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Abstract: Although gas desorption is a known phenomenon, modeling fluid flow in tight gas reservoirs often ignores the governing desorption effect, assuming that viscous transport is the predominant controller, resulting in an erroneous prediction of mass transport and fluid flow calculations. Thus, developing a new model accommodating all the major contributing forces in such a medium is essential. This work introduces a new comprehensive flow model suitable for tight unconventional reservoirs, including viscous, inertia, diffusion, and sorption forces, to account for fluid transport. Based on Langmuir law and Knudsen diffusion effect, three models were generated and compared with different known models using synthetic data. The model was solved and analyzed for different scenario cases, and parametric studies were conducted to evaluate the desorption effect on different reservoir types using MATLAB. Results show that the contribution of the sorption mechanism to the flow increases with the reducing permeability of the medium and lower viscosity of the flowing fluid and an additional pressure drop up to 10 psi was quantified.

Keywords: unconventional reservoirs; desorption; modeling; fluid flow

1. Introduction

Unconventional reservoirs embody the upcoming revolution in the oil and gas industry due to the rapid growth of world energy demand anticipated by the United States Energy Information Association Outlook [1] and the continuous draining of the current conventional hydrocarbon resources. The increase in demand has led to an aggressive investigation of unconventional accumulations that were once shelved due to production complexities to be considered for exploring opportunities. Unconventional reservoirs are reservoirs with divergent geological characteristics [2], inconstant geochemical characteristics, intricate petrophysical properties, eccentricities in fluid phase behavior, and various governing flow mechanisms/forces [3]. Unconventional reservoirs include various types of reservoirs including gas hydrates, tight gas and oil, heavy oil, and shale oil and gas.

In their natural form, gas hydrates consist of water molecules (ice molecules) that act as hosts [4]. In contrast, guest molecules are methane, propane, isobutene, and ethane, among other gases that are chemically bonded with van der Waals forces in low degrees of temperature and, at the same time, under high pressure. Natural hydrate gas is primarily white and has the same appearance as ice. Natural hydrates are commonly known to have methane, which can burn, thus having the name "fire ice". Natural gas hydrates have long been deemed a nuisance for blocking transmission pipes, endangering the foundations of deep-water platforms and pipelines, and risking more disruption to the output of deepwater oil and gas [5], maybe a significant possible source of energy in the future. In the permafrost and beneath the ocean floor, huge deposits of natural gas hydrates are widely dispersed [6].

Geologically, shale is the source rock where oil was originated and trapped with part migration to the reservoir rock where migration path was available. Shale oil is



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). mainly found in organic shale with nanoscale pore diameters [7,8]. The shale rock has two purposes: one is generating while the other is reserving shale oil. Shale oil exists in both adsorbed form and free state form. Generally, shale oil is lightweight with low viscosity levels as well. Due to the very low transmissibility of reservoir rock, the oil is hard to produce on a commercial scale. The term "shale oil" also applies to oil found in semi-previous shale where permeability is in micro-Darcies. In contrast to shale gas, shale oil was formed during the generative window of organic evolution. As the shale rock continues to produce, a large portion of shale oil is retained, thus making the reservoir saturated.

Coalbed methane (CBM), as the name implies, is primarily composed of methane generated in coal seams and stored in the adsorbed state. Its common name in coal mining is "marsh gas". Coalbed methane is more or less an unconventional gas that is mostly found in coal beds where coals are both the source rock as well as the reservoir. Ninety-five percent of coalbed methane is chiefly composed of methane and other dispensable amounts of hydrocarbons and nonhydrocarbons.

Tight oil corresponds to oil trapped in reservoirs where low or ultra-low rock permeability contributes to unfavorable reservoir flow efficiency. Rock matrix permeability is mostly of the range of 10 to 1 mD or less and has a porosity that ranges between 1% and 10%. For conventional growth, some sandstone and carbonate reservoirs may have even lower permeabilities [9]. Tight sandstone gas refers to gas originated in sandstone, which has a permeability matrix that is less than 10^{-1} mD and is characterized by a porosity level below 10%. Sandstone interbedded with shale-mudstone, resulting in reservoirs immediately in contact with sources, no obvious traps or direct caprocks, but regional seals are well developed [10].

The forces found in unconventional reservoirs that control the fluid movement are diffusion, viscous, convection, desorption, inertial, capillary, sorption, and viscoelastic. These mechanisms are classified into two groups based on their controlling effect: trapability and/or displacement [11]. Trapability forces aid in trapping the wetting phase fluid, while displacement controls fluid mobility through the porous medium in nano, micro, and macro scales. Note here that these mechanisms can become of importance when discussing fluid flow and other relevant issues related to CO_2 and hydrogen storage as the model that will be created later on involves a term that represents the sorption phenomena [12].

