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Modeling, estimation and optimization in coreflooding experiments for coalbed methane production ☆

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HIGHLIGHTS

- Coal coreflooding experiments for biogenic methane production were modeled.
- The coupled kinetics and transport model was validated against experimental data.
- Methane production was optimized by varying nutrient injection characteristics.
- Model reduction was performed based on active and exhausted reactions and modes.
- The model reveals that much of the methane produced is from the nutrient, tryptone.

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ABSTRACT

We extend a previously derived kinetic model for coal bioconversion and couple it with a transport model to simulate coreflooding experiments with packed crushed coal, which are representations of a coalbed methane (CBM) reservoir at the laboratory scale. We apply a tanks-in-series model to simulate plug flow in the core, and the nonlinear model is regressed against experimental data using particle swarm optimization. The validated model is used to analyze CBM production at different operating conditions and subsequently for the optimization of gas production. Model-based experimental design is applied to improve the accuracy of parameter estimation, and computational singular perturbation analysis is applied to develop a better understanding of the important species and reaction at each stage of the coreflooding experiment, and to develop reduced order kinetic models that can be used in process optimization.

1. Introduction

Gases produced and stored or trapped in coalbeds with multiple scales of porosity are known as coalbed methane (CBM). They are usually a mixture of methane (80–99% by volume) and minor amounts of carbon dioxide, nitrogen, hydrogen sulphide, sulphur dioxide and heavier hydrocarbons such as ethane, propane and butane. CBM is an unconventional resource of natural gas and is a better fuel than its precursor, coal, in terms of calorific value and impact on the environment. Interest in CBM extraction for commercial production began in the 1970s and has rapidly increased since the early 1990s.

CBM is produced by two major processes, biogenic and thermogenic. While thermogenic CBM is produced by thermal cracking at elevated pressure and temperature, biogenic methane is produced by anaerobic microbial attack on the organic matter in coal. Various events such as basin uplift/cooling, the flow of associated groundwater or dilution in salinity levels can trigger biogenic methane generation in coal beds that are no longer conducive to any microbial growth, and this methane is referred to as secondary biogenic CBM. Simulation of CBM production in the presence of ongoing microbial activity requires quantification of reaction kinetics along with characterization of the coalbeds. To address this, we have developed a simplified reaction pathway and a corresponding kinetic model based on experimental data from anaerobic microcosm studies conducted by us with crushed coal in serum bottles (Senthamaraikkannan et al., 2015) and existing literature on anaerobic digestion processes (Harris et al., 2008; Strapoc et al., 2011; Budwill et al., 2011). However, these closed system laboratory culture bottle experiments are conducted at

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very high ratios of medium to coal substrate. Since this is not the case in an actual CBM reservoir, kinetic models estimated with such experimental data cannot be applied directly for the simulation of biogenic CBM production at commercial field scales.

To overcome these limitations of the bottle experiments, coreflooding experiments, which are similar in principle to coreflooding experiments conducted by petroleum reservoir engineers for studies related to crude oil and gas recovery (Mazumder et al., 2008; Nobakht et al., 2008; Shen et al., 2009), were conducted by Stephen et al. (2014). These laboratory scale experiments mimic underground reservoir conditions more closely, in the sense that they treat the coal sample as a porous medium that permits migration of fluids (flow of water, microbes and flow/diffusion/sorption of gases) at high operating pressures. Data from these experiments is therefore more suitable for use in scale-up.

In this study, we have developed a fundamental model that includes reaction kinetics describing the coreflooding experiments of Stephen et al. (2014), conducted parameter estimation and model validation, analyzed the dynamic features of the model and used it for process optimization. First, we modify our previously developed enzymatic kinetic model (Senthamaraikkannan et al., 2015) to accommodate for varying nutrient limitations along with the integration of gas diffusion and sorption kinetics. A tanks-in-series model is then built to simulate the flow and changing species concentrations within the core. Particle swarm optimization is used for estimation of the parameters of the model to validate it against the production data from the experiment. The validated model is then used for model-based analysis of the effects of varying operating conditions, which subsequently enables optimization of gas production. In addition, we devise an optimal experimental design for parameter estimation based on a D-optimal measure. Analysis of the important species and reactions at different stages of the coreflooding experiments is also performed using computational singular perturbation (CSP).

