The Effects of the Urea and Mixture-T on Residual Oil Gasification Into Methane Under Reservoir Simulation System

Anpei Wei, Hengyu Hu, Yewei Sui, Shaomei Liu, Ziming Chen and Jing Li

ABSTRACT

A simulation reservoir system was designed to study the process of transforming residual oil into methane by indigenous microbes under initial pressure 10MPa, 55°C and the simulation time was 465 days. The Urea was used with four levels (U), U1 0mg/L, U2 200mg/L, U3 300mg/L, U4 400mg/L. the mixture-T (surfactant Tween 80 and complexing agent EDTA, proportion was 5:1) had five levels: 0CMC(Critical Micelle Concentration), 0.5CMC, 1CMC, 2CMC, 3CMC. The CMC was 14mg/L and the sterile treatments were control. When the urea concentration was 300mg/L or 400mg/L, the methane yield were both highest and the difference was not significant. When the additives mixture-T amount reached CMC, the methane yield was highest and among 1CMC, 2CMC and 3CMC treatments the difference was not significant. Meanwhile the urea and mixture T had additive effect on methane yield(3CMC-U4 treatment was highest), and oil removal efficiency had similar trend.¹

KEYWORDS

Simulation; Residual oil; Methane; Urea; Surfactant; Complexing Agent

¹Anpei Wei, Hengyu Hu*, Yewei Sui, Shaomei Liu, Ziming Chen, Jing Li, Key Laboratory of Soil and Water Conservation and Environmental Conservation in Shandong Province, College of Resources and Environment, LinYi University, Shan Dong LinYi, China
INTRODUCTION

On the residual oil degradation in reservoir, CH4 is recognized terminal degradation product. The running out of electron acceptor are the generation foundation of CH4 such as nitrate, tetravalent manganese, sulfate, ferric iron, etc [1]. Methanogenic archaea need to form a special kind of symbiotic relationship with other bacteria, accepting the electron to produce CH4 [1,3-5]. Meanwhile, in the reservoir, there are microbial community including microaerobic, facultative bacteria and anaerobic bacteria and they mainly degraded the fatty hydrocarbon of crude oil [2, 6]. On the reservoirs research, some scholars did a lot of studies about natural gas generation reason to speculate that there were many factors to influence anaerobic biodegradation methanogenesis of various organic matter (including crude oil, raw coal, etc.) [1,3,7-8] and the nutrients became the key factor for microorganisms using. Residual oil bio-degradation methanogenesis did not require large energy inputs, so it was regarded as a kind of advanced energy strategy. The bacteria could use some cheap resources which acted as activators to make available secondary products in reservoir [9]. The generation of these secondary products can increase the utilization rate of oil, including biological surface active agent, emulsifier, carboxylic acids, alcohols, and gas. On microbial enhancing oil extraction technology, nutrition and exogenous microbes injection could improve the utilization rate of oil [9]. In Muller [10] and Jack, etc [11] research note, in the laboratory, they first studied and proved that under the condition of the exogenous substances injection, the oil degradation produced methane and in some abandoned reservoir, residual oil could also be spontaneous to conduct this process. Recently a lot of scholars have proved the phenomenon and it became better prospect that injection the oil degradation methane-producing microbes to degrade petroleum hydrocarbon [1,3,4,8,12-13]. Moreover, the geological evidence indicated that through thousands years interior the earth reservoir the methane production was spontaneous, because the interior of the earth good provided the anaerobic methanogenesis conditions [1, 6,14-16]. In reservoir someone also found and identified all sorts of anaerobic bacteria group [17-22] and their research of metabolic mechanism confirmed the petroleum hydrocarbon degradation methanogenic facts in the anaerobic environment [5,22]. At the end of 2004, many American media reprinted and reported that the university of Oklahoma professor Sulfita used microorganisms to degrade residual oil into gas in the reservoir and pointed out that the successful application of this technology will have important impact on economic growth [23].
EXPERIMENTAL DESIGN

Collection of Samples

The water samples were taken from the oil well and filled several plastic buckets (about 7 liters). The oil well is using polymer flooding technology to extract the oil. Reservoir characteristics: continental phase, sandstone. The plastic bucket was tightly closed at 4°C, then sent to the laboratory immediately. The sampling block characteristics are shown in (Table 1).

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>Reservoir Temperature</th>
<th>Geothermal gradient</th>
<th>Density (g/cm³)</th>
<th>Viscosity (mPa•s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0±1.0</td>
<td>50°C-65°C</td>
<td>3.5°C/100m</td>
<td>0.935±0.02</td>
<td>325.6±5.0</td>
</tr>
</tbody>
</table>

TABLE. I. GEOLOGICAL INFORMATION OF SAMPLING BLOCK (CONTINUED).