1.1. Governing Forces

Several physical processes and mechanisms affect the flow in porous media. The effect of certain forces governs more than other forces depending on the reservoir types and conditions and the forces acting as trapability or displacement [11]. Thus, the currently used method—Darcy's equation—calculates pressure drop and flow concentration, but it lacks accuracy and validity as it ignores most of the governing forces. Diffusion is the movement of particles or materials (gas or liquid) in a substance from a high concentration area to a low concentration area. It is considered a displacement force [13]. Viscoelasticity describes the property of materials that can be either solids or liquid experiencing deformation forces, where both viscous and elastic characteristics forces can be observed [14,15]. The viscoelasticity force is composed of both displacement and trapability forces. Capillary pressure is a force that exists in saturated reservoirs with two or more immiscible fluids in reservoir rock's tiny pores [16]. The presence of capillary forces in a porous medium leads to hydrocarbon entrapment. Capillary forces are considered trapability forces due to their mechanism [17]. Inertial forces form due to the fluid momentum [18]. The fluid tends to resist velocity change by applying an equal or opposite force to the direction of the applied force. Inertial force is one of the forces affecting the displacement of fluid in unconventional reservoirs. Advection forces contribute to fluid and molecular movement through porous media, enhancing displacement and mass transfer [19]. Viscosity is the resistance of fluids to any alternations in shape or movement of nearby segments [18]. It could be described as internal friction within the fluid molecules, which resists velocity difference advancement. The viscosity of liquids decreases significantly as temperature increases, whereas the viscosity of gases increases as temperature increases. Sorption and desorption: by definition, sorption is the transfer of a substance from the gas phase or solution to the solid phase. Sorption has two types: adsorption and absorption [19]. Absorption occurs when molecules penetrate a solid medium. In contrast, adsorption occurs when gaseous molecules get attached to the surface of the solid and depend on the properties of the sorbate (gaseous molecules) and the sorbent (solid) [20]. Sorption is affected by many factors: pressure, temperature, porosity, permeability, the surface area of sorbent, and organic carbon content of the sorbate [20]. On the other hand, desorption occurs when reservoir pressure drops and the free gas that got sorbed by the sorbent gets released again [21–23].

1.2. Conventional Fluid Flow Models

1.2.1. Darcy's Law

Formulated by Henry Darcy, utilizing the homogenization principle, Darcy's law is considered one of the fundamental equations used to describe the fluid flow in porous media. Darcy's equation has been used in many industries and forms of engineering such as hydrogeology, electricity, etc. However, the multiple applications of Darcy's law led many scholars and researchers to adapt the physics of Darcy's equation to the petroleum industry, taking into consideration the resemblance of water movement in porous media to hydrocarbon flow through the reservoir's porous media. As a result, the derivation of Darcy's law in the petroleum industry was conducted assuming one-dimension, singlephase flow with a constant viscosity through a homogenous reservoir rock. Darcy's law describes the proportional relationship between the fluid velocity in porous media and the pressure drop over a given distance.

Darcy's equation is expressed as

$$v = -\frac{KA}{\mu}\frac{dp}{dx} \tag{1}$$

Fluids can coexist in the same basin in the subsurface, forming reservoirs with two or more fluid types, such as oil and gas; oil and water; and water, oil, and gas reservoirs. Such cases led to further investigations to improve Darcy's equation to accommodate the multiphase flow phenomena. Consequently, a comprehensive and intensive study utilized different resources, theoretical research, experimental observation, data processing, simulation, and field applications. As a result, many publications have been produced to describe and shape the multiphase flow in reservoirs that enriched the petroleum engineering research outcomes [24,25]. The measurement of oil, gas, and water flow; output; and assessment of primary and secondary oil recovery and reservoir dynamics focus on multiphase flow physics in reservoirs [26]. Due to the nature of Darcy's equation and its limitations, it is replaced by the Forchheimer equation at higher flow velocities [27].

1.2.2. Forchheimer's Equation

As Darcy's equation has limited validity in the low-velocity domain, a better flow correlation to estimate higher velocity flow was crucially required. Forchheimer's equation was one of the first equations that addressed this issue and improved fluid flow prediction and calculations. Forchheimer's equation is an empirical equation that relates pressure drop across a given distance with fluid velocity and friction across porous media. Forchheimer's equation of Darcy's equation to accommodate, describe and calculate the effect of non-Darcy flow in porous media [28].

Forchheimer's equation is expressed as

$$\frac{\partial P}{\partial x} = \frac{\mu}{k}v + \beta\rho v^2 \tag{2}$$

where β is the non-Darcy flow coefficient, which is measured using core samples in laboratories or determined from analysis of multi-rate pressure tests. The first term represents Darcy's equation, which denotes the viscous forces, while the second term denotes the inertial governing forces. Deviations in fluid flow behavior from Darcy's law have long been recognized in many applications [29,30]

1.3. Langmuir Adsorption Isotherm

In 1916, Irvin Langmuir developed the theory of Langmuir isotherm, which was used extensively to describe the sorption/desorption in the oil and gas industry. The theory is based on the following assumptions:

- One molecule is adsorbed in each adsorption location.
- No interaction between adsorbed gas molecules within the pores.
- The energy at sorption/desorption location is equal.

Langmuir isotherm equation is presented as follows:

$$V = V_L \frac{P}{P + P_L} \tag{3}$$

where *V* is the volume of the adsorbed gas, V_L is the Langmuir volume constant, P_L is the Langmuir pressure constant, and *P* is the pressure at the reservoir as shown in Figure 1.



Figure 1. Langmuir constants in adsorption vs. pressure.

