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POTENTIAL OF MICROBIAL FORMATION OF ACETIC ACID FROM HYDROGEN AND CARBON DIOXIDE FOR PERMEABILITY MODIFICATION IN CARBONATE RESERVOIRS

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Abstract

A considerable fraction of our remaining oil and bitumen reserves is found in carbonate reservoirs. Many of these are composed of sedimentary rock deposited in a marine environment and consist mostly of dolomite and limestone. Some of these reservoirs are characterized by extensive fracturing and karsting, as well as by heterogeneous porosity and permeability distributions. Heterogeneity on a multiplicity of scales and low permeability are major challenges for production from carbonate reservoirs. Fluid flow can be strongly dependent on the fracture network. The question addressed here is whether microbial acid production can improve permeability by dissolving carbonate rock. Organic acids, such as acetic acid, can be formed by fermentation of carbohydrates. In traditional MEOR technologies these are injected into the reservoir as an aqueous solution often together with the fermenting bacteria. However, acetic acid can also be produced by acetogenic bacteria from H_2 and CO_2, which are small, oil-soluble substrates diffusing into both oil- and water-filled pore spaces.

Produced water samples from a low temperature oil field contained high acetogenic microbial activity and formed up to 50 mM of acetic acid in two weeks with a significant decrease in pH. Interestingly, methane formation from H_2 and CO_2 was observed later and to a much lesser extent. Microbial conversion of the formed acetic acid to methane and CO_2 was not observed. The H_2 and CO_2 readily diffused from a gas phase through a heavy oil phase into an aqueous phase where the acetic acid was formed. Aqueous acetic acid dissolved core and crushed core obtained from a carbonate reservoir. Permeability enhancement of carbonate reservoirs by microbial production of acetic acid can thus potentially be achieved by injection of H_2 and CO_2, and this may offer advantages over the injection of higher molecular weight, purely aqueous carbohydrates such as molasses.

Introduction

Microbially enhanced oil recovery (MEOR) refers to a suite of technologies in which the activities of microbes are

used to improve production of oil.[1] The microbes used for this purpose are either native to the reservoir or are introduced. The goals can be to enhance oil properties (lower oil viscosity or interfacial tension) or to improve reservoir properties by blocking preferred water flow paths (conformance control) or by increasing permeability through dissolution of reservoir rock. The latter technology is aimed primarily at carbonate reservoirs because calcium carbonate dissolves at low pH:

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$……(1)

A well-known technology is the injection of carbohydrate (molasses) together with selected fermentative bacteria to produce acids, alcohols, gases, and biosurfactants. In a carefully documented field test, injection of molasses and a *Bacillus* strain gave *in situ* production of CO_2, acetate, lactate, ethanol, 2,3-butanediol and biosurfactant, which led to production of additional oil.[1] Microbial acid production and microbial gas production were cited as the two main mechanisms for production of additional oil from carbonate reservoirs.[2] Carbonate dissolution is considered important because the minimum permeability of carbonate rock is often very low (0.1 mD), precluding oil production by water flooding. Fermentation of carbohydrates has been used both in laboratory and in field studies to produce organic acids.[2,3] The pH in these tests often did not drop significantly, because of the buffering capacity of the dissolving reservoir rock (reaction 1). Direct injection of acids such as hydrochloric acid is less desirable, because that focuses the acid-dissolution to the near-injection wellbore region.[4,5] Synthetic organic acids have demonstrated that they are able to dissolve reservoir rock and are a good alternative for stimulating carbonate reservoirs.[4-6]

Injection of molasses (represented for simplicity as glucose, $C_6H_{12}O_6$) in a system with controlled pH will lead to formation of acetic acid ($C_2H_4O_2$):

$2H_2O+C_6H_{12}O_6 \rightarrow 2C_2H_4O_2+2CO_2+4H_2$ (2)

A class of fermenting bacteria referred to as homoacetogens can convert the CO_2 and H_2 formed into a third acetic acid:

$2CO_2 + 4H_2 \rightarrow C_2H_4O_2 + 2H_2O$……..(3)

The combination of the two reactions gives the overall equation:

$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$……(4)

