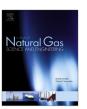
FISEVIER

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse



Shale gas reservoir treatment by a CO₂-based technology

CrossMark

Peng Pei ^{a, *}, Kegang Ling ^b, Jun He ^b, Zhongzhe Liu ^c

- ^a Institute for Energy Studies, University of North Dakota, 243 Centennial Drive, Upson II Room 366, Grand Forks, ND 58202, USA
- b Department of Petroleum Engineering, University of North Dakota, 243 Centennial Drive, Upson II Room 366, Grand Forks, ND 58202, USA
- ^c Department of Civil, Construction and Environmental Engineering, Marquette University, 1515 W. Wisconsin Ave., Milwaukee, WI 53233, USA

ARTICLE INFO

Article history: Received 29 December 2014 Received in revised form 17 March 2015 Accepted 18 March 2015 Available online 29 March 2015

Keywords: Shale gas Stimulation Desorption CO₂-enhanced gas recovery Cost analysis

ABSTRACT

The booming development and production of shale gas largely depends on extensive application of water-based hydraulic fracturing treatments and primary pressure depletion. Issues associated with this procedure include fast production rate drop, low recovery factor, high water consumption, and formation damage. It is necessary to develop new reservoir fracturing and enhanced gas recovery (EGR) technologies to reduce water usage and resource degradation, guarantee the environmental sustainability of unconventional resource developments, and boost individual well production. Building on gas storage and transport mechanisms in shales, this study investigated the feasibility of a new CO2-based reservoir treatment technology. CO₂ has a higher adsorptivity than CH₄, enabling it to liberate adsorbed natural gas in place. Therefore, gas production will be boosted by injecting CO2 to replace CH4. This novel reservoir treatment process will also open a large market for the beneficial utilization of CO₂. In this paper, the authors discuss the theoretical principles and feasibility of using CO2 in both the stimulation stage and the secondary gas recovery stage. Following that, the authors outline a case study performed to simulate applying the CO₂-EGR process in the Barnett, Eagle Ford, and Marcellus shale plays. The marginal revenue per thousand standard cubic feet (MSCF) of increased CH₄ production was calculated. The profitability was found to be largely determined by the prices of natural gas and available CO2. A cost breakdown analysis indicated that the CO₂ procurement expense was the main component in the total cost. The proposed CO₂-EGR process was mostly like to be successful in the Barnett shale.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Gas production from shales in the United States has continuously increased and has become one of the major domestic sources of energy. The boom of shale resource development and production largely depends on water-based hydraulic fracturing (fracking) (Wang et al., 2015). The driving mechanism is primary depletion of reservoir pressure (Sheng, 2009). The typical gas production rate from a single well usually drops rapidly in the first 1–2 years. The fast production rate drop significantly impacts the economics of individual wells and the overall development. During the fracking process, a large volume of water is mixed with proppants and other chemicals and injected into the reservoir at high pressures to create fractures in the rock face. A typical hydraulic facture operation requires three to five million gallons of water per well (Arthur et al., 2012). As natural gas is one of the cleanest and most abundant

energy sources, more shale gas reservoirs are expected to be developed in the next decades (Economides and Wood, 2009; Esfahani et al., 2015). In addition, there are increasing concerns about water usage and environmental footprints in unconventional field development (Ziemkiewicz et al., 2013). The water-based fracking process is also associated with some issues in formation damage, water-phase trapping, and flowback difficulty. During the development of shale gas plays, clays swell when they encounter fracking water, further reducing the available matrix permeability and preventing release of gas and oil in the matrix. Fracking fluids can get trapped in the liquid phase in rock pores next to the fractures due to the very low permeability in tight gas and shale formations. Because of the relatively high viscosity of the fracking fluid, control of proppants during the flowback procedure is also an issue from the views of economics and safety. Therefore, it is necessary to seek an alternative reservoir treatment process to reduce water usage as well as to improve production.

In this paper, we discuss the feasibility of a carbon dioxide (CO₂)-based reservoir treatment technology for gas shales. The

Corresponding author.

E-mail address: peng.pei@engr.und.edu (P. Pei).

proposed technology is waterless and reservoir friendly. It aims at improving reservoir performance by inducing fractures, liberating adsorbed methane, avoiding clay swelling, and boosting single well production. In the treatment, CO2 is used as the fracking fluid to stimulate the reservoir. During the secondary recovery stage, CO₂ is injected into the reservoir as a displacing fluid to liberate adsorbed methane (CH₄) and increase the CH₄ production rate. This is based on the principle that CO2 has a much higher sorption affinity to kerogen than CH₄. Herein the process is termed as CO₂-enhanced gas recovery (CO₂-EGR). In the following sections, the authors first review the gas storage and transport mechanism in the shale reservoir, and then discuss the obstacles in shale gas production. Following that, the principles and advantages of the CO₂-fracking and CO₂-EGR processes will be introduced. Finally, the authors outline a case study modeling the application of CO₂-EGR to the Barnett shale, Eagle Ford shale, and Marcellus shale plays to evaluate the cost components and potential profitability of the process.

2. Gas storage mechanisms and production obstacles

There are four major media in productive gas shales: organic matter, nonorganic matrix, natural fractures, and hydraulic fractures. It is observed that, in shale, the finely-dispersed kerogen material is imbedded within an inorganic material (Ambrose et al., 2010), and the organic matter is the main constituent of total pore volume associated with *in situ* generation and storage of gas (Kang et al., 2010). Gas is stored in shale in four basic forms: adsorbed gas on organic matter, free gas in pores and fractures, solution gas in liquid hydrocarbons, and solution gas in formation water (Lancaster and Hill, 1993; Boyer et al., 2005; Mengal, 2010). Free gas is natural gas that is trapped in the pore spaces of the shale; additionally, adsorption is the pressure-dependent attraction of gas molecules to the surface of a solid, resulting in a dense phase of gas at the surface. In the reservoir, the sorbed gas is in equilibrium with the free-phase gas (Lewis et al., 2004).

The fractured reservoir usually is depicted using the classic dual porosity model. The matrix is assumed to provide the storage capacity, and the fractures function as the main transport pathways for production. In the matrix, gas is transported by Fickian diffusion, while in the fractures with high permeability, gas is transported according to Darcy's law (Cui et al., 2009). The organic matter pores, which range in size from 5 to 1000 nm, can adsorb gases as well as store free gases. The porosity of the organic matter can be five times higher than that of the nonorganic matrix (Wang et al., 2009). Also, due to pore wall effects, density of the gas in the adsorbed phase is about two times higher than that of the bulk gas (Ambrose et al., 2010). By storing gas in a dense, liquid-like adsorbed phase, the overall storage capacity of the rock is enhanced compared to storing gas in the free phase alone (Kurniawan et al., 2006; Heller and Zoback, 2014). The amount of adsorbed gas is a function of kerogen type and content, pore structure, pore pressure, and temperature (Chalmers and Bustin, 2008; Ross and Bustin, 2009; Ambrose et al., 2010). Previous studies have concluded that total organic carbon (TOC) is the primary factor controlling the adsorptive capacity of the rock (Schettler et al., 1991; Lu et al., 1995; Heller and Zoback, 2014). Depending on the reservoir properties and conditions, adsorption may account for as much as 20%–85% of the gas in place in shales (Lancaster and Hill, 1993; Lewis et al., 2004; Pan and Connell, 2015). However, the majority of this adsorbed gas may not be recovered as the sorption isotherms only indicate an obvious steepness at lower pressures (Freeman et al., 2013).

The total gas in place, G_{st} (scf/ton), can be expressed as (Ambrose et al., 2010):

$$G_{st} = G_f + G_a + G_{so} + G_{sw} (1)$$

where $G_f(\text{scf/ton})$ is the gas content in the free phase, $G_a(\text{scf/ton})$ is the gas content in the adsorbed phase, $G_{so}(\text{scf/ton})$ is the solution gas in liquid hydrocarbons, and $G_{sw}(\text{scf/ton})$ is the solution gas in formation water.

