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Review article

A review on capillary condensation in nanoporous media: Implications for hydrocarbon recovery from tight reservoirs

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HIGHLIGHTS

- Insight into capillary condensation may improve gas recovery from tight reservoirs.
- Insight into capillary condensation is limited by the scarcity of experimental data.
- A review on the experimental data available in the literature is presented.
- A review on theories for modeling capillary condensation is presented.
- The extension of experimentally verified models to the reservoir scale is promoted.

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ABSTRACT

The key to understanding capillary condensation phenomena and employing that knowledge in a wide range of engineering applications lies in the synergy of theoretical and experimental studies. Of particular interest are modeling works for the development of reliable tools with which to predict capillary condensation in a variety of porous materials. Such predictions could prove invaluable to the petroleum industry where an understanding of capillary condensation could have significant implications for gas in place calculations and production estimations for shale and tight reservoirs. On the other hand, experimental data is required to validate the theories and simulation models as well as to provide possible insight into new physics that has not been predicted by the existing theories. In this paper, we provide a brief review of the theoretical and experimental work on capillary condensation with emphasis on the production and interpretation of adsorption isotherms in hydrocarbon systems. We also discuss the implications of the available data on production from shale and tight gas reservoirs and provide recommendations on relevant future work.

Contents

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1. Introduction

An improved understanding of the physical behavior of confined fluid is important to a multitude of disciplines and will allow for the development of better insights into catalysis [1–3], chemistry [4], geochemistry [5], geophysics [1], nanomaterials [1] and improved methods of battery design [2], carbon dioxide sequestration [6,7], drug delivery [2], enhanced coalbed methane recovery [8], lubrication and adhesion [1], materials characterization [9–13], micro/nano electromechanical system design [14], pollution control [1,7,15–17], and separation [2], as well as hydrocarbon production from shale and other tight formations [18–35]. In oil production, for example, full advantage of enhanced oil recovery by carbon dioxide injection into shale formations can only be taken once a better understanding of confined fluid behavior, including the phase equilibria, is gained [36,37].

It is well known that the physical behavior of fluids in confined spaces differs from that in the bulk [1,2,4,5,7,14,15,18,20–22,24,26–28,38–55]. In nanoporous media with pore diameters less than 100 nm [56] and greater than 2 nm, molecular size and mean free path cannot be ignored compared to pore size [1,23,57]. At this scale, due to confinement, distances are decreased among molecules, so intermolecular forces are large, and consequently, phase behavior becomes not only a function of fluid-fluid interactions, as it is in the bulk, but also a function of fluid-pore-wall interactions. Capillary and adsorptive forces [1,15,18,23,26,27,57] alter phase boundaries [1,2,7,15,18,21–24,26,27,42,45,49,50,52,55], phase compositions [1,27,52,58], interfacial tensions [22], fluid densities [1,5,23,24,49,51], fluid viscosities [18,22], and saturation pressures [20,24,42,43,46]. The extent to which the phase behavior is altered by confinement depends on the interplay of the fluid-fluid and the fluid-pore-wall interactions. Although pore size, shape, and interconnectivity; pore wall roughness, composition, and wettability; and fluid composition and molecular size are qualitatively known to influence the physical behavior of confined fluids [1,5,27,45,52], a quantitative understanding of the relative effects of each characteristic is presently lacking.

2. Capillary condensation of hydrocarbon gases in tight formations

Tight formations and their analogs, shale gas and shale oil reservoirs, are unconventional resources, which are defined as rock formations bearing large quantities of hydrocarbons in place that, as a result of reservoir rock and fluid properties, cannot be economically produced by conventional methods. Only in the past decade have the depletion of conventional reservoirs and the increasing worldwide demand for hydrocarbons generated enough interest in shale and tight reservoirs to establish technological innovations that make the production from these resources profitable.

Shale is "a laminated, indurated rock with [more than] 67% clay-sized minerals" [59]. The U.S. Energy Information Administration estimates that 345 billion barrels of recoverable oil and 7,299 trillion cubic feet of recoverable gas are stored in shale formations worldwide, making shale oil accountable for 9% of total (proven and unproven) oil reserves and shale gas accountable for 32% of total gas reserves [60]. Despite the abundance of hydrocarbons in shale and tight formations, impediments to production from them remain and are manifested in nanoscopic properties such as fine grain sizes [18,22], nanopores [18,22–24,27,61], low porosities (2–10%) [19], and nanodarcy permeabilities [18,19,22,24,33], as well as complex mineral compositions [62]. These characteristics limit conventional methods of reservoir evaluation [33], complicating estimations of original hydrocarbons in place and ultimate recovery [18,20] and culminating in an inability to accurately predict the profitability of a reservoir. Case in point, a good history match for oil production from wells in the middle Bakken formation is obtained only after considering the fluid phase behavior in small pores [24].

In estimating hydrocarbon recovery, the physicochemical properties of the reservoir fluids are combined with information about the petrophysical properties of the matrix in order to interpret well logs [20,21,61], compute original hydrocarbons in place [20,24], determine drainage areas, calculate well spacing [27], evaluate various production scenarios, and predict ultimate recovery. For shale and tight reservoirs, uncertainties in the determinations of water saturation [32], capillary pressure, and absolute and relative permeabilities [31,32] along with non-Darcy flow [33], delayed capillary equilibrium, and confined phase behavior necessitate comprehensive theoretical and experimental studies of these nanoscale phenomena and the development of specialized methods for estimating hydrocarbon recovery.

In shale gas reservoirs (i.e., at reservoir conditions), strong affiliation of reservoir fluids to pore walls is often present. Because hydrocarbon gases are predominately stored in the organic-matter nanopores [24] of the shale in which they are the wetting fluid [20,21], capillary condensation is highly probable, although more information is needed to understand how and when it occurs. Typical compositions of petroleum gases can be found in Table 1 for conventional geological formations and shale formations.

Capillary condensation has major implications for estimating hydrocarbons in place in shale and tight gas reservoirs. This is in strict contrast to conventional gas reservoirs where nanopores represent an inconsequential percentage of the total porosity in

Table 1
Typical compositions of conventional and unconventional petroleum gases.

Component	Mole fraction	
	Conventional[a]	Shale[b]
Methane	0.9500	0.6192
Ethane	0.0320	0.1408
Propane	0.0020	0.0835
n-Butane	0.0003	0.0341
Isobutene	0.0003	0.0097
n-Pentane	0.0001	0.0148
Isopentane	0.0001	0.0084
Hexane	0.0000	0.0179
Heptane	0.0000	0.0158
Octane	0.0000	0.0122
Nonane	0.0000	0.0094
Decane+	0.0000	0.0311
Nitrogen	0.0100	0.0013
Carbon Dioxide	0.0050	0.0018
Oxygen	0.0002	0.0000

[a] Typical composition of conventional natural gas composition taken from Driscoll and Maclachlan [63].
[b] Composition of Eagle Ford Shale gas taken from Deo and Anderson [64].