Homoacetogens can thus produce acetic acid from carbohydrate or from H_2 and CO_2. Interestingly, there are no reports on the use of CO_2 and H_2 as substrates for production of acetic acid in carbonate reservoirs through reaction 3, even though these substrates have some very attractive features: they are small and soluble in oil, allowing rapid diffusion through pore spaces that are occupied by either oil or water. Questions that need to be answered prior to considering this possibility are whether a significant population of acetogens is present in reservoirs and whether acetic acid is formed even when formation of methane from H_2 and CO_2 or conversions of acetic acid to methane or CO_2 occur as competing reactions (Figure 1):

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$……..(5)

$C_2H_4O_2 \rightarrow CH_4 + CO_2$……..……(6)

Materials and Methods

Sample Collection

Samples were obtained from the Medicine Hat Glauconitic C (MHGC) field near Medicine Hat, Alberta. This is a shallow (850 m), low temperature (30°C) field that produces heavy oil (API of 16°) from predominantly sandstone reservoir rock by water injection.[7,8] Produced

waters from producing wells 5 and 16 (5-PW and 16-PW) were collected in a 1 L Nalgene bottle that was filled to the brim to exclude air. Upon arrival in the lab these samples were stored in a Coy anaerobic hood with an atmosphere of 90% N_2 and 10% CO_2.

Incubations

To ten 120 mL serum bottles, 5 mL of sample and 45 mL of DSMZ acetogen medium were added. The bottles were closed with butyl rubber stoppers and given a headspace of 80% H_2 and 20% CO_2. H_2-CO_2 gas was regularly added to the incubations with the volume needed to bring the headspace back to 1 atmosphere being recorded. Acetic acid and methane production were monitored by HPLC and GC respectively, as described elsewhere.[8]

Diffusion of H_2 and CO_2 through oil

To 159 mL serum bottles, 5 mL of sample (5-PW or 16-PW) and 45 mL of acetogen medium were added. A layer of 10 mL of heavy oil (HO, 2300 cP at 20°C) or light oil (LO, 3.5 cP at 20°C) was then added. The bottles were closed with butyl rubber stoppers and filled with a headspace of 80% H_2 and 20% CO_2. H_2-CO_2 gas was regularly added and acetic acid and methane production was regularly monitored. Experiments were also done without oil. The gas headspace and the aqueous phase could be sampled through separate sampling ports without disturbing the intervening oil layer (Figure 2).

Use of carbonate core

Two carbonate samples (1.5 in diameter x 2 in length) were sliced into 1.5 x 0.4 in disks. One disk was added to each of a set of eight 250 mL wide mouth polypropylene bottles, together with either 100 mL of synthetic produced water (SPW), SPW with 0.02 M HCl, SPW with 0.1 M acetic acid, or CSB-K medium with 10% 5-PW. The bottles were closed with a cotton plug to allow gas exchange and were stored in a Forma anaerobic hood with an atmosphere of 85% N_2, 10% CO_2, and 5% H_2. Acetic acid was regularly monitored by HPLC. Two carbonate disks were gently crushed and a piece of approximately 0.1 g was added to eight 120 mL serum bottles, containing 50 mL of either SPW, SPW with 0.02 M HCl, SPW with 0.1 M acetic acid, or CSB-K medium with 10% 5-PW. The bottles were closed with butyl rubber stoppers and given a headspace of 80% H_2 and 20% CO_2. H_2-CO_2 was regularly added to and acetic acid and methane production were regularly monitored in the latter incubation.

Results

Formation of acetic acid and methane

Incubation of samples 5-PW or 16-PW in acetogen medium with a headspace of 80% H_2 and 20% CO_2 gave 80 to 90 mM acetic acid in the 50 mL aqueous phase within 10 days, while using approximately 700 mL of gas (Figure 3). After 40 days of incubation (86±8) mM of acetic acid was formed by 5-PW with uptake of (606±24) mL of gas. Trace amounts of methane were formed. With 16-PW, (75±8) mM of acetic acid was formed with uptake of (632±74) mL of gas after 40 days of incubation (Figure 3). A total of (2.18±2.15) mM of methane was formed in the headspace during this period. Acetic acid was therefore the main product in both incubations with maximal formation of approximately 2.5% methane. Variation of incubation conditions with sample 5-PW is shown in Table 1. All incubations contained a headspace of 80% H_2 and 20% CO_2. Use

of 5-PW without any further amendments gave low gas use, with little formation of acetic acid or methane and no pH drop. Amendment with nutrients (trace elements and selenite-tungstate) greatly increased gas use, acetic acid and methane production. This was also observed in acetogen media without added bicarbonate, which gave also as significant drop in pH, as well as in CSB-K media (Table 1). Hence, considerable acetogenic activity was observed under all conditions, except the first one.