1.4. Knudsen Diffusion

Knudsen diffusion, named after Martin Knudsen, occurs when the mean pore diameter is smaller than the mean free path of gas molecules, leading to collisions of gas molecules with the pore walls. Knudsen diffusion is considered a predominant transport mechanism.

The concentration flux can be calculated using the following equation:

$$J = -D_k \frac{\partial C}{\partial z} \tag{4}$$

in which, D_k is the Knudsen diffusivity and can be calculated using the following equation:

$$D_k = \frac{d_p}{2} \left(\frac{\pi kT}{2M}\right)^{1/2} \tag{5}$$

where d_p is the pore diameter, *T* is temperature, *M* is molar mass of gas, and *k* is the Boltzmann constant.

The present work aims to establish a new model based on Langmuir and Knudsen diffusion to better estimate the fluid flow in tight porous media. Additionally, it also targets to couple diffusion model to capture the actual behavior of the fluid. Several investiga-

tions were conducted using various case matrices and data from different unconventional reservoir types using MATLAB (developed by MathWorks in Massachusetts, USA) for simulation [22,31,32].

2. Materials and Methods

2.1. Model Creation

Several steps were taken to create the desired models, and a thorough comparison was conducted to determine the optimum model that quantitively represents viscous, inertial, diffusion, and desorption forces in a tight porous medium. The same concept that Forchheimer applied is implemented in this study to formulate a new equation that accounts for viscous, inertial, diffusion, and desorption forces. Note that Forchheimer's Model represents viscous and inertial forces only, and thus a new term that can represent both diffusion and desorption forces must be added.

The first step to formulate the desired model is to decide which Desorption/Diffusion law will be used to create the model and how it can be developed to fit the porous media characteristics. Three basic fundamental laws were used: Fick's law to represent diffusion forces, Knudsen law used in two primary forms: one to represent diffusion forces and the other to represent desorption forces, and Langmuir's law to represent desorption forces. Three models were developed in this study, and each will be discussed in detail in the following sections.

2.1.1. First Model

To create a credible model, a relationship between diffusion and desorption forces and the pressure drop should be established to add the desired term to Forchheimer's equation. The first term created is expected to capture the effect of both diffusion and desorption forces by coupling these two forces in a single term based on the understanding of Fick's and Langmuir's models. Note that Fick's first law was used to establish such a relationship as it states that the velocity is directly proportional to the pressure gradient. By understanding the merits of Fick's first law, it can be concluded that the concentration gradient controls diffusion. Furthermore, Langmuir's coefficient represented by the symbol θ is added to mathematically represent desorption forces as in Equation (8).

$$\theta = \frac{P_{Des}}{P_L + P_{Des}} \tag{6}$$

To conclude the addition of the following term developed the first model was created:

$$\frac{\partial P}{\partial x} = -v^2 \theta \frac{\partial C}{\partial x} \tag{7}$$

where

$$\frac{dP}{dx} = \frac{\frac{M}{LT^2}}{L} = \frac{M}{L^2T^2} \tag{8}$$

$$=\frac{L}{T}$$
(9)

$$\frac{dC}{dx} = \frac{\frac{M}{L^3}}{L} = \frac{M}{L^4} \tag{10}$$

 $\theta = Dimensionless.$

We perform a dimensional analysis to check the term's validity:

v

$$\frac{M}{L^2 T^2} = \frac{L^2}{T^2} \times \frac{M}{L^4}$$
(11)

$$\frac{M}{L^2 T^2} = \frac{M}{L^2 T^2}$$
(12)

2.1.2. Second Model

The second model was similarly created by adding a single term that represents both diffusion and desorption forces. It was generated using Fick's diffusion, Knudsen desorption, and Langmuir's models. The main difference between this model and the first model created is the added Knudsen desorption coefficient to enhance the model's accuracy and represent desorption forces better. It is believed that desorption forces cannot be represented by Langmuir's coefficient only. Similarly, the second model was developed by the addition of the following term:

$$\frac{\partial P}{\partial x} = -K_{Des}\theta v \frac{\partial C}{\partial x}$$
(13)

2.1.3. Third Model

The addition of two individual terms—one representing diffusion forces and the second representing desorption forces—distinctively created the third model. The diffusion term, which was initially developed by AlDhuhoori [33], was represented by a velocity term based on the original concept of Fick's partial pressure law, a diffusivity coefficient which was derived from Fick's first law was included to increase the accuracy of the model and to account for the diffusion of a particular phase into another. Furthermore, a non-Darcy term that includes both porosity and permeability of a medium was added to emulate reservoir properties and characteristics.