The free gas can be estimated using:

$$G_f = 32.0638 \frac{\phi(1 - S_W - S_O)}{\rho_b B_g} \tag{2}$$

where ϕ is the porosity, ρ_b (g/cm³) is the bulk density, S_W is the water saturation, S_O is the oil saturation, and B_g is the gas formation volume factor.

The amount of sorbed gas can be quantified by the Langmuir isotherms (Langmuir, 1916). This theory assumes that the gas is adsorbed as a monolayer on the rock surface. It describes the relationship between the adsorption of pure gas molecules on a coal or shale surface and gas pressure at a constant temperature.

$$G_a = V_L \frac{P}{P + P_I} \tag{3}$$

where V_L (scf/ton) is the Langmuir volume, P_L (psi) is the Langmuir pressure, and P (psi) is the reservoir pressure.

Solution gas is generally not significant in published volumetric calculations of gas in place. Adsorbed gas, on the other hand, might contribute significantly to the total gas volume of most shale gas plays (Euzen, 2011; Holmes et al., 2011). Using the Barnett shale as an example, laboratory tests indicated that adsorbed gas content ranges from 105 to 125 scf/ton at a reservoir pressure of 3800 psi, and the sorbed gas may account for as much as 50% of the total gas in place (Montgomery et al., 2005). Fig. 1 displays gas content of Barnett shale core samples. Total gas in place and the adsorbed gas isotherms are indicated in the diagram.

Shale gas production involves three main processes: depletion of free gas in fractures, depletion of free gas in matrix pores, and desorption of sorbed gas (Gault and Stotts, 2007). In the initial stage, the produced gas is dominated by free gas from the fracture network. Because of the limited amount of free gas in factures, the production curve usually declines drastically over the first 1–2 years (Fig. 2). Following that, free gas in the matrix and desorption of desorbed gas dominate the production. Numerical simulations suggest that desorption of gas maintains reservoir pressure for a longer period of time (Shabro et al., 2011).

The drastic drop of the gas production curve and the flat tail can

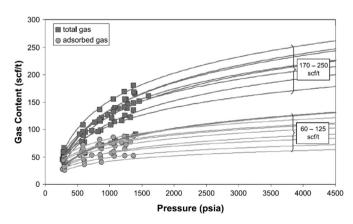


Fig. 1. Total gas and adsorbed gas content in the Barnett Shale (Montgomery et al., 2005).

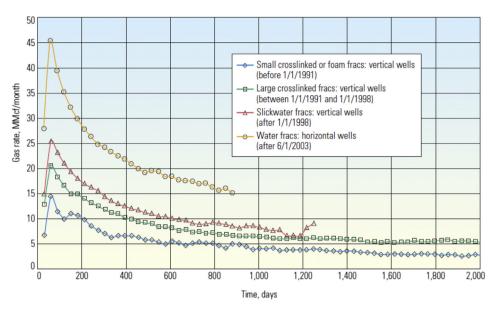


Fig. 2. Typical gas decline curves of Barnett Shale (Boyer et al., 2005).

be explained using the Langmuir isotherm of gas content vs. pressure. The adsorbed gas content is a function of pressure, and physical adsorption can be reversed by reducing the pressure of the adsorbed gas (White et al., 2005). In the example of Barnett shale shown in Fig. 1, it is clear from the isotherm curves that a significant drop will only occur if the pressure is below 1500 psi. This means that the adsorbed gas will not be released until the reservoir pressure is reduced to that level. However, in a typical reservoir/ production pressure range (>2000 psi), the gas content is not so sensitive to the pressure, and it is almost impossible to reduce the reservoir pressure to a level below 1500 psi. Therefore, the amount of adsorbed gas that can be released through pressure drop in production is limited. After the first 1–2 years of high production, which is mainly contributed by free gas in fractures, the production curve usually drops to a stable but low rate (Fig. 2). Desorption and diffusion are responsible for the characteristics of the flat production tails. As the production curve of a single well declines in the short term, the developer must continue investing and developing new wells in large scale to sustain the cash flow of the project. This, in turn, results in a larger environmental footprint and economic burden.

Table 1 lists the percentages of adsorbed gas and free gas in total gas in place for several gas shales in the U.S (Hill and Nelson, 2000; Jarvie et al., 2005; Patterson, 2009). In general, mature thermogenic shales have a higher free gas fraction. By contrast, biogenic shales, such as the Antrim shale, are predominantly saturated by adsorbed gas with a smaller amount of free gas (Boyer et al., 2005). As discussed, currently most of the produced gas from shales is

Table 1Free gas and adsorbed gas fractions in some representative shale plays in the U.S.

Play	Source	Free gas fraction	Adsorbed gas fraction
Barnett	Thermogenic	~50%—65%	~35%-50%
Marcellus	Thermogenic	~50%	~50%
Fayetteville	Thermogenic	~40%	~60%
Woodford	Thermogenic	~54%	~46%
Lewis	Thermogenic	~40%	~60%
Ohio	Thermogenic	~50%	~50%
New Albany	Mixed	~50%	~50%
Antrim	Biogenic	~30%	~70%

contributed by the free-phase gas; thus, the hard-to-recover sorbed gas portion presents a big potential to improve the production and economics of a single well.

3. CO₂-based treatment technology

To resolve the aforementioned challenges associated with shale gas production, the authors propose a novel CO₂-based treatment technology for shale gas reservoirs. During the stimulation procedure, CO₂ is used as a fracking fluid. In the enhanced recovery procedure, CO₂ is used as a displacing fluid. In this proposed technology, supercritical CO₂ is mixed with proppants and injected into the shale reservoir to frack the reservoir. As the pressure of CO₂-based fracking fluid overcomes the tensile strength of the rock, fractures are generated. Proppants carried by the fluids will hold the fracture open. In the EGR stage, since the organic surface of shale has a higher affinity for CO₂ than CH₄, CO₂ will replace CH₄ adsorbed on the surface, liberating CH₄ and improving gas recovery.

The CO₂-based treatment will improve economics and production from several aspects, including reducing water consumption, inducing artificial fractures, leaving reservoirs damage-free, improving fracking fluid clean-up, and maintaining gas production rate. CO2-based nonconventional fracturing fluid has been applied or discussed by several researchers (Harris et al., 1984; Gupta, 2009; Mazza, 1997). Liquid CO₂ as fracturing fluid is already commercially used in many tight gas applications in Canada and the U.S. (Gandossi, 2013), but supercritical CO2 use is at the concept stage. Studies have analyzed its potential use for fracturing shale formations, with positive conclusions (Ishida et al., 2012; Wang et al., 2012). Supercritical CO₂ exhibits a unique blend of high density and low viscosity. The liquid-like density allows supercritical CO₂ to be as capable of creating fractures and carrying proppants as water-based fluids. Low viscosity means the fluid has greater mobility, higher penetration rate, fast clean-up, and good recovery during flowback of the fracturing fluid. Under favorable reservoir conditions, injected liquid CO₂ may vaporize, leaving liquid-free proppants in the reservoir. In water-based fracking processes, clays swell when mixing with water, shrinking available channels in the pores for fluid flow. However, CO₂ does not cause this type of damage and is consequently considered to be "reservoir-friendly".

As mentioned in the previous section, there is a large amount of adsorbed gas in shales which is hard to release by pressure drop. It is known that shale has a preference to adsorb CO₂ over CH₄ (Krooss et al., 2009; Liu and Wilcox, 2012). Adsorption and desorption of CO₂ to and from coals and shales was also found to proceed more rapidly than that of CH₄. CO₂ and CH₄ adsorption on shale rocks have been measured by some researchers (Nuttall et al., 2005; Kang et al., 2010; Heller and Zoback, 2014). The selectivity of CO₂ over methane varies from 2 to higher than 5 at various temperatures and pressures (Vermylen, 2011). This selectivity provides the justification for the approach involving the use of CO₂ to liberate adsorbed CH₄. Therefore, injection of a high-affinity gas like CO₂ might be a potential way to sweep the reservoir and enhance CH₄ recovery (Li and Elsworth, 2014).