2. Coreflooding experiments of Stephen et al. (2014)

For clarity of exposition, we provide a brief description of the coreflooding experiments of Stephen et al. (2014), for which we develop a model in this work.

In their experiments, a core holder was filled with crushed coal of different mesh sizes simulating a heterogeneous porous medium as in an actual reservoir. Before starting the coreflooding experiment, 3 pore volumes of MSM-tryptone solution were injected (until saturation) followed by inoculation with 1.25 pore volumes of microbial culture and two weeks of incubation at room temperature. During the experiment, the core was continuously flooded with MSM-tryptone solution (nutrient) at 0.006 ml/min and the effluent sample was collected at the downstream section of the core holder. Dissolved gases were desorbed from the effluent by pressure reduction and were then analyzed for the presence of CH_4 and CO_2 in a gas chromatograph (GC) using two different methods. In one, the gas collected in a Tedlar bag was directly injected into the GC column, and in the other, the gas samples were transferred to a sealed vial before injection into the GC. Gas chromatography-mass spectrometry (GC-MS) was performed on the effluent to analyse the composition of the intermediate products (Stephen et al., 2014). Table 1 lists the properties of the coal sample and core holder used in these experiments.

Table 1
Coal and core holder properties for the experiments of Stephen et al. (2014).

Coal	
Mass	300.4 g
Average particle size	200 μm
Density	1422 kg/m ^{3}
Core	
Length	30.5 cm
Diameter	3.81 cm
Bulk volume	347.5 ml
Pore volume	131.95 ml

3. Kinetic model development

In our previous work (Senthamaraikkannan et al., 2015), the complicated reaction network for biogenic CBM production from coal was simplified by considering lumped species reacting in a series of enzymatic reaction blocks consisting of coal solubilization, hydrolysis, acidogenesis, acetogenesis and methanogenesis. The lumped components involved in each block are coal (C), solubilized coal (S), i.e., coal solubilized in water, fragmented coal (W) denoting the products of hydrolysis and represented by a common lignin monomer (syringic acid), benzoate (B) denoting the products of acidogenesis and represented by benzoate/benzoic acid, which is the most common aromatic ring intermediate found in these systems, acetate (A) denoting the products of acetogenesis and represented by acetate/acetic acid, and finally the products (P) of methanogenesis, which are methane, carbon dioxide and hydrogen. Thus, the simplified reaction pathway is

Coal **C** → Solubilized coal **S** → Fragmented coal **W** →
Benzoate **B** → Acetate **A** → Products **P**

A kinetic model was proposed for this reaction scheme using a series of Monod models which was then validated against experimental data from various closed static low pressure anaerobic microcosm studies conducted in bottles with crushed coal (Senthamaraikkannan et al., 2015). Various assumptions were considered in the development of the kinetic model, including assuming that carbon is the only limiting substrate while nitrogen (from the nutrient, tryptone) is present in excess for the entire microbial chain. This was reasonable in the case of bottle experiments where the medium to substrate ratios were high. However, in the case of coreflooding experiments, the concentration of nitrogen (from tryptone) is not in excess in different parts of the core at all times. For instance, for a core with volume $V=347.5$ ml and tryptone supplied at a feed flow rate of $F=0.006$ ml/min, there is a constant fresh supply of tryptone at the inlet, while there is a fresh supply only every 40 days (the residence time) at the outlet. Thus, nitrogen limitations due to low tryptone concentrations have to be introduced into the kinetic model for coal breakdown.

A table of notation is for all the variables introduced in the following sections is provided at the end of the manuscript.

3.1. Nitrogen as a limiting substrate

Tryptone, which is the nutrient used in the experiment, is an assortment of peptides providing a source of amino acids (i.e., supply of nitrogen [N]) to growing bacteria. The growth rate in the presence of heterogeneous limiting substrates, i.e., the carbon and nitrogen sources ([C] and [N] respectively), can be expressed by modifying the Monod model as (Davidson, 1996)

$$\mu = \mu_m \frac{[N]}{K_N + [N]} \frac{[C]}{K_C + [C]} \tag{1}$$

Since the nitrogen is derived from tryptone, [N] is replaced by [Nu], which denotes the concentration of the external nutrient supply (tryptone). It is to be noted that complex structures such as peptides and amino acids present in tryptone are usually broken