Diffusion of H_2 and CO_2 through oil

The results of oil containing incubations are summarized in Table 2. Similar concentrations of acetic acid (10 to 20 mM) and methane (5 to 8 mM) were formed in this experiment under all incubation conditions. The only difference was in the volume of gas used. Which was higher in the absence of oil (235 to 260 mL) than in the presence of LO (144 to 164 mL) or HO (53 to 84 mL). One would expect similar volumes of gas to be used for production of similar concentrations of acetic acid and methane. Possible dissolution of H_2 and CO_2 in the oil phase when the experiment was started may explain this difference. The data in Table 2 show that acetic acid was readily formed in an aqueous phase even if the substrates H_2 and CO_2 needed to diffuse through an intervening oil phase of considerable viscosity.

Dissolution of carbonate core

Sliced core was incubated in 100 mL of SPW with either no addition, 0.02 M HCl or 0.1 M acetic acid, as well as in 100 mL CSB-K medium with 10% 5-PW under conditions of gas exchange with the anaerobic hood atmosphere (5% H_2, 10% CO_2, 85% N_2). Crushed core (~0.1 g) was incubated in 50 mL of these same aqueous media in closed serum bottles with a 70 mL headspace of 80% H_2 and 20% CO_2. Visual inspection indicated that crushed core disappeared completely in the incubation with 0.1 M acetic acid. Incubations in CSB-K medium with 5-PW gave 25 mM acetic acid with sliced core and 15 mM acetic acid with crushed core within 3 weeks of incubation. These preliminary experiments indicate that carbonate core is dissolved by acetic acid, which can be produced by acetogenic bacteria from H_2 and CO_2.

Discussion

As indicated in the introduction a potentially promising MEOR technology is the production of additional oil from tight carbonate reservoirs by increasing permeability though acidic carbonate dissolution. We have shown here that samples from a low temperature heavy oil field have significant acetogenic activity. Acetogenic bacteria can form up to 80 mM acetic acid in the aqueous phase from H_2 and CO_2 in a short period of time (Figure 3) with variable concentrations of methane also being formed (Table 1). The H_2 and CO_2 can diffuse through a heavy or light oil phase, producing acetic acid in a distant aqueous phase (Figure 2, Table 2), which may dissolve carbonate rock as indicated in Figure 4. Features needed for this technology to succeed are (i) the presence of acetogenic bacteria in the carbonate reservoir, (ii) activation of these bacteria through injection of H_2 and CO_2 as well as of (iii) potentially other nutrients such as trace elements and selenite-tungstate (Table 1). The work shown here is a first step along this path. Its novelty is in the use of H_2 and CO_2 rather than of carbohydrates such as molasses to produce acetic acid. H_2 and CO_2 substrates diffuse more rapidly than

carbohydrates and are soluble in oil, whereas carbohydrates dissolve in water only. These features allow the synthesis of acetic acid wherever water and acetogenic bacteria are present in the reservoir. Future experiments will use oil-filled carbonate core to determine whether incubation with H_2 and CO_2 can increase permeability and subsequent oil production.

Conclusion

Production of acetic acid from H_2 and CO_2 by acetogenic bacteria has promise as a novel MEOR technology. High concentrations of acetic acid can be formed in relatively short periods of time. These can dissolve carbonate rock increasing permeability and oil production.