In addition, CO₂ capture and storage has been proposed as a major effort to reduce anthropogenic CO₂ emissions and mitigate global climate change. Favored storage options are saline aquifers, depleted gas and oil reservoirs, or unminable coal seams (Freund and Ormerod, 1997; Holloway, 1997; Hitchon et al., 1999; Hattenbach et al., 1998; Bachu, 2000; IPCC, 2005). Shale has a higher storage capacity for CO₂ than CH₄. Due to the large surface areas of pores, organic-rich shale may provide a huge potential for CO₂ storage through the adsorption trapping mechanism (Lawrence et al., 2006; Busch et al., 2008; Kang et al., 2010). Moreover, the organic matter functions as a molecular sieve which allows CO₂, with its linear molecular geometry, to accumulate in smaller pores where other gases like CH₄ cannot access (Kang et al., 2010). Therefore, the CO₂-EGR process can also utilize the significant adsorption potential of gas in shales, making shales viable media for CO₂ sequestration.

There are two major challenges associated with this proposed technology: the availability of CO₂ sources, and the ability of fracking fluid to carry proppants. These challenges will require additional research. Due to the large surface area and high CO₂ adsorption capability in shales, large quantities of CO₂ would be consumed during the treatment process. This provides an opportunity in beneficial utilization of CO₂. Currently, industry has prioritized CO₂ utilization over CO₂ sequestration. However, the demand for CO₂ in the market comprises only a small portion of the annual emissions from industry sources. If this technology is applied successfully, a new, potentially large, CO₂ market will be unlocked.

Because of the low viscosity of the CO₂-based fluid, its ability to carry the proppants may be constrained. This issue can be resolved by using a properly structured CO₂/water two-phase fluid with a high internal phase ratio. Laboratory experiments and field tests in Anakarko Basin indicated that a foam comprising 70% CO₂ could maintain typical properties of good proppant transport and low fluid loss (Harris et al., 1984). If two-phase foam is not employed, new proppants which are lightweight and strong must be developed for effective long-term use.

4. Application potential

4.1. Modeling approach

To assess the application potential of the proposed technology, a case study was performed to simulate the CO₂-EGR process. The authors selected three representative shale gas plays in the U.S. to model: the Barnett shale, the Eagle Ford shale, and the Marcellus shale. A common analogy to the CO₂-EGR process is CO₂-enhanced coalbed methane (CO₂-ECBM) recovery. Experience and lessons from the CO₂-ECBM technology can be applied to the proposed CO₂-EGR process. Both the shale gas and coalbed methane (CBM) reservoirs are continuous gas accumulations. Pilot tests of CO₂-ECBM have been carried out in many places, and a large amount of

data has been published characterizing coals from various coal basins worldwide for their gas sorption capacity (Gray, 1987; Busch and Gesterblum, 2011; Cai et al., 2013; Liu et al., 2014). In primary CBM recovery, the seam is first dewatered to low pressure and then allowed to naturally depressurize with time. CH₄ present in the coal diffuses from an area of higher pressure within the coal to an area of low pressure at the bore holes. During ECBM recovery, CO₂ injection increases the production of CH₄ by reducing the partial pressure of CH₄ in coal and displacing of CH₄ from sorption sites. The sorbed CO₂—CH₄ front is expected to grow elliptically out from the injection wells due to coal anisotropy (White et al., 2005).

However, one should note that there are several important differences between coal and shale in terms of gas storage and transport (Hartman et al., 2008; Jenkins and Boyer, 2008): a) coals contain more than 50% by weight (wt%) organic matter, whereas shales contain less than 50 wt% organic matter; b) nearly all coalbed gas is sorbed gas, whereas shale gas is a combination of sorbed gas and free gas; c) shale-gas reservoirs typically are thicker (>100 ft) with lower sorbed gas content than coalbed, and contain a much larger volume of free gas in the pore space; and d) shale gas reservoirs usually have much lower permeabilities than the coalbed, with values in the nano-to microdarcy range.

In the case studies models, several assumptions were made as follows:

- The reservoir had been fractured using the CO₂-based stimulation process described previously;
- Primary recovery of the shale gas was driven by natural depressurization and CO₂-EGR was applied after the steep drop stage in primary recovery;
- The CO₂ injection wells and natural gas production wells were arrayed next to each other, and the injection wells were converted from production wells;
- When CO₂ injection was started, the reservoir is adsorbed by CO₂ and CH₄;
- The reservoir pressure was maintained at an approximately constant level during CO₂ injection;
- Gas adsorption in the rock followed the Langmuir monolayer adsorption theory;
- The increased production of CH₄ by CO₂ injection was equal to the desorbed CH₄ from the surface of the rock;
- The project was terminated when CO₂ broke through in the production well, which was set as 10 years based on experience in CO₂ –ECBM operations (White et al., 2005).

When CO₂ is injected into the reservoir and present in free phase, it will compete with CH₄ for adsorption sites; thus, the adsorption and desorption of the gases are not independent from one another. The adsorption characteristics of the rock are described by the binary isotherms, which are generated by laboratory testing. Many previous studies have provided the binary or ternary isotherms of coals for the purpose of examining the feasibility of CO₂-ECBM (Rupper et al., 1972; Arri et al., 1992; Hall et al., 1994; Clarkson and Bustin, 2000; Harpalani et al., 2006). However, currently there is little literature providing the binary isotherms of shale rocks. In such cases, the extended Langmuir isotherms were used for representing the adsorption isotherm data of mixures of gases. The binary sorption was estimated using pure gas isotherms (Myers and Prausnitz, 1965; Ruthven, 1984; Yang, 1987; Arri et al., 1992). The extended Langmuir isotherm is expressed as:

$$G_{a,i} = \frac{V_{L,i} \frac{P_i}{P_{L,i}}}{1 + \sum_{j} \frac{P_j}{P_{L,j}}} \tag{4}$$

where $G_{a,i}$ (scf/ton) is the gas content of gas component i, $V_{L,i}$ (scf/ton) is the Langmuir volume of gas component i, $P_{L,i}$ (psi) is the Langmuir pressure of gas i, and P_i (psi) is the partial pressure of gas component i:

$$P_i = P y_i \tag{5}$$

where P (psi) is the pore pressure and y_i is the volume fraction of gas i in the free phase.

With the extended Langmuir isotherm, the gas content of each component can be directly calculated from its partial pressure. Only the Langmuir constants from pure gas sorption are required. The selectivity ratio, α , is defined as (Arri et al., 1992):

$$\alpha = \frac{\left(\frac{V_{L,i}}{P_{L,i}}\right)}{\left(\frac{V_{L,j}}{P_{L,j}}\right)} \tag{6}$$

The amount of CH₄ liberated through CO₂ injection, ΔG_{CH_4} (scf/ton), is calculated by:

$$\Delta G_{CH_4} = G_{CH_{40}} - G_{a,CH_4} \tag{7}$$

where $\Delta G_{CH_{4,0}}$ (scf/ton) is the CH₄ gas content before CO₂ injection and G_{a,CH_4} (scf/ton) is the CH₄ gas content at any point after CO₂ injection.