As for the separate desorption term, generated by understanding the merits of Knudsen desorption law, it includes a viscosity term, a velocity term, a length term that represents the length of the reservoir (since it plays a significant role in estimating Knudsen desorption coefficient, which was also added to the new term). The new addition to Forchheimer's model can be represented mathematically by adding two terms represented in the following equation:

$$\frac{\partial P}{\partial x} = -Dv\beta \frac{\partial C}{\partial x} - \frac{v\mu K_{Des}}{L^2}$$
(14)

2.2. Mathematical Formulation

The same concept that Forchheimer applied is implemented in this study to formulate a new equation that accounts for viscous, inertial, diffusion, and desorption forces. The new modifications to the model address the fluid transport phenomena into three scales incorporating a diffusion–desorption term while accounting for the porous media properties. A detailed derivation of the second model is shown in this section to explain the mathematical expression and steps taken to reach the final form of the model and to achieve the main goal of the derivation: to be able to represent these forces in both time and space. The first step is to add the modified diffusion/desorption term to the equation, and thus we get

$$-\frac{\partial P}{\partial x} = \frac{\mu}{k}v + \beta\rho v^2 + K_{Des}\theta v \frac{\partial C}{\partial x}$$
(15)

Taking the derivative of both sides of the equation with respect to *x*:

$$-\frac{\partial^2 P}{\partial x^2} = \frac{\mu}{k} \frac{\partial v}{\partial x} + 2\beta \rho v \frac{\partial v}{\partial x} + K_{Des} \theta \frac{\partial v}{\partial x} \frac{\partial C}{\partial x} + K_{Des} \theta v \frac{\partial^2 C}{\partial x^2}$$
(16)

By rearranging we get

$$\frac{\partial^2 P}{\partial x^2} = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta \frac{\partial C}{\partial x}\right] \left(-\frac{\partial v}{\partial x}\right) - K_{Des}\theta v \frac{\partial^2 C}{\partial x^2}$$
(17)

This is the continuity equation in 1-D form for a single steady-state system, or

$$v\frac{\partial\rho}{\partial x} + \rho\frac{\partial v}{\partial x} = -\phi\frac{\partial\rho}{\partial t}$$
(18)

By rearranging, we get

$$-\frac{\partial v}{\partial x} = \frac{\phi}{\rho}\frac{\partial\rho}{\partial t} + \frac{v}{\rho}\frac{\partial\rho}{\partial x}$$
(19)

By substituting the continuity equation from above in the previous equation, we get

$$\frac{\partial^2 P}{\partial x^2} = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta\frac{\partial C}{\partial x}\right] \left(\frac{\phi}{\rho}\frac{\partial\rho}{\partial t} + \frac{v}{\rho}\frac{\partial\rho}{\partial x}\right) - K_{Des}\theta v\frac{\partial^2 C}{\partial x^2}$$
(20)

Using the chain rule,

$$\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial P} \frac{\partial P}{\partial t}$$
(21)

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial P} \frac{\partial P}{\partial x}$$
(22)

We get

$$\frac{\partial^2 P}{\partial x^2} = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta\frac{\partial C}{\partial x}\right] \left(\frac{\phi}{\rho}\frac{\partial\rho}{\partial P}\frac{\partial P}{\partial t} + \frac{v}{\rho}\frac{\partial\rho}{\partial P}\frac{\partial P}{\partial x}\right) - K_{Des}\theta v\frac{\partial^2 C}{\partial x^2}$$
(23)

Moreover, taking

$$\frac{\partial \rho}{\partial P} = \rho c \tag{24}$$

We get

$$\frac{\partial^2 P}{\partial x^2} = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta\frac{\partial C}{\partial x}\right] \left(\frac{\phi}{\rho}(\rho c)\frac{\partial P}{\partial t} + \frac{v}{\rho}(\rho c)\frac{\partial P}{\partial x}\right) - K_{Des}\theta v\frac{\partial^2 C}{\partial x^2}$$
(25)

Or on simplifying and rearranging

$$\frac{\partial^2 P}{\partial x^2} + K_{Des}\theta v \frac{\partial^2 C}{\partial x^2} = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta \frac{\partial C}{\partial x}\right]\phi c \frac{\partial P}{\partial t} + \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta \frac{\partial C}{\partial x}\right]v c \frac{\partial P}{\partial x}$$
(26)

which can be written as

$$\frac{\partial^2 P}{\partial x^2} + A \frac{\partial^2 C}{\partial x^2} = B \frac{\partial P}{\partial t} + C \frac{\partial P}{\partial x}$$
(27)

$$A = K_{Des}\theta v \tag{28}$$

$$B = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta\frac{\partial C}{\partial x}\right]\phi c$$
⁽²⁹⁾

$$C = \left[\frac{\mu}{k} + 2\beta\rho v + K_{Des}\theta \frac{\partial C}{\partial x}\right]vc$$
(30)

Note that the other two models were formulated using almost the same steps.

2.3. Numerical Modeling

A unique synthetic environment consisting of 1-D mass transport of a single gaseous phase has been created to study the validity of various models generated above. The conceptual design of model has the following assumption:

- Homogenous one-dimensional medium
- Finite boundaries
- Single gaseous phase
- Constant temperature throughout the tested area
- Gravity and capillary effects neglected

By applying the finite difference method to the investigated models, derivatives were transformed to partial equations and initial boundaries were selected. Additionally, tight

reservoir characteristics and features were adequately selected to ensure that parametric values properly represent the reservoir rock and fluid properties. Proper boundaries were selected, and the models were then discretized evenly to different blocks for numerical simulation. The central point of the block method was selected for better estimation of pressure and concentration solutions, using the implicit method of second-order partial derivatives, central and forward methods for the first order of partial derivatives. The following equations were generated and substituted in the generated model to solve via MATLAB Simulator:

