{z_{i,j+1,k}} - H_{z_{i,j,k}}}{}\Delta x
\]

\[
C_{z}^{H_{i,j+k/2}} = \frac{H_{z_{i,j+1,k}} - H_{z_{i,j,k}}}{\Delta x} - \frac{H_{x_{i,j,k+1/2}} - H_{x_{i,j,k}}}{\Delta y}
\]

By normalizing the magnetic field, we can obtain similar order of magnitude for the both the E and H fields.

\[
\vec{H} = \sqrt{\frac{\mu_{o}}{\epsilon_{o}}} \vec{H}
\]
\[ \nabla \times \vec{E} = -\frac{[\mu_r]}{c_o} \frac{\partial \vec{H}}{\partial t} \]

\[ \nabla \times \vec{H} = -\frac{[\varepsilon_r]}{c_o} \frac{\partial \vec{E}}{\partial t} \]

If we normalise the electric field

\[ \vec{E} = \sqrt{\frac{\varepsilon_o}{\mu_o}} \frac{\vec{E}}{n_o} = \frac{1}{n_o} \vec{E} \]

\[ \vec{D} = \frac{1}{\sqrt{\mu_o \varepsilon_o}} \vec{D} = c_o \vec{D} \]

By substituting the normalised fields, we can rewrite the Maxwell’s equation as

\[ \nabla \times \vec{H} = \frac{1}{c_o} \frac{\partial \vec{D}}{\partial t} \]

\[ \nabla \times \vec{E} = -\frac{\mu_o}{c_o} \frac{\partial \vec{H}}{\partial t} \]

\[ \vec{D} = \varepsilon_r \vec{E} \]

Expansion of the curl equation and only concentrating on 2-D solution of the equation, our resulting equations can be summarised below
\[ \nabla \times \vec{E} = -\frac{\mu}{c_o} \frac{\partial \vec{H}}{\partial t} \]

\[ \nabla \times \vec{H} = \frac{1}{c_o} \frac{\partial \vec{D}}{\partial t} \]

\[ D = \varepsilon_r E \]

\[ \vec{D} = \varepsilon_{xx} \vec{E}_x + \varepsilon_{xy} \vec{E}_y + \varepsilon_{xz} \vec{E}_z \]

\[ \vec{D} = \varepsilon_{yx} \vec{E}_x + \varepsilon_{yy} \vec{E}_y + \varepsilon_{yz} \vec{E}_z \]

\[ \vec{D} = \varepsilon_{zx} \vec{E}_x + \varepsilon_{zy} \vec{E}_y + \varepsilon_{zz} \vec{E}_z \]

By assuming only diagonal tenors

\[ \frac{\partial \vec{E}_y}{\partial y} - \frac{\partial \vec{E}_z}{\partial z} = -\frac{1}{c_o} \mu_{xx} \frac{\partial H_x}{\partial t} \]

\[ \frac{\partial \vec{E}_z}{\partial z} - \frac{\partial \vec{E}_x}{\partial x} = -\frac{1}{c_o} \mu_{yy} \frac{\partial H_y}{\partial t} \]

\[ \frac{\partial \vec{E}_x}{\partial x} - \frac{\partial \vec{E}_y}{\partial y} = -\frac{1}{c_o} \mu_{zz} \frac{\partial H_z}{\partial t} \]
\[ D_x = \varepsilon_{xx} E_x \]
\[ D_y = \varepsilon_{yy} E_y \]
\[ D_z = \varepsilon_{zz} E_z \]

The curl terms can now be calculated separately

\[
C_x^E = -\frac{\mu_0}{c_0} \frac{\partial H_x}{\partial t} = \frac{\partial \tilde{E}_y}{\partial z} - \frac{\partial \tilde{E}_z}{\partial y}
\]

\[
C_y^E = -\frac{\mu_0}{c_0} \frac{\partial H_y}{\partial t} = \frac{\partial \tilde{E}_z}{\partial x} - \frac{\partial \tilde{E}_x}{\partial z}
\]

\[
C_z^E = -\frac{\mu_0}{c_0} \frac{\partial H_z}{\partial t} = \frac{\partial \tilde{E}_x}{\partial y} - \frac{\partial \tilde{E}_y}{\partial x}
\]

\[
C_x^H = \frac{\partial H_x}{\partial y} - \frac{\partial H_y}{\partial z}
\]

\[
C_y^H = \frac{\partial H_y}{\partial z} - \frac{\partial H_z}{\partial x}
\]

\[
C_z^H = \frac{\partial H_z}{\partial x} - \frac{\partial H_x}{\partial y}
\]

