MODELING THE KINETICS OF BIOGENIC GAS PRODUCTION DURING MICROBIAL ENHANCED OIL RECOVERY

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Abstract— This work presents a study on the reaction kinetics surrounding the formation of biogenic gases in a reservoir undergoing a MEOR process. Bacteria growth kinetics is modeled using the Monod and Michaelis-Menten equation. Chemical reaction equations of the biogenic gases are presented and subsequently solved assuming the formation of an intermediate complex, making the reaction system of a three-lump nature. The developed models are developed with special reference to a scenario of methane formation, adopting data from a laboratory core study. Sensitivity plots of the bacteria concentration, biogas formation and the crude oil concentration are presented. The growth plot shows a good linear correlation as predicted by the Monod model. The study is however limited by its assumption of a steady state scenario to ease the resolution process in the absence of a MEOR simulator.

Index Terms—Bacteria growth; Biogenic gases; Kinetics; MEOR; Methane; Reaction kinetics; Three-lump kinetics

1 INTRODUCTION

HIS With the ever-increasing demand for oil in the world of energy, it has become clearer that petroleum and its products with their associated versatile application are the main stay of the energy industry. While seeking out new crude oil accumulations via exploration and drilling, it is evident that methods to improve oil recovery are vital in satisfying the world's energy demand. These methods include, but are not limited to, thermal techniques like steam flooding and electric heating, chemical techniques like alkali, surfactant and polymer flooding and the Microbial Enhanced Oil Recovery technology

Microbial enhanced oil recovery (MEOR) is a mechanism that employs the use of microbes to degrade or ferment hydrocarbons and produce by-products such as surfactants, polymers, gases and biofilms that are useful in the recovery of oil [1], [2]. It encompasses a multiplicity of methods ranging from the injection of microbes to those depending upon the stimulations of the in-situ micro-flora. Microbial methods for increasing oil recovery are potentially cost effective even at relatively low crude oil prices. They can be applied in a variety of ways including permeability modification treatments and microbial enhanced water flooding. The flexibility and potential cost effectiveness of the technology makes it attractive, but further understanding of the transport mechanism and the development of a sound engineering methodology for optimizing microbial and injection strategies are needed to realize its potential [3].

Before a particular microorganism is used for MEOR, the bacteria must be able to grow and survive under reservoir conditions. A bacterium growth is very well dependent on nutrient concentration and is often divided into different phases [4].The practical application of microbial culture to subsurface oil reservoirs imposes several restrictions on the microbial culture. The microbes must be able to migrate, transported deep within the reservoir for any in-situ applications to be of practical significance to oil recovery. The microbes must remain biologically active at elevated temperature and pressure [5]. As such, microbes intended to be used in petroleum reservoirs should be tested with reservoir fluids at subsurface conditions of temperature, pressure and salinity [5], [6].

Donaldson and Thomas [7] reported that the range of metabolic products from microbial activity on crude oil is very broad, depending on the prevailing conditions, the presence of nutrients available for cell metabolism and the choice of microbe selected for the investigation of its interaction with the crude oil. In general terms, metabolites could be gases (methane, hydrogen, Carbon dioxide, Hydrogen sulphide), Carboxylic acids (formic, acetic, valeric), solvents (alcohols, ketone, aldehydes), polymers (proteins, polysaccharides), surface-active compounds (poly anionic lipids) and many other compounds ranging from simple to very complex macromolecules [8]. Biogases are products of the biological breakdown of organic matter in the absence of oxygen. These biogases when produced subsurface have the capacity to re-pressurize the reservoir as well as reducing heavy crude viscosity. Some of these biogenic gas producers include Bacillus, pseudomonas and methanogens that produce about 60% methane and 40% carbon dioxide [9].

Biogenic gases are products of the metabolism of microbes in the reservoir. The gases that are formed depend on the Oxygen level of the reservoir, the microbes that act on the crude oil in place and the nutrients injected. Some microbes may survive with or without the availability of nutrients. Typical biogenic gases are Carbon dioxide (CO_2), Hydrogen Sulphide (H_2S), Methane (CH_4), Nitrogen (N_2) and Hydrogen (H_2), either of which could dissolve in the oil to reduce the crude oil viscosity or form a secondary gas cap to repressurize the reservoir.