The increased amount of CO_2 (ΔG_{CO_2} , scf/ton) in the reservoir is equal to the injected amount of CO_2 (G_{CO_2} , scf/ton):

$$\Delta G_{CO_2} = G_{CO_2} \tag{8}$$

Here the ratio of production (R_{prd}) is defined as a parameter to represent how many volumes of CO_2 must be injected to liberate one unit volume of CH_4 :

$$R_{prd} = \frac{\Delta G_{CO_2}}{\Delta G_{CH_4}} \tag{9}$$

The single phase CO_2 injection rate (q_{CO_2} , MSCF/D) of a horizontal well can be estimated using the Economides et al. (1993) model:

$$q_{CO_2} = \frac{k_H h \left(p_{wf}^2 - p_e^2 \right)}{1424 \mu Z T \left[\ln \left(\frac{a + \sqrt{a^2 - (L/2)^2}}{L/2} \right) + \frac{I_{ani} h}{L} \left(\ln \frac{I_{ani} h}{r_w (I_{ani} + 1)} \right) \right]}$$
(10)

where $r_w(\mathrm{ft})$ is the well radius, $h(\mathrm{ft})$ is the pay zone thickness, $T(^{\circ}\mathrm{R})$ is the reservoir temperature, $K_H(\mathrm{mD})$ is the horizontal permeability in the fractures, $L(\mathrm{ft})$ is the length of the horizontal section, I_{ani} is the permeability anisotropy, μ (cp) is the viscosity, Z is the gas compressibility, and $a(\mathrm{ft})$ is the semimajor axis of the drainage ellipsoid formed by a horizontal well of length L, calculated by Equation (11):

$$a = \frac{L}{2} \left\{ 0.5 + \left[0.25 + \left(\frac{r_{eH}}{L/2} \right)^4 \right]^{0.5} \right\}^{0.5}$$
 (11)

where r_{eH} (ft) is the hydraulic drainage radius.

In this study, the cost associated with the CO₂-EGR process was broken into capital cost and operation cost. Since the CO₂ injection wells were converted from the original natural gas production wells, drilling and completion cost was not included in the EGR cost

estimation. The capital cost items include:

- CO₂ compressor capital cost, C_{comp} (\$)
- CO₂ well abandonment cost, C_{aband,CO₂} (\$)
- CH₄ well abandonment cost, C_{aband,CH_4} (\$)

The operating cost items are:

- Fixed operation cost of CO₂ well, C_{F.O.CO₂} (\$/month)
- Variable operation cost of CO_2 well, $C_{V.O.CO_2}$ (\$/MSCF)
- Fixed operation cost of CH₄ well, C_{F.O.CH₄} (\$/month)
- Variable operation cost of CH₄ well, C_{V,O,CH₄} (\$/MSCF)
- Electricity cost of CO₂ compressor, C_{elec} (\$/month)
- CO₂ purchase expense, Expex_{CO2} (\$/month)

The annualized capital cost CO_2 compressor (A_{comp} , \$/year) is calculated by Mian (2011):

$$A_{comp} = C_{comp} \left[\frac{i_e (1 + i_e)^t}{(1 + i_e)^t - 1} \right]$$
 (12)

where i_e is the annual interest rate and t (year) is the project life. The annualized abandonment cost of the wells (A_{aband} , \$/year) is calculated by Mian (2011):

$$A_{aband} = C_{aband} \left[\frac{i_e (1 + i_e)^t}{(1 + i_e)^t - 1} \right]$$
 (13)

The net revenue of the CO₂-EGR process was the sale income of CH₄ less the associated costs listed above. The calculation flow diagram is displayed in Fig. 3. Assumptions relating to the CO₂ compressor and well arrangement are listed in Table 2.

Using the methods and equations described in the last section, the authors estimated the potential applicability of the $\rm CO_2$ -EGR process in the Barnett, Eagle Ford, and Marcellus shale plays. The revenue from each increased production volume of $\rm CH_4$ (\$/MSCF) was calculated as a function of three factors:

- Injection pressure was set as 1.2, 1.5, and 1.8 times of the reservoir pressure;
- CO₂ price from \$15/ton to \$45/ton;
- Natural gas price from \$3.00/MMBTU to \$8.00/MMBTU.

The authors also calculated the percentage of each cost component in the total cost, including the cost of the $\rm CO_2$ compressor, costs associated with the $\rm CO_2$ injection well, costs associated with the $\rm CH_4$ production well, and costs associated with $\rm CO_2$ procurement. The cost and revenue were expressed in 2014 U.S. dollars.

4.2. Barnett shale

The input parameters for the model of Barnett shale are listed in Table 3. Fig. 4 displays the Langmuir parameters of the Barnett shale rocks measured by Heller and Zoback (2014).

Using Equation (9), the production ratio, R_{prd} , was calculated as 2.04; that is, to increase the CH₄ production by 1 SCF from the Barnett shale, 2.04 SCF of CO₂ needs to be injected into the reservoir. Fig. 5 shows the revenue per increased MSCF of CH₄ through CO₂ injection to the Barnett shale, at a fixed natural gas price of \$5.50/MMBTU. The revenue is expressed as a function of CO₂ price and injection pressure. It is obvious that the CO₂ price had a more significant impact than the injection pressure. If the CO₂ price is higher than \$40/ton, the project is not profitable.

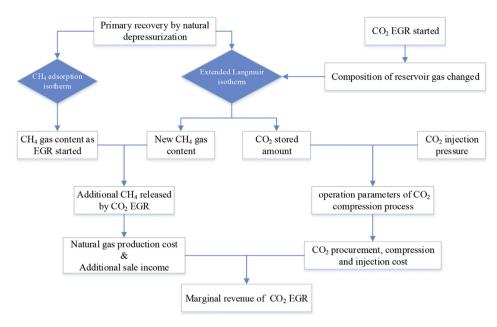


Fig. 3. Calculation flow diagram.

Table 2 Assumptions of CO_2 compressor and well arrangement.

5000	ft
3200	ft
1746.5	ft
0.5	ft
15	Years
85	
500,000	\$
2000	\$/month
0.1	\$/MSCF
0.06	\$/kWh
10	%
•	3200 1746.5 0.5 15 85 500,000 2000 0.1 0.06

Table 3 Inputs for the case study of Barnett shale.

Reservoir depth, D	7000	ft
Pay zone thickness, h	300	ft
Original reservoir pressure, P_0	3800	psi
Reservoir temperature, T	640	°R
Horizontal permeability in fracture, K_H	0.25	mD
Permeability anisotropy, I_{ani}	71	
Primary recovery year, t _{primary}	5	years
Reservoir external pressure during EGS, P_{EGR}	3400	psi

Fig. 6 shows the revenue per increased MSCF of CH_4 produced as a function of natural gas price and injection pressure, at a fixed CO_2 price of \$30/ton. Similarly, the natural gas price was the determining factor compared to the injection pressure. The CO_2 -EGR process becomes profitable when the natural gas price is over \$4.00/MMBTU.

Table 4 lists the percentage of each cost component. As mentioned above, CO_2 price was the determining factor in profitability, and the CO_2 purchase cost comprised the largest share in the total cost, ranging from 63% to 87%.

4.3. Eagle Ford shale

The input parameters for the Eagle Ford shale model are listed in Table 5. Fig. 7 depicts the Langmuir constants of the Eagle Ford

shale rocks measured by Heller and Zoback (2014). Compared to the Barnett shale, the Eagle Ford shale has a lower storage capacity for both CO₂ and CH₄.

The production ratio, R_{prd} , was calculated as 2.88; that is, to increase the CH₄ production by 1 MSCF from the Eagle Ford reservoir, 2.88 MSCF of CO₂ must be injected. This production ratio is higher than that calculated for the Barnett shale. Fig. 8 is the

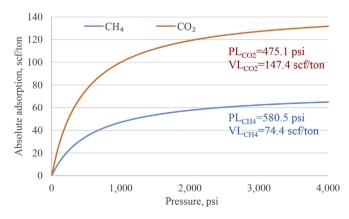


Fig. 4. CO₂ and CH₄ adsorption isotherms on Barnett samples (after Heller and Zoback, 2014).

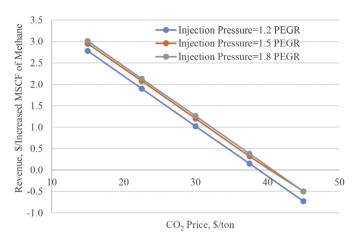


Fig. 5. Revenue sensitivity as a function of injection pressure and ${\rm CO_2}$ price (CH₄ price = \$5.50 MMBTU), Barnett shale.