Approximation using the finite difference

\[
C_x^{E,i,j,k} = \frac{E_{y,i,j,k+1} - E_{y,i,j,k}}{\Delta y} - \frac{E_{z,i,j,k+1} - E_{z,i,j,k}}{\Delta z}
\]

\[
C_y^{E,i,j,k} = \frac{E_{x,i,j,k+1} - E_{x,i,j,k}}{\Delta z} - \frac{E_{y,i+1,j,k} - E_{y,i,j,k}}{\Delta x}
\]

\[
C_z^{E,i,j,k} = \frac{E_{x,i+1,j,k} - E_{x,i,j,k}}{\Delta x} - \frac{E_{y,i,j,k+1} - E_{y,i,j,k}}{\Delta y}
\]

And now
\[ C^E_{x l} \frac{\partial}{\partial \Delta t} H_x \frac{\partial}{\partial \Delta x} - H_x \frac{\partial}{\partial \Delta x} - H_x \frac{\partial}{\partial \Delta x} - H_x \frac{\partial}{\partial \Delta x} \]

\[ C^E_{y l} \frac{\partial}{\partial \Delta t} H_y \frac{\partial}{\partial \Delta y} - H_y \frac{\partial}{\partial \Delta y} - H_y \frac{\partial}{\partial \Delta y} - H_y \frac{\partial}{\partial \Delta y} \]

\[ C^E_{z l} \frac{\partial}{\partial \Delta t} H_z \frac{\partial}{\partial \Delta z} - H_z \frac{\partial}{\partial \Delta z} - H_z \frac{\partial}{\partial \Delta z} - H_z \frac{\partial}{\partial \Delta z} \]

And finally

\[ C^H_{x l} \frac{\partial}{\partial \Delta t} - \frac{\partial}{\partial \Delta t} \]

\[ C^H_{y l} \frac{\partial}{\partial \Delta t} - \frac{\partial}{\partial \Delta t} \]

\[ C^H_{z l} \frac{\partial}{\partial \Delta t} - \frac{\partial}{\partial \Delta t} \]

\[ D_x |_{\Delta t} = (\epsilon_{xx} |_{\Delta t}) E_x |_{\Delta t} \]

\[ D_y |_{\Delta t} = (\epsilon_{yy} |_{\Delta t}) E_y |_{\Delta t} \]

\[ D_z |_{\Delta t} = (\epsilon_{zz} |_{\Delta t}) E_z |_{\Delta t} \]

Reduction to 2 dimension

For 2D, \( \frac{\partial}{\partial z} = 0 \) meaning no wave propagation in the z direction.


\[
\begin{align*}
C_x^{E,j} & = \frac{E_x^{i,j+1} - E_x^{i,j}}{\Delta y} \\
C_y^{E,j} & = -\frac{E_y^{i+1,j} - E_y^{i,j}}{\Delta x} \\
C_z^{E,j} & = \frac{E_z^{i,j+1} - E_z^{i,j}}{\Delta y} - \frac{E_y^{i,j+1} - E_y^{i,j}}{\Delta y} - \frac{E_x^{i,j+1} - E_x^{i,j}}{\Delta y}
\end{align*}
\]

\[
\begin{align*}
C_x^{H,j} & = \frac{H_x^{i,j+1} - H_x^{i,j}}{\Delta y} \\
C_y^{H,j} & = -\frac{H_y^{i+1,j} - H_y^{i,j}}{\Delta x} \\
C_z^{H,j} & = \frac{H_z^{i,j+1} - H_z^{i,j}}{\Delta y} - \frac{H_y^{i,j+1} - H_y^{i,j}}{\Delta y} - \frac{H_x^{i,j+1} - H_x^{i,j}}{\Delta y}
\end{align*}
\]

\[
\begin{align*}
\tilde{D}_x^{i,j} & = \left( \epsilon_{xx} \right)^{i,j} \tilde{E}_x^{i,j} \\
\tilde{D}_y^{i,j} & = \left( \epsilon_{yy} \right)^{i,j} \tilde{E}_y^{i,j} \\
\tilde{D}_z^{i,j} & = \left( \epsilon_{zz} \right)^{i,j} \tilde{E}_z^{i,j}
\end{align*}
\]