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Microbes that are able to generate gases are Desulfovibrio, SRB (Sulphate-Reducing Bacteria), Clostridium acetogenic bacteria etc. Some of the reactions that lead to the evolution of the gases are given below:

$4H_2 + HCO_3^- + H^+ \longrightarrow CH_4 + 3H_2O$ (1)

for Hydrogen generation using Methanogenes and Desulfovibrio; and

$CH_3CH_2CH_2COO^- + 2H_2O \longrightarrow 2CH_3COO^- + 2H_2 + H^+$ (2)

for Hydrogen generation using Acetogenic Bacteria

All these reactions take place under aerobic and anaerobic conditions. The most common anaerobic microbial mechanism is the aerobic production of CO_2 and alcohol. A suggestion that this metabolic pathway could produce enough carbon dioxide to improve reservoir sweep must consider that the Oxygen present in the evolved gas is derived from the use of a carbohydrate as a substrate rather than a hydrocarbon. The other rate form of anaerobic mechanism that occurs with some rate of reaction is that of sulphur reduction in certain groups of bacteria that lead to the formation of biogenic gases.

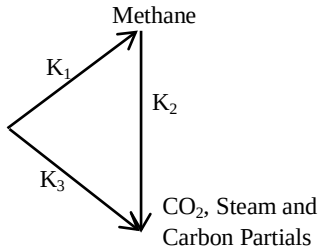
2 METHODOLOGY

Kinetics deals with the chemical reaction between the microbes and nutrients, and the rate of the path of the chemical reaction. An important part of any kinetic investigation I the measurement of rates of change of reactant and product concentrations.in this work, it is assumed that the reaction occurs in a system in which there is no change in the total volume as the reaction proceeds.

2.1 Kinetics Model for Biogenic Gases Production

D Studies have shown that in the presence of appropriate microbes and under suitable conditions, the reaction between the microbes takes place at a relatively low concentration and energy. However, by assuming that microbes react with the carbon source and momentarily forms a complex compound which will decompose according to the three-lump kinetics, one can use the postulates of this theory to infer what occurs downhole and thus demonstrate the qualitative relationship between microbial performance characteristics and operating conditions. The three-lump arrangement is shown below:

Enzyme + Substrate $\longrightarrow$ Enzyme + Unstable Intermediate Complex (3)



The Michaelis-Menten rate law will be used to predict the production of unstable intermediate complex from the enzyme and substrate in the first balance [10]. The general formula for biomass generation/biogenic gas production is given as:

$[Z] + [S] \rightleftharpoons [ZS] \longrightarrow [S] + [P]$ (4)

The rate of increase in the microbes-substrate complex is resolved to be:

$$\frac{d[KS_{CH_4}]}{dt} = K_1[S][Z_{CH_4}] - K_{-1}[ZS_{CH_4}] - K_p[ZS_{CH_4}] \quad (5)$$

where P = Product

At equilibrium, it is assumed that the substrate entering the control region from the reactant side and that which is exiting from the product side are equal. Mathematically, this is written as:

$$K_1[S][Z_{CH_4}] = K_{-1}[SZ_{CH_4}] \quad (6)$$

$$\frac{K_1}{K_{-1}} = \frac{[S][Z_{CH_4}]}{[SZ_{CH_4}]} \quad (7)$$

Making SZ_{CH_4} the subject of the formula,

$$[SZ_{CH_4}] = \frac{K_1}{K_{-1}}[S][Z_{CH_4}] \quad (8)$$

The rate of the reaction can be determined by:

$$\frac{dP}{dt} = K_p[SZ_{CH_4}] = \sigma N = R \quad (9)$$

Substituting (8) into (9) will yield:

$$R = \frac{K_p}{K_s}[S][Z_{CH_4}] \quad (10)$$

Where $K_s = K_{-1}/K_i$

Assuming steady state conditions, the rate of accumulation of the complex is zero, (5) is resolved to give:

$$[SZ_{CH_4}] = \frac{[S_T][Z_{CH_4}]}{[Z_{CH_4}]+[K_d]} \quad (11)$$

Where $K_d = \frac{K_1+K_p}{K_1}$

The velocity of the reaction (i.e., rate) becomes:

$$V = K_p[SZ_{CH_4}] = \frac{K_p[S_T][Z_{CH_4}]}{[Z_{CH_4}]+[K_d]} \quad (12)$$

Equation (12) is best used to approximate the velocity of the reaction if v is measured early in the reaction. Rewriting the equation in terms of the initial velocity (V_i) gives:

$$V_i = \left(\frac{dP}{dt}\right)_i = K_p[SZ_{CH_4}] = \frac{K_p[S_T][Z_{CH_4}]}{[Z_{CH_4}]+[K_d]} \quad (13)$$

where V_i = Initial velocity

This model can be adapted to different biogenic gases such as Carbon dioxide (CO_2), Hydrogen Sulphide (H_2S) etc.