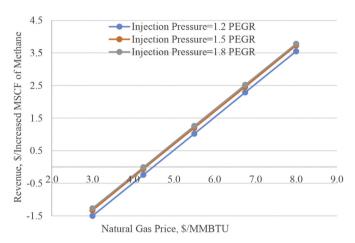


Fig. 6. Revenue sensitivity as a function of injection pressure and CH_4 price (CO_2 price = \$30/ton), Barnett shale.

revenue per increased MSCF of CH_4 production at a fixed natural gas price of \$5.50/MMBTU. The revenue was estimated as a function of CO_2 price and injection pressure (Fig. 8). Similar to the case of Barnett shale, the CO_2 price was the major factor in determining the profitability. If the CO_2 price is higher than \$30/ton, the project is not profitable. Fig. 9 shows the revenue per increased MSCF of CH_4

Table 5Input for the case study of Eagle Ford shale.

Reservoir depth, D	9000	ft
Pay zone thickness, h	200	ft
Original reservoir pressure, P_0	6400	psi
Reservoir temperature, T	715	°R
Horizontal permeability in fracture, K_H	0.25	mD
Permeability anisotropy, I_{ani}	71	
Primary recovery year, t _{primary}	5	years
Reservoir external pressure during EGS, P_{EGR}	3000	psi

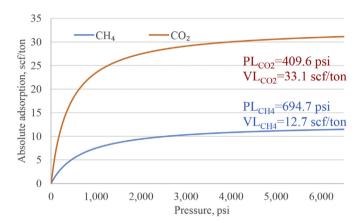


Fig. 7. CO₂ and CH₄ adsorption isotherms on Eagle Ford samples (after Heller and Zoback, 2014).

as a function of natural gas price and injection pressure, at a fixed $\rm CO_2$ price of \$30/ton. The $\rm CO_2$ -EGR process became profitable when the natural gas price is over \$6.00/MMBTU.

Table 6 lists the percentage of each cost component. CO₂ price was again the determining factor in profitability, and CO₂ purchase cost comprised the largest portion in the total cost, ranging from 65% to 88%.

4.4. Marcellus shale

The input parameters for the Marcellus shale model are listed in Table 7. Fig. 10 shows the Langmuir parameters of the Marcellus shale rocks measured by Heller and Zoback (2014).

Using Equation (9), the production ratio of the Marcellus shale, R_{prd} , was 2.46. This is lower than that of the Eagle Ford shale but higher than that of the Barnett shale. Fig. 11 shows the revenue

Table 4 Fractions of each cost component in CO₂-EGR, Barnett shale case.

Injection Pressure Ratio	CO ₂ price	Production cost of CH ₄	CH ₄ well Share %	CO ₂ well Share %	CO ₂ compressor Share %	CO ₂ purchase Share %
	\$/ton	\$/increased MSCF CH ₄				
1.2	15.0	2.78	7%	20%	9%	63%
1.5	15.0	2.61	7%	16%	9%	67%
1.8	15.0	2.55	7%	15%	10%	69%
1.2	22.5	3.66	5%	16%	7%	72%
1.5	22.5	3.48	5%	12%	7%	76%
1.8	22.5	3.43	5%	11%	7%	77%
1.2	30.0	4.54	4%	13%	6%	77%
1.5	30.0	4.36	4%	10%	6%	80%
1.8	30.0	4.30	4%	9%	6%	82%
1.2	37.5	5.42	4%	10%	5%	81%
1.5	37.5	5.24	4%	8%	5%	84%
1.8	37.5	5.18	3%	7%	5%	85%
1.2	45.0	6.29	3%	9%	4%	84%
1.5	45.0	6.12	3%	7%	4%	86%
1.8	45.0	6.06	3%	6%	4%	87%

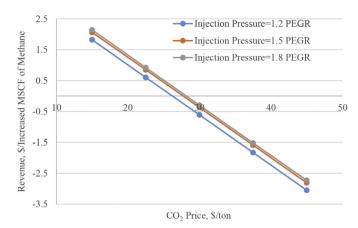


Fig. 8. Revenue sensitivity as a function of injection pressure and CO_2 price (CH₄ price = \$5.50 MMBTU), Eagle Ford shale.

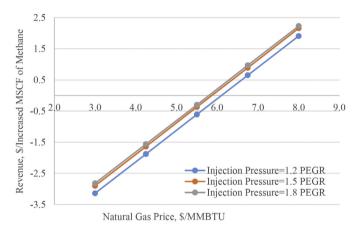


Fig. 9. Revenue sensitivity as a function of injection pressure and CH_4 price (CO_2 price = \$30/ton), Eagle Ford shale.

per increased MSCF of CH_4 through CO_2 injection at a fixed natural gas price of \$5.50/MMBTU. The revenue was expressed as a function of CO_2 price and injection pressure. Similar to the cases of the Barnett and Eagle Ford shales, the CO_2 price was the major factor in determining the profitability. When the CO_2 price was higher than approximately \$33/ton, the project was not profitable.

Table 7 Input for the case study of Marcellus shale.

Reservoir depth, D	5000	ft
Pay zone thickness, h	100	ft
Original reservoir pressure, P_0	4000	psi
Reservoir temperature, T	565	°R
Horizontal permeability in fracture, K_H	0.25	mD
Permeability anisotropy, I _{ani}	71	
Primary recovery year, $t_{primary}$	5	years
Reservoir external pressure during EGS, P_{EGR}	3500	psi

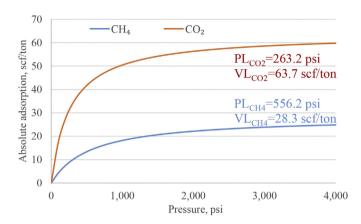


Fig. 10. CO_2 and CH_4 adsorption isotherms on Marcellus samples (after Heller and Zoback, 2014).

Fig. 12 shows the revenue per increased MSCF of CH₄ as a function of natural gas price and injection pressure, at a fixed CO₂ price of \$30/ton. The CO₂-EGR process became profitable when the natural gas price is over approximately \$5.00/MMBTU. Table 8 lists the percentage of each cost component. As mentioned above, the CO₂ price is the determining factor in profitability, and CO₂ purchase cost comprised the largest portion of the total cost, ranging from 63% to 87%.

4.5. Discussion of case study results

From the calculation results above, it can be concluded that CO_2 procurement was the biggest share of the total cost in CO_2 -EGR process for all the three shale plays. The sum of the well abandonment cost, well operation cost, and CO_2 compression cost was less than the CO_2 purchase expense. The CO_2 and CH_4 prices had the

Table 6 Fractions of each cost component in CO₂-EGR, Eagle Ford shale case.

	CO ₂ price		CH ₄ well Share %	CO ₂ well Share %	CO ₂ compressor Share %	CO ₂ purchase Share %
	\$/ton					
1.2	15.0	3.74	6%	21%	8%	65%
1.5	15.0	3.50	5%	16%	8%	70%
1.8	15.0	3.42	5%	15%	9%	71%
1.2	22.5	4.96	4%	16%	6%	74%
1.5	22.5	4.71	4%	12%	6%	78%
1.8	22.5	4.64	4%	11%	6%	79%
1.2	30.0	6.17	3%	13%	5%	79%
1.5	30.0	5.93	3%	10%	5%	82%
1.8	30.0	5.86	3%	9%	5%	83%
1.2	37.5	7.39	3%	11%	4%	82%
1.5	37.5	7.15	3%	8%	4%	85%
1.8	37.5	7.08	3%	7%	4%	86%
1.2	45.0	8.61	2%	9%	4%	85%
1.5	45.0	8.37	2%	7%	4%	87%
1.8	45.0	8.29	2%	6%	4%	88%

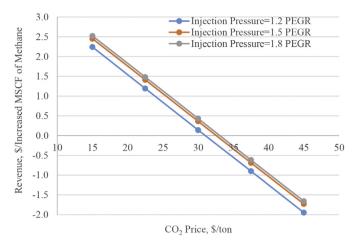


Fig. 11. Revenue sensitivity as a function of injection pressure and CO_2 price (CH₄ price = \$5.50 MMBTU), Marcellus shale.