We can notice that the Maxwell’s equations have been decoupled into two distinct sets of equations of \( E_z \) and \( H_z \).
\[
C_x^{E} \frac{\hat{m}_x^{j}}{\Delta t} = -\frac{\hat{E}_x^{j+1} - \hat{E}_x^{j}}{\Delta y} \\
C_y^{E} \frac{\hat{m}_y^{j}}{\Delta t} = -\frac{\hat{E}_y^{j+1} - \hat{E}_y^{j}}{\Delta x} \\
C_x^{E} \frac{\hat{m}_x^{j}}{\Delta t} = -\frac{\hat{m}_x^{j+1} H_x^{j+\Delta t/2} - H_x^{j-\Delta t/2}}{\Delta t} \\
C_y^{E} \frac{\hat{m}_y^{j}}{\Delta t} = -\frac{\hat{m}_y^{j+1} H_y^{j+\Delta t/2} - H_y^{j-\Delta t/2}}{\Delta t} \\
C_x^{H} \frac{\hat{m}_x^{j}}{\Delta t} = \frac{H_x^{j+1} - H_x^{j-1}}{\Delta y} \\
C_y^{H} \frac{\hat{m}_y^{j}}{\Delta t} = \frac{H_y^{j+1} - H_y^{j-1}}{\Delta y} \\
C_z^{H} \frac{\hat{m}_x^{j}}{\Delta t} = \frac{H_z^{j+1} - H_z^{j-1}}{\Delta x} \\
C_z^{H} \frac{\hat{m}_y^{j}}{\Delta t} = \frac{H_z^{j+1} - H_z^{j-1}}{\Delta x} \\
C_z^{H} \frac{\hat{m}_z^{j}}{\Delta t} = \frac{1}{c_o} \frac{\tilde{D}_x^{j} - \tilde{D}_x^{j-1}}{\Delta t} \\
\tilde{D}_x^{j} \frac{\hat{m}_x^{j}}{\Delta t} = (\epsilon_{xx}^{j+1}) \tilde{E}_x^{j} \\
\tilde{D}_y^{j} \frac{\hat{m}_y^{j}}{\Delta t} = (\epsilon_{yy}^{j+1}) \tilde{E}_y^{j} \\
\tilde{D}_z^{j} \frac{\hat{m}_z^{j}}{\Delta t} = (\epsilon_{zz}^{j+1}) \tilde{E}_z^{j}
\]

For the \( H_z \)
Update equations can now be written for solving the future time values of the fields associated with the \( E_z \) and \( H_z \) modes.

\[
H_x^{i,j}_{b+\Delta t/2} = H_x^{i,j}_{b-\Delta t/2} + \left( \frac{c_o \Delta t}{\mu_{xx}} \right) C_{x}^{E,i,j}_{b}
\]

\[
H_y^{i,j}_{b+\Delta t/2} = H_y^{i,j}_{b-\Delta t/2} + \left( \frac{c_o \Delta t}{\mu_{yy}} \right) C_{y}^{E,i,j}_{b}
\]

\[
\tilde{D}_x^{i,j}_{v+\Delta t} = \tilde{D}_x^{i,j}_{v-\Delta t} + \left( c_o \Delta t \right) C_{x}^{H,i,j}_{v+\Delta t/2}
\]

\[
\tilde{E}_z^{i,j}_{v+\Delta t} = \left( \frac{1}{\varepsilon_{zz}} \right) D_{z}^{i,j}_{v+\Delta t}
\]

Likewise \( H_z \) mode

\[
H_z^{i,j}_{b+\Delta t/2} = H_z^{i,j}_{b-\Delta t/2} + \left( \frac{c_o \Delta t}{\mu_{zz}} \right) C_{z}^{E,i,j}_{b}
\]

\[
\tilde{D}_x^{i,j}_{v+\Delta t} = \tilde{D}_x^{i,j}_{v-\Delta t} + \left( c_o \Delta t \right) C_{x}^{H,i,j}_{v+\Delta t/2}
\]

\[
\tilde{D}_y^{i,j}_{v+\Delta t} = \tilde{D}_y^{i,j}_{v-\Delta t} + \left( -c_o \Delta t \right) C_{y}^{H,i,j}_{v+\Delta t/2}
\]

\[
\tilde{E}_x^{i,j}_{v+\Delta t} = \left( \frac{1}{\varepsilon_{xx}} \right) D_{x}^{i,j}_{v+\Delta t}
\]

\[
\tilde{E}_y^{i,j}_{v+\Delta t} = \left( \frac{1}{\varepsilon_{yy}} \right) D_{y}^{i,j}_{v+\Delta t}
\]