2.2 Microbial Kinetics

When a microorganism undergoes biochemical reactions, for dynamic studies, the general conservation for a steady state must be modified to give the following unsteady state mass balance:

$$\frac{d}{dt}\begin{bmatrix}\text{Biomass in the}\\ \text{Reservoir System}\end{bmatrix} = \begin{bmatrix}\text{Rate of addition of}\\ \text{microorganism within}\\ \text{the reservoir system}\end{bmatrix} - \begin{bmatrix}\text{Rate of removal of}\\ \text{Microorganism in}\\ \text{the reservoir system}\end{bmatrix} + \begin{bmatrix}\text{Rate of production}\\ \text{of gases within the}\\ \text{reservoir system}\end{bmatrix} \quad (14)$$

Assuming that the rate of production within the reservoir system and the rate of removal of microorganism from the reservoir system are equal to zero, (14) becomes:

$$\frac{d}{dt}\begin{bmatrix}\text{Biomass in the}\\ \text{Reservoir System}\end{bmatrix} = \begin{bmatrix}\text{Rate of production}\\ \text{of gases within the}\\ \text{reservoir system}\end{bmatrix} \quad (13)$$

Assuming that the concentration of biomass in the reservoir is σ and that the rate of production of biogenic gases in the reservoir system is σμ, the statement of mass balance can be reduced to give:

$$\sigma = \frac{1}{t}\ln\frac{\mu}{\mu_o} \quad (14)$$

where t = duration

The microbial growth kinetics is modeled using the Monod equation given below:

$$\sigma = \frac{\sigma_{max}[S]}{K_m+[S]} \quad (15)$$

where

σ_{max} = maximum cell growth rate

[S] = Substrate Concentration

σ = Cell growth rate

K_m = Dissociation constant of microbes

5 RESULTS AND DISCUSSION

The production of biogenic gases during microbial enhanced oil recovery is a function of the decomposition of the complex. The rate at which the complex separates leads to the formation of methane (CH_4) and Carbon dioxide (CO_2) as expressed in the rate equation presented. Adaptation of these models to a laboratory core model dosed with microbes and nutrient agar [11], [12] leads to the results presented below.

TABLE 1
CRUDE OIL CONCENTRATION AFTER 14 DAYS OF INOCULATION OF MICROBES IN SYNTHETIC CORE MODEL

Time (days)	Crude Oil Concentration (mol/cm³)
0	1.0
2	0.8
4	0.56
6	0.4
8	0.2
10	0.2
12	0.2
14	0.05

The continual decline in the concentration of crude oil is best expressed in the plot below. This is attributable to the action of the biogenic gas on the crude oil.

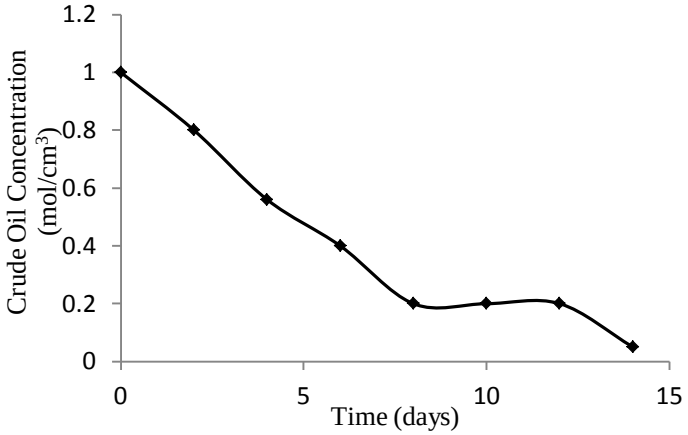


Fig. 1 Crude Oil Concentration with time

The rate at which product is formed is a function of microbial growth. The concentration of the product formed with time is given in table below.