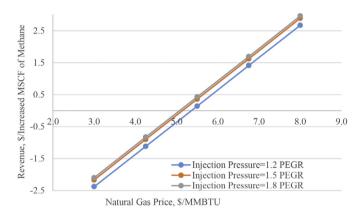


Fig. 12. Revenue sensitivity as a function of injection pressure and CH_4 price (CO_2 price = \$30/ton), Marcellus case.

greatest influence on the profitability of the project. The injection pressure in all cases had a smaller impact on the net revenue. Hence, there are two market factors that would play a significant role in applying the proposed EGR process: the prices of natural gas and CO₂. Recent natural gas wellhead prices in the U.S. are lower than \$4/MMBTU (U.S. Energy Information Administration, 2015), which is not high enough to support the EGR process according to

the simulated results. The typical cost of capturing CO₂ from flue gas using conventional capture technologies, such as amine scrubbing, is in the \$40–100/ton CO₂ range (Figueroa et al., 2008). The capture cost can be less than \$40 per ton from some industrial sources, such as natural gas processing plants, hydrogen plants, ammonia plants, and refineries (U.S. Energy Information Administration, 2011). Considering additional transport costs, the CO₂ price would be higher than the acceptable range according to the case study. In summary, the current market environment might not be favorable for the CO₂-EGR process. Reducing CO₂ price and rebounding natural gas prices will definitely advance the feasibility of CO₂-EGR.

Among these three shale plays in the case study, the proposed CO₂-EGR process was mostly like to be successful in the Barnett shale, mainly because the Barnett shale had the lowest R_{prd} (2.04), which means less CO₂ was required to increase one unit volume of natural gas production in the EGR process. Therefore, the R_{prd} value can be used as one of the criteria in assessing the feasibility of CO₂-EGR. A lower R_{prd} value indicates favorable conditions in terms of economics, but will also limit the CO₂ storage capacity of the reservoir.

5. Conclusion

More shale gas is expected to be developed to meet the everincreasing worldwide energy consumption. To substantiate shale gas production in a more efficient and environmentally-friendly way, novel reservoir stimulation and enhanced gas recovery methods are needed. In this paper:

- The authors have reviewed the storage and transport fundamentals of shale gas, discussed the causes of fast drop production rate in shale gas production, and proposed a CO₂-based reservoir treatment technology for gas shales.
- Using CO₂-based fracking fluid will bring advantages including reduced water consumption, averted reservoir damage, and expedited fracking fluid flow-back.
- Through CO₂ injection during the EGR process, natural gas production will be boosted by the displaced sorbed gas, resulting in benefits of improved single well production and economics, reduced large-scale well drilling, and more limited environmental footprints.
- Results of the case study indicate that CO₂ procurement was the biggest cost for the EGR process, higher than the sum of other cost components.

Table 8 Fractions of each cost component in CO₂-EGR, Marcellus shale case.

Injection Pressure Ratio	CO ₂ price \$/ton	Prod. cost of CH ₄ \$/increased MSCF CH ₄	CH ₄ well Share %	CO ₂ well Share %	CO ₂ compressor Share %	CO ₂ purchase Share %
1.5	15.0	3.11	7%	17%	10%	67%
1.8	15.0	3.04	6%	15%	10%	69%
1.2	22.5	4.37	5%	16%	7%	72%
1.5	22.5	4.15	5%	12%	7%	76%
1.8	22.5	4.08	5%	11%	7%	77%
1.2	30.0	5.42	4%	13%	6%	77%
1.5	30.0	5.20	4%	10%	6%	80%
1.8	30.0	5.13	4%	9%	6%	82%
1.2	37.5	6.46	3%	11%	5%	81%
1.5	37.5	6.25	3%	8%	5%	84%
1.8	37.5	6.18	3%	7%	5%	85%
1.2	45.0	7.51	3%	9%	4%	84%
1.5	45.0	7.29	3%	7%	4%	86%
1.8	45.0	7.22	3%	6%	4%	87%

- Prices of CO₂ and CH₄ were the key factors in determining the profitability of the EGR process.
- The proposed CO₂-EGR process was mostly like to be successful in the Barnett shale since it has the lowest *R*_{prd} (2.04).

To push the proposed technology to be applicable in practice, more research activities and a favorable market atmosphere are necessary. Some scientific and engineering questions need to be further investigated, including adsorption characteristics of multiple gases in shales, properly constructed CO₂-based fracking fluid development, and multiphase transport phenomenon studies in shale matrices and fractures. A higher natural gas market price will be a driving force, and a stable decrease of CO₂ price through developing more advanced capture and transport technologies is also of significance.

Acknowledgments

The authors are grateful for the support from the Institute for Energy Studies at the University of North Dakota.

Nomenclature

Symbols

A annualized capital cost (\$/year)

a large half-axis of the drainage ellipsoid (ft)

Bg gas formation volume factor

C cost (\$)

D reservoir depth (ft)
 G gas content (scf/ton)
 h pay zone thickness (ft)
 I_{ani} permeability anisotropy

i_e annual interest ratek permeability (mD)

L length of well horizontal section (ft)

P pressure (psi)

 P_L Langmuir pressure (psi) q gas flow rate (MSCF/D) R_{prd} production ratio of CO_2/CH_4 r_{eH} hydraulic drainage radius (ft)

 r_w well radius (ft)

Relec. electricity price (\$/kWh)

S saturation T temperature (°R) t project life (year)

*V*_L Langmuir volume (scf/ton)

W well spacing (ft)
 wt% weight percentage
 y gas volume fraction
 Z gas compressibility
 α selectivity ratio

 ΔG change of gas content (scf/ton)

 ρ_b bulk density (g/cm³)

 ϕ porosity η efficiency μ viscosity (cp)

Subscripts

a adsorbed phase
 Aband. well abandonment
 Comp. CO₂ compressor
 f free phase
 F.O. fixed operation cost
 H horizontal

i gas componentj gas component

O oil

so solution gas in oil st gas in total

sw solution gas in water *V.O.* variable operation cost

W water0 original

Abbreviations

CBM coalbed methane

ECBM enhanced coalbed methane EGR enhanced gas recovery

PEGR reservoir pressure during enhanced gas recovery

TOC total organic carbon

Units

cp centipoise ft feet kW kilowatt mD millidarcy

MMBTU million British Thermal Unit
MSCF thousand standard cubic feet
MSCF/d thousand standard cubic feet to

MSCF/d thousand standard cubic feet per day

nm nanometer

psi pounds per square inch R degree Rankine scf standard cubic feet ton short ton

\$ 2014 U.S. Dollar

References

Ambrose, R.J., Hartman, R.C., Diaz-Campos, M., Akkutlu, I.Y., Sondergeld, C.H., 2010. New pore-scale consideration in shale gas in-place calculations. In: SPE 131772, Paper Presented in the SPE Unconventional Gas Conference, February 23–25, Pittsburgh, Pennsylvania. http://dx.doi.org/10.2118/131772-MS

Arri, L.E., Yee, D., Morgan, W.D., Jeansonne, M.W., 1992. Modeling coalbed methane production with binary gas sorption. In: SPE Paper 24363, Presented at the SPE Rocky Mountain Regional Meeting, May 18-21, Casper, Wyoming.

Arthur, D.J., Uretsky, M., Wilson, P., 2012. Water resources and use for hydraulic fracturing in the Marcellus Shale Region. In: Presented at AIPG Meeting on May 5-6. Pittsburgh. Pennsylvania.

Bachu, S., 2000. Sequestration of CO₂ in geological media: criteria and approach for site selection in response to climate change. Energy Convers. Manag. 41 (9), 953–970. http://dx.doi.org/10.1016/S0196-8904(99)00149-1.

Busch, A., Alles, S., Gensterblum, Y., Prinz, D., Dewhurst, D., Raven, M., Stanjek, H., Krooss, B., 2008. Carbon dioxide storage potential of shales. Int. J. Greenh. Gas Control 2 (3), 297–308. http://dx.doi.org/10.1016/j.ijggc.2008.03.003.