<table>
<thead>
<tr>
<th>Saturated fraction(%)</th>
<th>Aromatic fraction(%)</th>
<th>Colloid(%)</th>
<th>Asphaltene(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.9±0.7</td>
<td>32.7±0.7</td>
<td>28.6±0.6</td>
<td>4.9±0.1</td>
</tr>
</tbody>
</table>

Enrichment Culture and Design

First, 50ml water samples and 30ml inorganic salt culture medium were both added into 120ml sterile anaerobic bottle. At the same time, the oxygen was removed by Hungate [24], then the bottle remained strictly anaerobic condition. These were placed in the incubator in dark condition. 100 days later, methane was detected by gas chromatography (analyzing headspace gas), so it is used as inoculum for enrichment culture.

Second, 5ml inoculum (the upper clear liquid and filtered) mentioned above was added into the oil reservoir simulation reactors (The volume: 115mL), shown in (in supply information). An additional 5ml crude oil, 40ml inorganic salt culture medium were added to each reactor. In this study, the main temperature could be set as: 55°C and initial pressure was 10MPa. The simulation time was 465 days and we used gas chromatograph to measure the methane quantities. Through the high pressure gas source, the nitrogen was added into simulation reactors. The experiment adopted orthogonal experimental design with three reduplications. Main factor was the Urea.
(U) with four levels, U1:0mg/L, U2:200mg/L, U3:300mg/L, U4:400mg/L; Sub-factor was the mixture-T (surfactant Tween 80 and complexing agent EDTA, proportion was 5:1) with five levels: 0CMC (Critical Micelle Concentration), 0.5CMC, 1CMC, 2CMC, 3CMC. The CMC was 14mg/L and the sterile treatments were control. In order to better simulate the real reservoir conditions, the reservoir conditions simulated system (Figure 1) was designed in this experiment.

![Figure 1. The oil reservoir conditions simulated system](image)

A: High pressure gas source; B: Temperature control area; C: main reactor part; D: Pressure control valve; E: Flowmeter; F: Sampler 1; G: Pressure sensor; H: Filtrating equipment; I: Sampler 2; P: Pressure display; T: Temperature sensor; Z: Four-way valve.

Description: Inorganic salts culture medium formula: KH2PO4, 5.0g; K2HPO4, 5.0g; NH4Cl, 5.0g; NaCl, 1.0g; MgCl2, 2.0g; CaCl2, 0.1g; trace element solution, 5ml; deionized water volume to 1L; pH: 7.0-7.2; resazurin; boiling deoxygenizing and fed with pure nitrogen by Hungate device [25], until the pink medium to colorless and add Na2S • 9H20 (0.5g) and NaHCO3 (2.0g).

**Gas And Oil Analysis**

Gas composition: SHIMADZU GC gas chromatograph. Carrier gas: 99.99% helium, 50kPa; combustion gas: hydrogen 50kPa; supporting gas: Air 40kPa; Detector: FID 300°C; gasifier injector 300°C; Column: PONA elastic quartz capillary column (50m×0.2mm×0.5μm); Column temperature: initial temperature of 35°C, 15min; 2°C/min heating to 220°C, 5min. injection volume: 0.5mL, the standard gas is diluted with pure nitrogen to different concentrations, the analysis was under the above conditions, the gas content was quantified by modified area normalization method, data acquisition and handling was computer assisted.
Oil saturated hydrocarbon GC-MS analysis (according to SY/T 5779-1995), Instrument: Agilent 6890N GC/5975i mass spectrometry. Test conditions: inlet temperature: 300°C, the transmission line: 280°C, chromatographic carrier gas: 99.999% helium, column: HP-5MS elastic quartz capillary column (60m×0.25mm×0.25μm), column temperature (temperature-programmed): initial temperature: 50°C/min, then 20°C/min heating to 120°C, 4°C/min heating to 250°C, then 3°C/min heating to 310°C, keep it for 30min, carrier gas flow rate: 1mL/min. MS EI source, 70eV, multiplier voltage: 1200V, filament current: 100μA, full scan [25-27].

**Measurement of Petroleum Hydrocarbons Degradation Rate**

The crude oil culture after degradation was transferred to a 250mL separating funnel and was then acidified with hydrochloric acid to a pH value of ≤2, followed by washing with 20 mL of CCl4, with the extract transferred to an Erlenmeyer flask and the remainder left in the separating funnel. The extract after being diluted to a definite factor was analyzed by infrared spectroscopy to measure the hydrocarbon content (HJ 637-2012, China), and the petroleum hydrocarbons degradation rate was calculated [28].

**RESULTS**

**Methane Yield of Different Treatments**

![Graph showing methane yield over time for different treatments](image)
Figure 2. The methane yield change of different treatments with time-variation
U, Urea; CMC, Critical Micelle Concentration; O1: Control group, sterile treatment;
The data are means ± SD (n = 3).

TABLE II. THE OIL REMOVAL EFFICIENCY OF DIFFERENT TREATMENTS AFTER 465 DAYS SIMULATION (%).