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Nomenclature

5-PW	=	MHGC produced water from well #5
16-PW	=	MHGC produced water from well #16
CaCO3	=	calcium carbonate
CH_4	=	methane
$C_2H_4O_2$	=	acetic acid
$C_6H_{12}O_6$	=	glucose
CO_2	=	carbon dioxide
CSB-K	=	Coleville synthetic brine K
H_2	=	hydrogen
HO	=	heavy oil
LO	=	light oil
MEOR	=	microbially enhanced oil recovery
MHGC	=	Medicine Hat Glauconitic C field
SPW	=	synthetic produced water

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Table 1. Formation of aqueous acetic acid and gas phase methane from gas phase H_2 and CO_2 under various conditions, as explained in the text. Gas use and the pH attained are also indicated. The data were those observed following 32 to 35 days of incubation.

Media type	Gas used (mL)	Acetic acid (mM)	Methane (mM)	pH
5-PW only	20 ± 14	0.91 ± 0.63	0.11 ±0.05	8.4 ± 0.1
5-PW with trace elements and selenite-tungstate	242 ± 57	17.7 ± 5.3	6.1 ± 1.8	8.5 ± 0.1
Acetogen media without bicarbonate (10% 5-PW)	148 ± 35	13.8 ± 1.5	0.01± 0.01	4.8 ± 0.1
CSB-K (10% 5-PW)	416 ± 4	25.6 ± 6.7	9.8 ± 0.05	6.9 ± 0.2

Table 2. Formation of aqueous phase acetic acid from gas phase H_2 and CO_2, separated from the aqueous phase by a layer of oil. The formation of methane in the gas phase and H_2-CO_2 gas usage is also indicated. Data were following 47 days of incubation.

Incubation	Gas use (mL)	Acetic acid (mM)	Methane (mM)
5-PW	235.2 ± 1.6	15.6 ± 8.0	7.1 ± 0.7
16-PW	260.0 ± 1.7	10.7 ± 4.8	7.6 ± 0.05
5-PW-LO	143.8 ± 2.5	14.0 ± 1.9	6.8 ± 0.3
16-PW-LO	164.8 ± 2.2	19.7 ± 1.5	7.6 ± 0.03
5-PW-HO	84.4 ± 2.5	17.1 ± 3.8	5.3 ± 0.4
16-PW-HO	52.8 ± 6.3	12.7 ± 5.2	6.0 ± 1.4

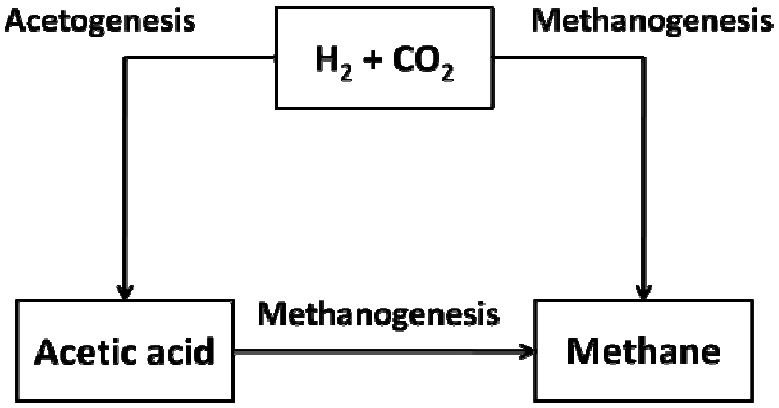

Figure 1. Production of acetic acid and of methane from H_2 and CO_2.

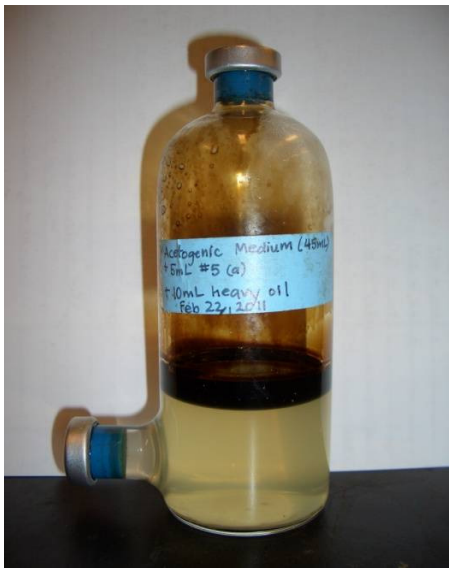

Figure 2. Serum bottle used to monitor production of acetic acid in the aqueous phase, separated from the gas phase by a layer of heavy oil (as shown) or light oil.