Busch, A., Gesterblum, Y., 2011. CBM and CO₂-ECBM related sorption process in coal: a review. Int. J. Coal Geol. 87 (2), 49–71. http://dx.doi.org/10.1016/j.coal.2011.04.011.

Boyer, C., Kieschnick, J., Lewis, R., 2005. Producing gas from its source. Schlumb. Oilfield Rev. 36–49 autumn 2006.

Cai, Y., Liu, D., Pan, Z., Yao, Y., Li, J., Qiu, Y., 2013. Pore structure and its impact on CH₄ adsorption capacity and flow capability of bituminous and subbituminous coals from Northeast China. Fuel 103, 258–268. http://dx.doi.org/10.1016/j.fuel.2012.06.055.

Chalmers, G.R., Bustin, R.M., 2008. Lower Cretaceous gas shales in northeastern British Columbia, part I: geological controls on methane sorption capacity. Bull. Can. Pet. Geol. 56 (1), 1–21. http://dx.doi.org/10.2113/gscpgbull.56.1.1.

Clarkson, C.R., Bustin, R.M., 2000. Binary gas adsorption/desorption isotherms: effect of moisture and coal composition upon carbon dioxide selectivity over methane. Int. J. Coal Geol. 42 (4), 241–271. http://dx.doi.org/10.1016/S0166-5162(99)00032-4.

Cui, X., Bustin, A.M.M., Bustin, R.M., 2009. Measurements of gas permeability and diffusivity of tight reservoir rocks: different approaches and their applications. Geofluids 9, 208–223. http://dx.doi.org/10.1111/j.1468-8123.2009.00244.x.

Economides, M.J., Hill, D.A., Ehilig-Economides, C., 1993. Petroleum Production Systems. Prentice-Hall Inc, Upper Saddle River, New Jersey.

Economides, M.J., Wood, D.A., 2009. The state of natural gas. J. Nat. Gas Sci. Eng. 1

- (1), 1-13. http://dx.doi.org/10.1016/j.jngse.2009.03.005.
- Esfahani, S., Baselizadeh, S., Hemmati-Sarapardeh, A., 2015. On determination of natural gas density: least square support vector machine modeling approach. J. Nat. Gas Sci. Eng. 22, 348–358. http://dx.doi.org/10.1016/ i.ingse.2014.12.003.
- Euzen, T., October 2011. Shale Gas a Overview. IFP Canada internal report. http:// ifp-canada.com/wp-content/uploads/2014/01/IFP_Canada_Shale_Gas_Report.
- Figueroa LD Fout T Plasynski S McIlyried H Srivastava R D 2008 Advances in CO₂ capture technology — the U.S. Department of Energy's carbon sequestration program. Int. J. Greenh. Gas Control 2, 9–20. http://dx.doi.org/10.1016/S1750-5836(07)00094-1.
- Freeman, C.M., Moridis, D., Blasingame, T.A., 2013. A numerical study of performance for thigh gas and shale gas reservoir systems. J. Pet. Sci. Eng. 108, 22-39. http://dx.doi.org/10.1016/j.petrol.2013.05.007.
 Freund, P., Ormerod, W.G., 1997. Progress toward storage of carbon dioxide. Energy
- Convers. Manag. 38, S199-S204.
- Gandossi, L., 2013. An Overview of Hydraulic Fracturing and Other Formation Stimulation Technologies for Shale Gas Production. http://dx.doi.org/10.2790/99937. Report of the Joint Research Center for the European Commission
- Gault, B., Stotts, G., March 2007. Improve Shale Gas Production Forecasts. Exploration & Production. http://www.epmag.com/EP-Magazine/archive/Improveshale-gas-production-forecasts 306.
- Gray, I., 1987. Reservoir engineering in coal seams: part 1-the physical process of gas storage and movement in coal seams. SPE Reserv. Eng. 2 (1), 28-34. http://dx. doi.org/10.2118/12514-PA.
- Gupta, D., 2009. Nonconventional fracturing fluids. In: Presented in SPE Hydraulic Fracturing Technology Conference, 19–21 January, The Woodlands, Texas.
- Hall, F.E., Zhou, C., Gasem, K.A.M., Robinson Jr., R.L., Yee, D., 1994. Adsorption of pure methane, nitrogen, and carbon dioxide and their binary mixtures on wet fruitland coal. In: SPE Paper 29194, Proceedings of The1994 Eastern Regional Conference and Exhibition, Charleston, WV, pp. 329-344.
- Harpalani, S., Prusty, B., Dutta, P., 2006. Methane/CO₂ sorption modeling for coalbed methane production and CO₂ sequestration. Energy & Fuel 20 (4), 1591-1599. http://dx.doi.org/10.1021/ef050434l.
- Harris, P., Haynes, R., Egger, J., June 1984. The Use of CO₂ -based Fracturing Fluids in the Red Fork Formation in the Anadarko Basin. Society of Petroleum Engineers of AIME, Oklahoma, pp. 1003-1008.
- Hartman, R.C., Lasswell, P., Bhatta, N., 2008. Recent advances in the analytical methods used for shale gas reservoir gas-in-place assessment. In: AAPG Search and Discovery Article #40317, Presented at AAPG Annual Convention, April 20-23, San Antonio, Texas.
- Hattenbach, R.P., Wilson, M., Brown, K.R., 1998. Capture of carbon dioxide from coal combustion and its utilization for enhanced oil recovery. In: Presented at GHGT-4 Conference, August 30-September 2, Interlaken, Switzerland.
- Heller, R., Zoback, M., 2014. Adsorption of methane and carbon dioxide on gas shale and pure mineral sample. J. Unconv. Oil Gas Resour. 8, 14-24. http://dx.doi.org/ 10.1016/j.juogr.2014.06.001.
- Hill, D.G., Nelson, C.R., 2000. Gas Productive Fractured Shales; an Overview and Update: GasTIPS (Summer). Hart Energy Publishing, Houston, Texas.
- Hitchon, B., Gunter, W.D., Gentzis, T., Bailey, R.T., 1999. Sedimentary basins and greenhouse gases: a serendipitous association. Energy Convers. Manag. 40 (8), 825-843. http://dx.doi.org/10.1016/S0196-8904(98)00146-0.
- Holloway, S., 1997. Safety of the underground disposal of carbon dioxide. Energy Convers. Manag. 38, 241–245. http://dx.doi.org/10.1016/S0196-8904(96)
- Holmes, M., Holmes, D., Holmes, A., 2011. A petrophysical model to estimate free gas in organic shales. In: AAPG Search and Discovery Article #40781, AAPG Annual Convention and Exhibition, April 12, Houston, Texas.
- IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, Cambridge, United Kingdom.
- Ishida, T., Aoyagi, K., Niwa, T., Chen, Y., Murata, S., Chen, Q., Nakayama, Y., 2012. Acoustic emission monitoring of hydraulic fracturing laboratory experiment with supercritical and liquid CO2. Geophys. Res. Lett. 39, L16309. http:// dx.doi.org/10.1029/2012GL052788.
- Jarvie, D.M., Hill, R.J., Pollastro, R.M., 2005. Assessment of the Gas potential and yields from shales: the barnett shale model. In: Proceedings of Unconventional Gas of the Southern Mid-continent Symposium, March 9-10, Oklahoma City,
- Jenkins, C., Boyer, C., 2008. Coalbed- and shale-gas reservoirs. J. Pet. Technol. 60 (2), 92-99. http://dx.doi.org/10.2118/103514-JPT.
- Kang, S.M., Fathi, E., Ambrose, R.J., Akkutlu, I.Y., Sigal, R.F., 2010. CO2 Storage capacity of organic-rich shales. In: SPE Paper 134583, Presented in SPE Annual Technical Conference and Exhibition, September 19-22, Florence, Italy. http://dx.doi.org/ 10.2118/134583-MS.
- Krooss, B., Busch, A., Gensterblum, Y., Prinz, D., 2009. Sorption and desorption processes of methane and carbon dioxide on coals and shales - experiments and theory. In: AAPG Search and Discovery Article #90078, Presentation at AAPG Annual Convention, April 20-23, San Antonio, TX.
- Kurniawan, Y., Bhatia, S.K., Rudolph, V., 2006. Simulation of binary mixture adsorption of methane and CO2 at supercritical conditions in carbons. AICHE J. 52 (3), 957-967. http://dx.doi.org/10.1002/aic.10687.
- Lancaster, D., Hill, D., 1993. A multilaboratory comparison of isotherm measurements on Antrim shale samples, Otsego County, Michigan. In: SCA Paper No.