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Oil removal efficiency, %</th>
<th>Treatments</th>
<th>Oil removal efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0CMC-U1</td>
<td>10.2±0.9k</td>
<td>0CMC-U3</td>
<td>33.6±0.4e</td>
</tr>
<tr>
<td>0.5CMC-U1</td>
<td>9.3±0.9k</td>
<td>0.5CMC-U3</td>
<td>34.9±0.6d</td>
</tr>
<tr>
<td>1CMC-U1</td>
<td>18.2±0.6i</td>
<td>1CMC-U3</td>
<td>40.4±0.3c</td>
</tr>
<tr>
<td>2CMC-U1</td>
<td>17±0.4j</td>
<td>2CMC-U3</td>
<td>41.2±0.3abc</td>
</tr>
<tr>
<td>3CMC-U1</td>
<td>17±0.8j</td>
<td>3CMC-U3</td>
<td>40.5±0.5bc</td>
</tr>
<tr>
<td>0CMC-U2</td>
<td>20.7±0.5h</td>
<td>0CMC-U4</td>
<td>32.9±0.5e</td>
</tr>
<tr>
<td>0.5CMC-U2</td>
<td>21.2±0.9h</td>
<td>0.5CMC-U4</td>
<td>32.7±0.7e</td>
</tr>
<tr>
<td>1CMC-U2</td>
<td>27.7±0.6g</td>
<td>1CMC-U4</td>
<td>41.5±0.3ab</td>
</tr>
<tr>
<td>2CMC-U2</td>
<td>28.7±0.6fg</td>
<td>2CMC-U4</td>
<td>42±0.4a</td>
</tr>
<tr>
<td>3CMC-U2</td>
<td>29.6±0.2f</td>
<td>3CMC-U4</td>
<td>41.5±1.1ab</td>
</tr>
</tbody>
</table>

Means followed by the same letter in each column are not significantly different at P<0.05 (LSD-test);
The data are means ± SD (n=3); U, Urea; CMC, Critical Micelle Concentration; U1, 0mg/L; U2, 200mg/L; U3, 300mg/L; U4, 400mg/L.

The microbes degradation of petroleum hydrocarbons was simulated in a simulation reactor (Figure 1). Through the cultivation of 465 days, it showed (in the Figure 2 A) the methane yield change of different treatments with time-variation. The U1 methane yield was rare in the early time. After 275 days adaptation we can...
start to detect methane generation and the U2 methane yield had 220 days adaptation period and the U3, U4 had 125 days adaptation. Meanwhile, each treatment had a rapid period of methane generation. In the same Urea level the 0CMC and 0.5CMC treatments had the near methane yield and the difference was not significant (P<0.01). Meanwhile, in the same Urea level the 1CMC, 2CMC and 3CMC had the near methane yield and the difference was not significant. In the same CMC level with addition of the Urea, the treatment U2 methane yield was more than treatment U1 and the treatment U3, U4 were more than U2 and the difference was both significant. But, the treatment U3 methane yield was near by U4 and the difference was not significant (P<0.01). After 465 days simulation it showed (in the Figure 2 A) that the methane yield means of U3,U4 were 1325 μmol, 1361 μmol respectively and the sterile treatments were not found methane generation(in the Figure 2 B).

**Oil Removal Efficiency of Different Treatments**

After 465 days simulation it showed (in the Table 2) that the oil removal efficiency of 0CMC, 0.5CMC were near and the difference was not significant (P<0.05) and the oil removal efficiency of 1CMC, 2CMC, 3CMC were near and the difference was not significant (P<0.05). Meanwhile, in the same CMC level with addition of the Urea, the treatment U2 oil removal efficiency was more than treatment U1 and the treatment U3, U4 were more than U2 and the difference was both significant. But, the treatment U3 oil removal efficiency was near by U4 and the difference was not significant (P<0.05). The 3CMC-U4 oil removal efficiency mean was very high of 41.5%.

**DRSCUSSION**

In this paper, a simulation system of oil reservoir was innovatively designed to study the process by using indigenous microbes to transform residual oil into methane under initial 10MPa, 55°C (Fig. 1). Microbes commonly existed in a petroleum reservoir which was lower than 80°C. The methanogenic microbes were hard to survive when the temperature is higher than 80°C [17,29-31], while under the temperature 40°C, their growth have the maximum. The methanogenic microbes can be found everywhere in the world from 5°C to 110°C. These microbes played an important role in the carbon cycle by decomposing the organic matter. In general, the oil reservoir temperature was below 80°C [32] and pressure was below 10MPa. Base on the investigation we chose 55°C as the temperature in our experiment and maintain the pressure 10MPa to simulate the real reservoir conditions.
CONCLUSIONS

A simulation oil reservoir system was built to study the process of using indigenous microbes to transform residual oil into methane and the conclusion was summed as follows: The urea and mixture T which can promote anaerobic degradation of petroleum hydrocarbons to produce methane were revealed. When the urea concentration was 300mg/L or 400mg/L, the gas production was both maximum and the difference was not significant. When the mixture T concentration reached the CMC, gas production reached maximum, and the difference among 1CMC, 2CMC and 3CMC treatment was not significant.

ACKNOWLEDGMENTS

Project name: study on isotope tracer high-efficiency degrading flora of pollutants.

REFERENCES