Finite difference formula for $\frac{\partial P}{\partial t}$:

$$\left.\frac{\partial P}{\partial t}\right|_{x=x_i} \approx \frac{P_i^{n+1} - P_i^n}{\Delta t} \tag{31}$$

Finite difference formula for $\frac{\partial P}{\partial r}$:

$$\left.\frac{\partial P}{\partial x}\right|_{t=t_n} \approx \frac{P_{i+1}^n - P_{i-1}^n}{2\Delta x} \tag{32}$$

Finite difference formula for $\frac{\partial^2 P}{\partial r^2}$:

$$\frac{\partial^2 P}{\partial x^2}\Big|_{t=t_n} \approx \frac{P_{i+1}^n - 2P_i^n + P_{i-1}^n}{\Delta x^2}$$
(33)

Finite difference formula for $\frac{\partial^2 C}{\partial r^2}$:

$$\frac{\partial^2 C}{\partial x^2}\Big|_{t=t_n} \approx \frac{C_{i+1}^n - 2C_i^n + C_{i-1}^n}{\Delta x^2}$$
(34)

An iterative approach was employed, where at each time step, the model calculates concentration based on the pressure values. As for the pressure estimation, the model calculates the pressure at each time step based on the pressure estimated at the previous time step, considering the reservoir characteristics and fluid properties during the process. All the numerical models are set up to follow the same process and iterative approach.

3. Results and Discussion

3.1. Synthetic Case Study Validation

The synthetic case study shows a gaseous fluid with two slightly different concentrations and a reservoir with two main different boundary pressure conditions. The reservoir rock parameters are assumed to be constant, and thus this case is entirely homogenous. Additionally, fluid properties are assumed to be constant.

Furthermore, a grid system of 100 grid blocks is used to represent the 500 ft long reservoir. Table 1 summarizes the data used in the gas–gas phase medium containing mainly methane [32–35].

Parameter	Value	Unit
Viscosity	0.01402	cP
Permeability	0.001	md
Porosity	0.07	
Compressibility	$4.40 imes10^{-10}$	psi^{-1}
Beta	2.3767×10^{6}	1/ft
Density	0.0417	ibf/ft ³
Length	500	ft
K _{des}	$8.26706 imes 10^{7}$	
Velocity	0.005 - 0.00005	ft/hr
Pressure at boundary in	500	psia
Pressure at boundary out	400	psia
Concentration at boundary in	1000	ppm
Concentration at boundary out	500	ppm

Table 1. Synthetic data utilized for modeling of poor permeability medium.

Several plots have been constructed in MATLAB to simulate the behavior of a tight unconventional reservoir for both pressure and concentration drop during a specific time and distance until pressure and concentration steady-state times are reached. The newly derived models were tested for validation by utilizing the data provided in Table 1, representing a tight unconventional reservoir gas–gas case.

Figure 2 shows the results of the Desorption M3 model, created to represent the pressure distribution within a porous media, the concentration, and the rest of the model's pressure profiles results. Additionally, the pressure gradient and the concentration gradient at different time iterations in terms of hours until we reach a pressure steady-state time and a concentration steady-state time. Note that calculations showed that the time required for concentration to reach the steady-state condition for each model is less than the time required for the pressure to reach the steady-state phase for all the models.



Figure 2. Desorption M3 pressure and concentration profiles.

3.2. Comparison of the Newly Developed Models Pressure Gradients

By comparing the pressure gradients of the three newly developed models, it can be observed that the velocity and the pressure gradient have a directly proportional relationship (Figure 3). As the velocity increase, so does the pressure gradient. Additionally, Desorption Model 1 has a much higher pressure gradient estimation compared to the other two models created, which showed almost the same result/trend with a pressure differential of almost ten psi. The initial presumption observed at this stage is that the first model is overestimating the pressure differential compared to the other two models despite being theoretically accurate. In the following section, a comparison will be carried out to investigate the credibility of all three models by comparing them to previously published desorption models.



Figure 3. Desorption models pressure gradient vs. velocity comparison.

3.3. Comparison of Different Flow Models with the Newly Developed Models

A comparison between Darcy's model, Forchheimer's model, diffusion, and the newly developed model in the gas–gas case is performed to compare the pressure gradient drop using the three models. Figure 4 shows the predicted pressure drop across the porous medium at steady-state conditions using the models. Where the new models should accommodate the following forces: inertial loss, diffusion, and desorption.



Figure 4. Comprehensive comparison of flow models: Darcy, Forchheimer's, diffusion, and desorptions.

Figure 4 shows the newly developed model, which exhibited a semi-exponential behavior. Compared to the diffusion model created by Aldhuhoori [33], Forchheimer's model, and Darcy's model, Desorption M1 experiences a high-pressure gradient estimation of a difference of 66.402 psi with Diffusion model, a difference of 71.25 psi compared with Forchheimer's, and a difference of 142.650 psi with Darcy's. The first model overestimates the pressure drop, which indicates that this model failed to quantify the effect of both desorption and diffusion. On the other hand, Desorption M2 lays precisely on Forchheimer's Models as the difference of pressure between Desorption M2 and Forchheimer's is zero as shown in Table 2, leading to lower pressure drop. Moreover, the Desorption M3 model represented viscous, inertia, diffusion, and desorption effects and resulted in a higher pressure gradient than the diffusion model. So far, the third desorption model is showing promising results. It can capture the effects of both diffusion and desorption without overestimating compared to the other two models.