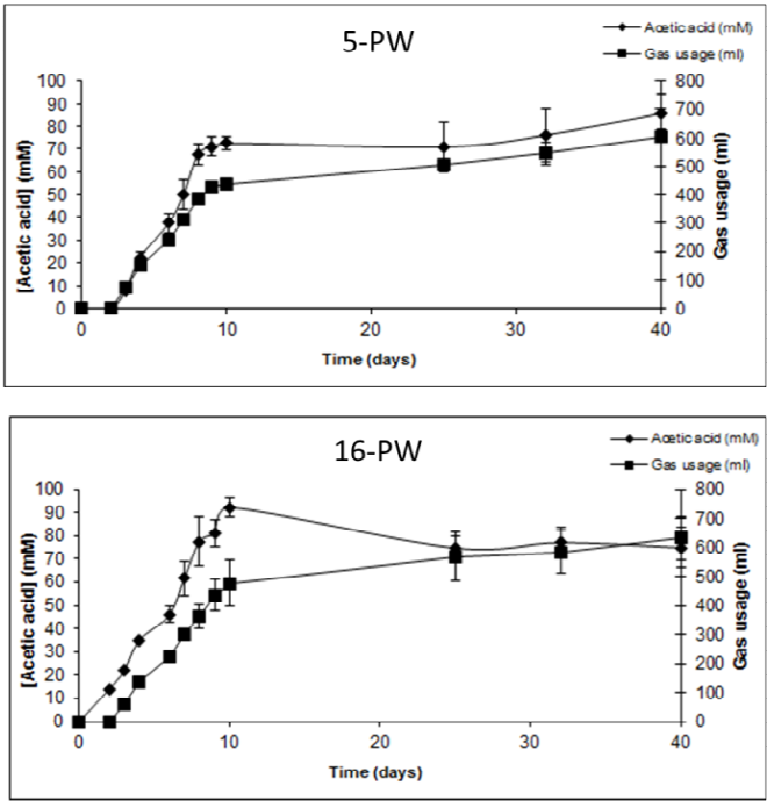

Figure 3. Production of acetic acid and gas use by samples 5-PW (top) and 16-PW (bottom) upon incubation with a headspace of 80% H_2 and 20% CO_2.

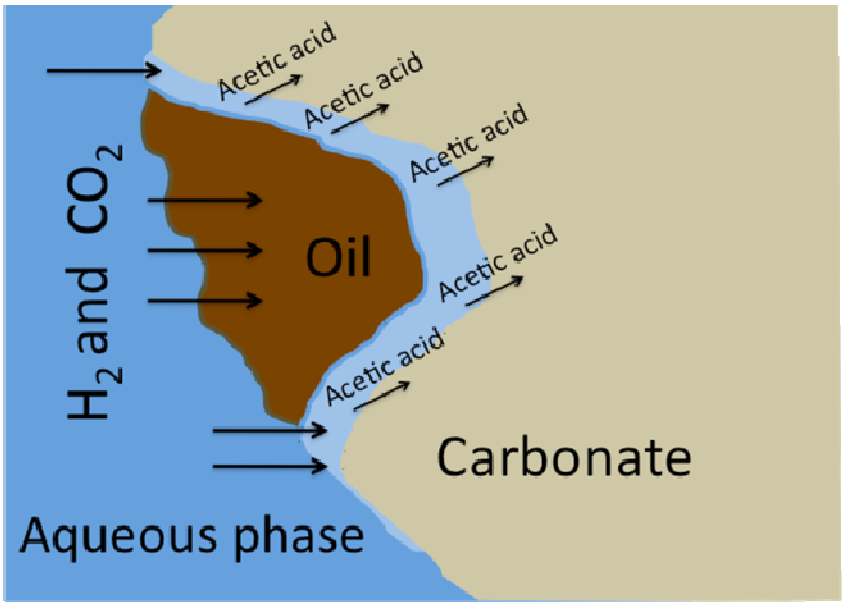

Figure 1. Dissolution of carbonate through formation of acetic acid from H_2 and CO_2 following their diffusion through an oil phase.