- 9303, 15 p., Proceedings of Society of Core Analysis Annual Technical Conference, August 9–11, Houston, Texas.
- Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids: part I, solids. J. Am. Chem. Soc. 38 (11), 2221–2295.
- Lawrence, W., Venteris, E., Slucher, E., Carter, K., McDonald, J., Rupp, J., Greb, S., Baum, G., Harrison, W., Hohn, M., 2006. Geologic storage options and capacities for carbon dioxide sequestration in the Midwest Regional Carbon Sequestration Partnership (MRCSP). In: Presented in the Fifth Annual Conference on Carbon Capture and Sequestration, May 8-11, Pittsburgh, Pennsylvania.
- Lewis, R., Ingrahma, D., Pearcy, M., Williamson, J., Sawyer, W., Frantz, J., 2004, New evaluation techniques of gas shale reservoirs. In: Proceedings of the 2004 Schlumberger Reservoir Symposium.
- Li X Elsworth D 2014 Effect of CO₂ injectivity on enhanced shale gas recovery. In: Paper Presented on the 48th US Rock Mechanics/Geomechanics Symposium. June 1-4. Minneapolis, Minnesota.
- Liu, H., Mou, J., Cheng, Y., 2014. Impact of pore structure on gas adsorption and diffusion dynamics for long-flame coal. J. Nat. Gas Sci. Eng. 22, 203-213. http:// dx.doi.org/10.1016/j.jngse.2014.11.030.
- Liu, Y., Wilcox, J., 2012. Molecular simulation studies of CO₂ adsorption by carbon model compounds for carbon capture and sequestration applications. Environ. Sci. Technol. 47 (1), 95-101. http://dx.doi.org/10.1021/ es3012029.
- Lu, X.C., Li, F.C., Watson, A.T., 1995. Adsorption measurement in Devonian shales. Fuel 74 (4), 599–603. http://dx.doi.org/10.1016/0016-2361(95)98364-K. Mazza, R., 1997. Liquid-free stimulations — CO_2 \sand dry-frac. In: Proceedings of
- Conference of Emerging Technologies for Natural Gas Industry. http://www. netl.doe.gov/KMD/cds/Disk28/NG10-5.PDF.
- Mengal, S., 2010. Accounting for Adsorbed Gas and its Effect on Production Behavior of Shale Gas Reservoirs (Master thesis). Texas A&M University.
- Mian, M.A., 2011. Project Economics and Decision Analysis In: Deterministic Models, second ed., vol. 1. PennWell Corp, Tulsa, Oklahoma.
- Montgomery, S., Jarvie, D., Bowker, K., Pollastro, R., 2005. Mississippian Barnett shale, Fort Worth basin, north-central Texas: gas-shale play with multi-trillion cubic foot potential. Am. Assoc. Pet. Geol. Bull. 89, 155-175. http://dx.doi.org/ 10.1306/09170404042.
- Myers, A.L., Prausnitz, J.M., 1965. Thermodynamics of mixed-gas adsorption. AIChE J. 11 (1), 121-127.
- Nuttall, B.C., Eble, C.F., Drahovzal, J.A., Bustin, R.M., 2005. Analysis of Devonian Black Shales in Kentucky for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas Production. Report of Kentucky Geological Survey/University of Kentucky (DE-FC26-02NT41442).
- Pan, Z., Connell, L., 2015. Reservoir simulation of free and adsorbed gas production form shale. J. Nat. Gas Sci. Eng. 22, 359-370. http://dx.doi.org/10.1016/ j.jngse.2014.12.013.
- Patterson, C., June 2009. Barnett VS Marcellus A Comparison of Two Shale Gas Giants. XTO Energy.
- Ross, D.J., Bustin, R.M., 2009. The importance of shale composition and pore structure upon gas storage potential of shale gas reservoirs. Mar. Pet. Geol. 26 (6), 916-927. http://dx.doi.org/10.1016/j.marpetgeo.2008.06.004.
- Rupper, T.C., Grein, C.T., Bienstock, D., 1972. Adsorption of methane/enthane mixtures on dry coal at elevated temperatures. Fuel 51, 297-303.
- Ruthven, D.M., 1984. Principles of Adsorption and Adsorption Process. John Wiley & Sons, Hoboken, New Jersey.
- Schettler, P.D., Parmely, C.R., Juniata, C., 1991. Contributions to total storage capacity in Devonian shales. In: SPE Paper, 23422, Presented in the SPE Eastern Regional Meeting, October 22-25, Lexington, Kentucky. http://dx.doi.org/10.2118/23422-
- Shabro, V., Torres-Verdin, C., Javadpour, F., 2011. Numerical simulation of shale-gas production: from pore-scale modeling of slip-slow, Knudsen diffusion, and Langmuir desorption to reservoir modeling of compressible fluid. In: SPE 144355, Presented in 2011 North American Unconventional Gas Conference and Exhibition, June 14-16, Woodlands, Texas.
- Sheng, J., 2009. Enhanced oil recovery in shale reservoirs by gas injection. J. Nat. Gas Sci. Eng. 22, 252–259. http://dx.doi.org/10.1016/j.jngse.2014.12.002.
- U.S. Energy Information Administration, 2011. Assumptions to the Annual Energy Outlook 2011. http://pbadupws.nrc.gov/docs/ML1209/ML12090A838.pdf (accessed March 2015).
- U.S. Energy Information Administration, 2015. U.S. Natural Gas Wellhead Price. http://www.eia.gov/dnav/ng/hist/n9190us3m.htm (accessed March 2015).
- Vermylen, J.P., 2011. Geomechanical Studies of the Barnett, Texas, USA (Ph.D. Dissertation). Texas A\$M University.
- Wang, F.P., Reed, R.M., John, A., Katherine, G., 2009. Pore network and fluid flow in gas shales. In: SPE Paper 124253, Presented at the SPE Annual Technical Conference and Exhibition, October 4-7, New Orleans, Louisiana. http://dx.doi.org/ 10.2118/124253-MS.
- Wang, H., Li, G., Shen, Z., 2012. A feasibility analysis on shale gas exploitation with supercritical carbon dioxide. Energy Sources Part A Recovery Util. Environ. Eff. 34 (5), 1426-1435. http://dx.doi.org/10.1080/15567036.2010.529570.
- Wang, W., Su, Y., Sheng, G., Cossio, M., Shang, Y., 2015. A mathematical model considering complex fractures and fractal flow for pressure transient analysis of fractured horizontal wells in unconventional reservoirs. J. Nat. Gas Sci. Eng. 23, 139–147. http://dx.doi.org/10.1016/j.jngse.2014.12.011.
 White, C.M., Smith, D.H., Jones, K.L., Goodman, A.L., Jikich, S.A., LaCount, R.B.,
- Dubose, S.B., Ozdemir, E., Morsi, B.I., Schroeder, K.T., 2005. Sequestration of

carbon dioxide in coal with enhanced coalbed methane recovery — a review. Energy & Fuels 19 (3), 659—724. http://dx.doi.org/10.1021/ef040047w.
Yang, R.T., 1987. Separation by Adsorption Process. Butterworths Publishers, London, United Kingdom.

Ziemkiewicz, P.F., Quaranta, J.D., Darnell, A., Wise, R., 2013. Exposure pathways related to shale gas development and procedures for reducing environmental and public risk. J. Nat. Gas Sci. Eng. 16, 77–84. http://dx.doi.org/10.1016/j.jngse.2013.11.003.