Table 2. Press	sure gradient	different for	different models	at velocity	[•] 0.005 ft/h
	0				

	Darcy	Forchhei Mer's	Diffusion	Desorption 1	Desorption 2	Desorption 3
Desorption 1	142.650	71.250	66.402		71.250	57.707
Desorption 2	71.400	0.000	-4.848	-71.250		-13.543
Desorption 3	84.943	13.543	8.695	-57.707	13.543	

3.4. Comparison of Newly Developed Models with Well-Known Published Models

Furthermore, the newly developed model was compared with two different wellknown publication models to study the sorption effect only. The two models were developed by Shabro [36] and Boosari [37].

It can be observed in Figure 5 that compared with Shabro's and Boosari's models, Desorption M3 generates a more accurate pressure gradient compared with the other desorption models. In comparison, Desorption M1 has an overestimating pressure gradient, while Desorption M2 model is underestimating the pressure gradient and hence the first and second desorption models will be discarded, and further studies will be conducted to thoroughly investigate the effect of the third desorption model and its effectiveness in estimating the pressure drop.



Figure 5. Comparison on desorption effect using previous published models.

3.5. Comparison of Newly Developed Models Using Different Permeabilities

Over the years, many definitions and methods to distinguish unconventional reservoirs from conventional reservoirs were developed by many researchers [38,39]. They mainly focused on a certain property or a specified characteristic to distinguish between those reservoirs. A couple of the most famous criteria used to characterize and distinguish reservoirs are based on the permeability of the porous media in a specified reservoir. In this sensitivity study, the newly developed model will be tested against different permeabilities representing different types of reservoirs to examine the effectiveness of the desorption forces utilizing a criterion developed by Belhaj [40].

Belhaj classified various types of reservoirs based on permeability values ranging from 10^{-4} mD up to 100 mD. It includes five main types of reservoirs: shale, tight reservoirs, limestone, CBM, and conventional reservoirs as summarized in Table 3. To investigate the effect of permeability on the newly developed model, Darcy's model, Forchheimer's, and AlDhuhoori's diffusion model are included in this study. Figure 6 shows the criteria developed by Belhaj to classify different types of reservoirs based on reservoir permeability.

Permeability, mD	Reservoir Type
0.0001	Ultra Tight
0.001	Very Tight
0.01	Tight
0.1	Low Permeability
5	Moderate Permeability
50	High Permeability

Table 3. Permeabilities values for different reservoir types.



Reservoir Quality Matrix

Figure 6. Belhaj's classification matrix of conventional and unconventional reservoirs.

The four models were compared at different permeabilities ranging from 10^{-4} mD up to 10^{-1} mD. As indicated from Figure 7 as the velocity increases, the difference between the pressure drop estimation using the newly developed model and Forchheimer's model becomes clear. The diffusion and desorption effects become much more noticeable.



Figure 7. Pressure gradient comparison for different permeabilities of Darcy, Forchheimer's, diffusion, and desorption M3.

It can be concluded that as the permeability increases, the difference between the pressure drop calculated using the newly developed model and Forchheimer's model decreases until both models generate the same result at a permeability of 10^{-1} mD and thus indicating that the diffusion and desorption effects decrease as the permeability increases. Thus, it is apparent that the newly developed model can adequately capture the effect of diffusion and desorption forces in extremely tight media such as shale, tight reservoirs, and some limestones and fails to characterize that effect in higher permeability reservoirs such as CBM and conventional reservoirs in general. Note that at low permeabilities, the model exhibited the same trend as that of Forchheimer's, but at higher velocities, the model fails to capture those effects. Therefore, the model can only predict the pressure drop at low permeabilities.

It can also be observed that the desorption effects tend to have exponential behavior with low permeabilities, while with higher permeability, it tends to have a straight line behavior.

4. Conclusions

The following points summarize the work done on investigating the effect of diffusion forces in modeling fluid flow in tight unconventional reservoirs and highlights the main conclusions:

- A new 1-D linear and radial mathematical models were derived, tested, and numerically simulated to investigate and address the effect of diffusion/desorption forces in tight unconventional reservoirs.
- The newly developed model proved the importance of the contribution of diffusion/desorption forces to fluid flow in the porous media, as initially hypothesized. The significant effect of both forces is noted as the reservoir deviated towards unconventionality.
- Like the establishment of steady-state time for pressure gradient, the concept of steady-state time for concentration gradient is introduced for the first time. This newly introduced concentration gradient steady-state time means that the medium reached a constant concentration gradient throughout the pores system (constant slope).

5. Patents

A new desorption model has been created that better estimates the desorption effect along with the diffusion effect. The new proposed model will be able to address the pressure drop in porous media by adhering to the diffusion and desorption effect.