TABLE 2
PRODUCT FORMATION (CH_4) AFTER 14 DAYS OF INOCULATION OF MICROBES IN SYNTHETIC CORE MODEL

Time (days)	Production formation, CH_4 (mol/cm³)
0	0
1	2
2	4
4	8
8	10
10	12
11	14
12	18
13	19
14	20

The values from the table are used to generate the plot given below. The period of slight decline in the product formation is observed. This may be attributed to the period after any inoculation exercise when the microbes undergo a brief period of stunted growth called the lag phase where the microbes spend time to adapt to their new environment.

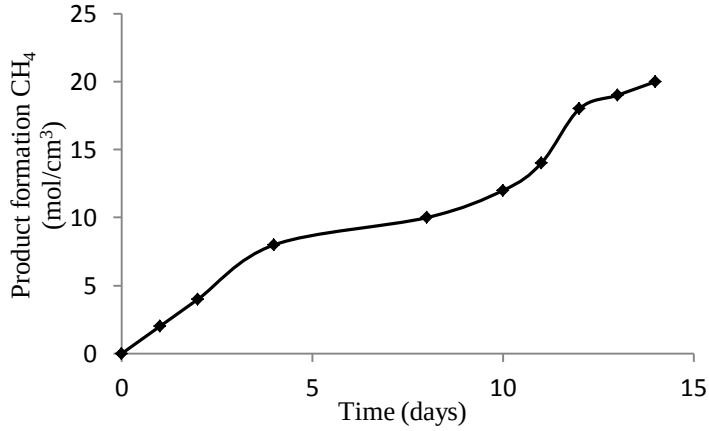


Fig. 2. Concentration of Methane formed with time

The bacteria growth with time computed with the Monod

equation is given in the table below.

TABLE 3
BACTERIA GROWTH RATE WITH TIME

t	N_t
2	218.39
4	11923.83195
6	651019.1657
8	35544442.08
10	1940660782
12	1.05956E+11
14	5.78503E+12
16	3.15852E+14
18	1.72449E+16
20	9.41541E+17
22	5.14064E+19
24	2.80669E+21
26	1.5324E+23
28	8.36664E+24
30	4.56803E+26
32	2.49406E+28
34	1.36171E+30
36	7.43469E+31
38	4.0592E+33
40	2.21625E+35

The relationship is best expressed in the logarithmic plot of N_t versus time shown below.

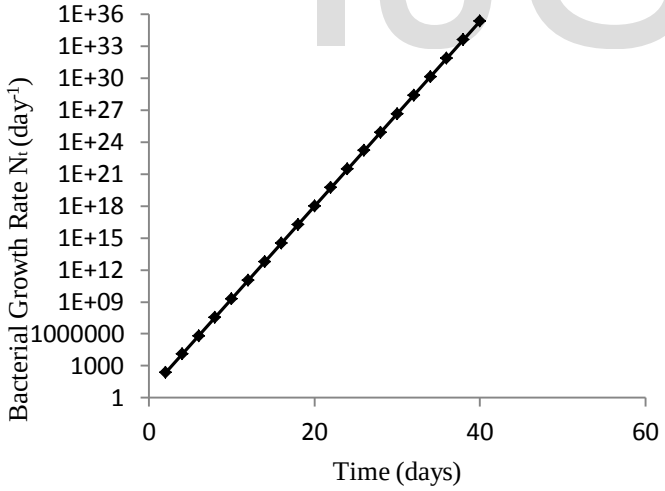


Fig. 3 Plot of the Bacteria growth rate N_t (in log scale) with time

The microbial growth kinetics depends on the concentration of the injected nutrients. The injected nutrient in this case is a solution of beef extract, yeast extract, peptone and sodium chloride.

4 CONCLUSION

The study presents an absent look into the reaction kinetics of biogenic gases formation in a reservoir undergoing a MEOR process. The gas produced depends on the Oxygen level in the reservoir. The underlying reaction kinetics is modeled using the Michaelis-Menten law and the Monod equation for the bacteria growth. However, the absence of an adequate simulator to describe the behaviour of the MEOR reservoir scenario retards studies on MEOR. It is hoped that with the aid of such a simulator, one would be able to incorporate other aspects of the kinetics such as chemotaxis, keeping the assumptions to a minimum.

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