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References

- 1. U.S. Energy Information Administration—EIA—Independent Statistics and Analysis. Short-Term Energy Outlook—U.S. Energy Information Administration (EIA). (n.d.). Available online: https://www.eia.gov/outlooks/steo/ (accessed on 7 June 2021).
- 2. Harris, C. What Is Unconventional Resources? AAPG Annual Convention and Exhibition: Long Beach, CA, USA, 2012.
- 3. Chengzao, J.; Zheng, M.; Zhang, Y. Unconventional hydrocarbon resources in China and the prospect of exploration and development. *Pet. Dev.* 2012, *39*, 139–146.
- Hassanpouryouzband, A.; Joonaki, E.; Farahani, M.V.; Takeya, S.; Ruppel, C.; Yang, J.; English, N.J.; Schicks, J.M.; Edlmann, K.; Mehrabian, H.; et al. Gas hydrates in sustainable chemistry. *Chem. Soc. Rev.* 2020, *49*, 5225–5309. [CrossRef] [PubMed]
- 5. Sloan, E.D., Jr.; Koh, C.A. Clathrate Hydrates of Natural Gases; CRC Press: Boca Raton, FL, USA, 2007.
- 6. Rutqvist, J.; Moridis, G.J.; Grover, T.; Collett, T. Geomechanical response of permafrost-associated hydrate deposits to depressurization-induced gas production. *J. Pet. Sci. Eng.* **2009**, *67*, 1–12. [CrossRef]
- Zou, C.; Zhang, G.; Yang, Z.; Tao, S.; Hou, L.; Zhu, R.; Yuan, X.; Ran, Q.; Li, D.; Wang, Z. Concepts, characteristics, potential and technology of unconventional hydrocarbons: On unconventional petroleum geology. *Pet. Explor. Dev.* 2013, 40, 413–428. [CrossRef]
- 8. Foroozesh, J.; Abdalla, A.I.M.; Zhang, Z. Pore Network Modeling of Shale Gas Reservoirs: Gas Desorption and Slip Flow Effects. *Transp. Porous Media* **2018**, 126, 633–653. [CrossRef]
- Moridis, G.J.; Blasingame, T.A.; Freeman, C.M. Analysis of mechanisms of flow in fractured tight-gas and shale-gas reservoirs. In Proceedings of the SPE Latin American and Caribbean Petroleum Engineering Conference. Society of Petroleum Engineers, Lima, Peru, 1–3 December 2010.
- 10. Zou, C.N.; Yang, Z.; Tao, S.Z.; Yuan, X.J.; Zhu, R.K.; Hou, L.H.; Wu, S.T.; Sun, L.; Zhang, G.S.; Bai, B.; et al. Continuous hydrocarbon accumulation over a large area as a distinguishing characteristic of unconventional petroleum: The Ordos Basin, North-Central China. *Earth-Sci. Rev.* **2013**, *126*, 358–369. [CrossRef]
- 11. Hadi, B.; Rabab, Q.; Bisweswar, G.; Saqer, R. Modeling Fluid Flow in Tight Unconventional Reservoirs: Nano Scale Mobility/Trapability Mechanistic Approach! In Proceedings of the SPE Gas & Oil Technology Showcase and Conference, Dubai, United Arab Emirates, 21–23 October 2019. [CrossRef]
- 12. Hassanpouryouzband, A.; Joonaki, E.; Edlmann, K.; Haszeldine, R.S. Offshore Geological Storage of Hydrogen: Is This Our Best Option to Achieve Net-Zero? *ACS Energy Lett.* **2021**, *6*, 2181–2186. [CrossRef]
- 13. Wang, J.; Feng, L.; Zhao, L.; Snowden, S. China's natural gas: Resources, production and its impacts. *Energy Policy* **2013**, *55*, 690–698. [CrossRef]
- 14. Christensen, R.M. *Theory of Viscoelasticity*, 2nd ed.; Dover Publications: New York, NY, USA, 2003. Available online: https://searchebscohost-com.libconnect.ku.ac.ae/login.aspx?direct=true&db=cat06281a&AN=kul.35983&site=eds-live&scope=site (accessed on 29 September 2021).
- De, A.; Kuipers, J.A.M.; Peters, E.A.J.F.; Padding, J.T. Viscoelastic flow simulations in random porous media. J. Non-Newton. Fluid Mech. 2017, 248, 50–61. [CrossRef]
- Shapiro, A.A.; Stenby, E.H. Effects of Capillary forces and Adsorption on Reserves Distribution. In Proceedings of the SPE European Petroleum Conference, Milan, Italy, 22–24 October 1996. Paper SPE-36922.

- 17. Legait, B.; Sourieau, P.; Combarnous, M. Inertia, viscosity, and capillary forces during two-phase flow in a constricted capillary tube. *J. Colloid Interface Sci.* **1983**, *91*, 400–411. [CrossRef]
- Belhaj, H.A.; Agha, K.R.; Butt, S.D.; Islam, M.R. Simulation of Non-Darcy Flow in Porous Media Including Viscous, Inertial and Frictional Effects. In Proceedings of the 2003 SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 21 October 2003. Paper SPE 84879.
- 19. Guo, L.; Peng, X.; Wu, Z. Dynamical characteristics of methane adsorption on monolith nanometer activated carbon. *J. Chem. Ind. Eng.* **2008**, *11*, 2726–2731.
- Zhang, C. Soil and Groundwater Remediation—Fundamentals, Practices, and Sustainability; John Wiley & Sons: Hoboken, NJ, USA, 2020. Available online: https://app.knovel.com/hotlink/toc/id:kpSGRFPS01/soil-groundwater-remediation/soil-gro
- 21. Rolando, M.A. Roque-Malherbe (2007) Adsorption and Diffusion in Nanoporous Materials, 6000 Broken Sound Parkway NW, Suite 300; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2007.
- 22. Em, K.G.; Ali, B.; Narayan, A. Microflows and Nanoflows Fundamentals and Simulation; Springer: New York, NY, USA, 2005.
- 23. Mahmoud, M. Effect of Gas Adsorption on the Estimation of Gas in Place (GIP) in Conventional and Unconventional Reservoirs. *Arab. J. Sci. Eng.* **2019**, *44*, 6205–6214. [CrossRef]
- 24. Neuman, S.P. Theoretical derivation of Darcy's law. Acta Mech. 1977, 25, 153–170. [CrossRef]
- 25. Whitaker, S. Flow in porous media I: A theoretical derivation of Darcy's law. *Transp. Porous Media* **1986**, *1*, 3–25. [CrossRef]
- 26. Papathanasiou, T.D.; Markicevic, B.; Dendy, E.D. A computational evaluation of the Ergun and Forchheimer equations for fibrous porous media. *Phys. Fluids* **2001**, *13*, 2795–2804. [CrossRef]
- Freij-Ayoub, R.; Mühlhaus, H.B.; Walshe, J.L. 2-Phase Convective Multicomponent Reactive Transport Model. In *Computational Mechanics–New Frontiers for the New Millennium*; Elsevier: Amsterdam, The Netherlands, 2001; pp. 803–808.
- 28. Evans, R.; Faruk, C. Characterization of Non-Darcy Multiphase Flow in Petroleum Bearing Formations. Annual Status Report, 14 May 1991–13 May 1992; Association of Information and Image Management: Maryland, LA, USA, 14 May 2021. [CrossRef]
- 29. Katz, D.L.V.; Lee, R.L. *Natural Gas Engineering: Production and Storage*; McGraw-Hill Economics Department: New York, NY, USA, 1990.
- 30. Zeng, Z.; Grigg, R. A Criterion for Non-Darcy Flow in Porous Media. Transp. Porous Media 2006, 63, 57–69. [CrossRef]
- Camacho-Velazquez, R.; Padilla-Sixto, R.; Vasquez-Cruz, M. Inflow Performance Relationships with Inertial Effects in the Reservoir. In Proceedings of the Production Operations Symposium, Oklahoma City, OK, USA, 21–23 March 1993. Paper SPE-25481.
- Yu, P.; Dian, F.; Chen, S. A Novel Approach to Determine Gas Velocity Profile in Entire Knudsen Number Regime for Nanoporous Shale with Various Pore Geometries. In Proceedings of the SPE/AAPG/SEG Unconventional Resources Technology Conference, Virtual, 22 July 2020; 1553. [CrossRef]
- 33. Aldhuhoori, M.A.; Belhaj, H.; Alkuwaiti, H.K.; Ghosh, B.; Fernandes, R.; Qaddoura, R. Role of viscous, diffusion and inertial mechanisms in modeling fluid flow through unconventional reservoir. *J. Pet. Sci. Eng.* **2021**, 205, 108772. [CrossRef]
- Mydland, S.; Yusra, I.; Whitson, C.H.; Dahouk, M.M.; Carlsen, M.L. Gas EOR Processes in Tight Unconventionals. In Proceedings
 of the SPE Improved Oil Recovery Conference. Society of Petroleum Engineers, Virtual, 31 August–4 September 2020.
- Javadpour, F. Nanopores and Apparent Permeability of Gas Flow in Mudrocks (Shales and Siltstone). J. Can. Pet. Technol. 2009, 48, 16–21. [CrossRef]
- 36. Shabro, V.; Torres-Verdín, C.; Sepehrnoori, K. Forecasting Gas Production in Organic Shale with the Combined Numerical Simulation of Gas Diffusion in Kerogen, Langmuir Desorption from Kerogen Surfaces, and Advection in Nanopores. In Proceedings of the SPE Annual Technical Conference and Exhibition, San Antonio, TX, USA, 8–10 October 2012. [CrossRef]
- Boosari, H.; Sina, S.; Aybar, U.; Eshkalak, M.O. The Effect of Desorption-induced Porosity-Permeability Changes and Geomechanics on Production from U.S. Shale Gas Formations. In Proceedings of the 49th U.S. Rock Mechanics/Geomechanics Symposium, San Francisco, CA, USA, 28 June–1 July 2015.
- 38. Bahadori, A. Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs; Elsevier: Amsterdam, The Netherlands, 2018.
- 39. Hoss, B.; Ebrahim, F.; Fatemeh, B. *Hydraulic Fracturing in Unconventional Reservoirs—Theories, Operations, and Economic Analysis,* 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2019.
- Belhaj, H.A.; Agha, K.R.; Nouri, A.M.; Butt, S.D.; Islam, M.R. Numerical and Experimental Modeling of Non-Darcy Flow in Porous Media. In Proceedings of the SPE Latin American and Caribbean Petroleum Engineering Conference, Port-of-Spain, Trinidad and Tobago, 27–30 April 2003. [CrossRef]