

# The Supercritical CO<sub>2</sub> Huff-n-puff Experiment of Shale Oil Utilizing Isopropanol

Shengxiang Shang<sup>1</sup>, Mingzhe Dong<sup>2</sup> and Houjian Gong<sup>1</sup>

<sup>1</sup>School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, China 266580

<sup>2</sup>Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, AB, Canada T2N 1N4

\*Corresponding author e-mail: 13506480728@163.com

**Abstract.** In this study, the supercritical CO<sub>2</sub> huff-n-puff experiment of shale oil has been investigated. Experimental data shows that the addition of isopropanol can greatly improve the recovery of shale oil. And this provides a new way to improve the recovery of shale oil. In this paper, it is also tried to analyze the influencing factor of isopropanol on the recovery of shale oil by analyzing the MMP.

## 1. Introduction

The world oil industry is moving from conventional oil and gas to unconventional oil and gas, and the development of shale gas and tight oil has achieved good results. Shale oil is rich in reserves and possess good quality of crude oil, which can alleviate the contradiction of energy supply and demand in China. However, the shale oil exists in the form of adsorption and isolation and mainly in the nanoscale pore throat and fracture system. And shale oil reservoirs possess extremely low permeability, strong heterogeneity and high organic matter. So shale oil is low in degree of producing reserves.

The supercritical fluid has been applied for the production of oil shale. The main reasons is that supercritical exploitation can increase yields, improve oil quality and selective the nature of production. This method can be utilized for the exploitation of oil shale. Comparing to liquid solvents, supercritical CO<sub>2</sub> has a higher diffusivity and lower viscosity. So it can improve mass transfer properties during extraction. And supercritical CO<sub>2</sub> can easily be used to exploit certain classes of compounds by the change of temperature and pressure. At the same time, the use of CO<sub>2</sub> can effectively mitigate the greenhouse effect. So the CO<sub>2</sub> EOR method can both enhance oil recovery and CO<sub>2</sub> sequestration to reduce greenhouse gas emissions.

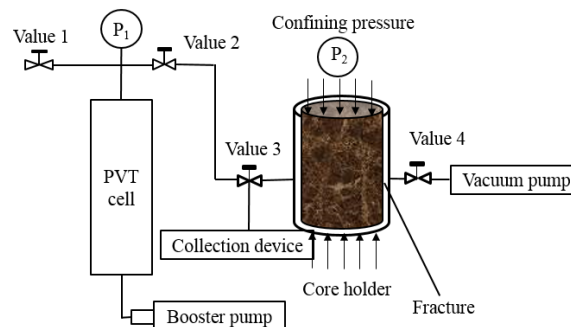
Bondar et al. [1] studied the supercritical fluid extraction of oil shale and utilized supercritical CO<sub>2</sub> to extract specific class of solvency from complex matter. Erol et al. [2] investigated the supercritical fluid extraction of two Turkish lignite and oil shale with toluene mixtures. Tucker et al. [3] compared the recovery of nitrogen retorting, carbon dioxide retorting, CO<sub>2</sub> supercritical fluid extraction and SC-H<sub>2</sub>O. The oil yield obtained using CO<sub>2</sub> supercritical fluid extraction and SC-H<sub>2</sub>O was higher than nitrogen retorting and carbon dioxide retorting. Although the oil quality obtained using SC-CO<sub>2</sub> was better than that obtained when using SC-H<sub>2</sub>O.

This paper aims to study the effect of isopropanol on the recovery of supercritical CO<sub>2</sub> huff-n-puff experiment.



## 2. The supercritical CO<sub>2</sub> huff-n-puff experiment

Studies show that huff-n-puff injection is preferred to gas flooding to improve oil recovery in shale oil reservoirs. Since Wan et al. [4] first proposed huff-n-puff method to improve oil recovery in shale oil reservoirs. Sheng and Chen [5] used simulation method to indicate that huff-n-puff method has the highest potential to enhance oil recovery in shale oil reservoirs. In this paper, the huff-n-puff experiment was conducted to study the recovery of shale oil by carbon dioxide injection. The experimental device is shown in Figure 1.



**Figure 1.** The device of the supercritical CO<sub>2</sub> huff-n-puff experiment.

The supercritical CO<sub>2</sub> huff-n-puff experiment was performed utilizing isopropanol as co-solvent, at different concentration of isopropanol. The experimental pressure is 12MPa and the temperature is 60°C. Dodecane was used as experimental oil in the experiment. The parameters of the rock sample A and B are shown in table 1.

**Table 1.** Parameters for core sample.

sample	Lithology	Length (cm)	Diameter (cm)	Mass (g)	BET Surface (g/m <sup>3</sup> )	BJH Pore Diameter (nm)	TOC (wt.%)
A	shale	3.982	2.48	39.177	1.37	21.35	4.62
B	shale	3.23	2.48	34.111	2.73	21.39	11.29

The experimental results are shown in Table 3. Results have indicated that when using isopropanol as co-solvent, matrix recovery of shale core has been significantly improved. Therefore, it is feasible to improve the recovery of shale oil by adding isopropanol to carbon dioxide. With the increase of isopropanol concentration, the recovery rate is further improved.

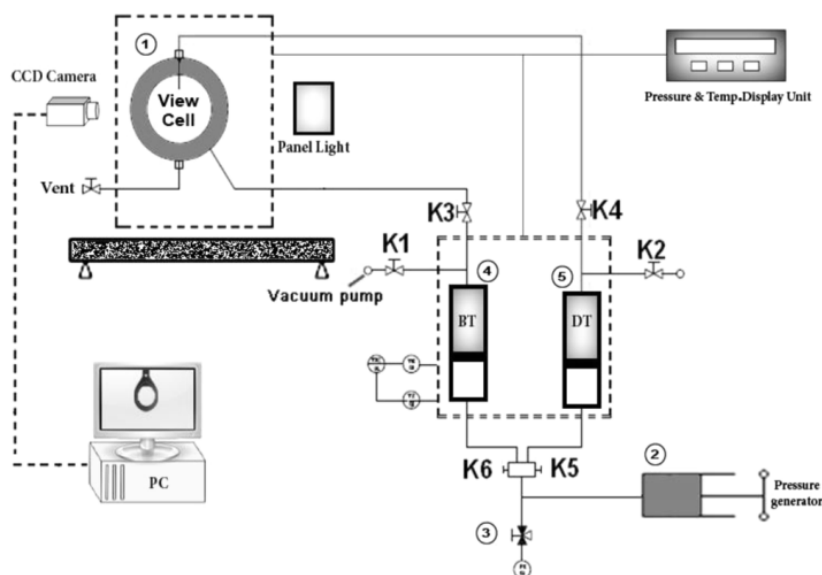
**Table 2.** Experimental results of huff-n-puff injection.

Core Number	Isopropanol concentration	Saturated oil	Produced oil	Matrix recovery
A	0	1.83g	0.882g	0.482
A	1%	1.909g	1.063g	0.557
A	2%	1.85g	1.103g	0.596
B	0	0.711g	0.271g	0.364
B	1%	0.828g	0.381g	0.46
B	2%	0.83g	0.45g	0.542

### 3. The MMP between hexadecane and supercritical CO<sub>2</sub>

#### 3.1. Experimental method

Recently, various MMP prediction methods has been provided.[6,7] The vanishing interfacial tension (VIT) technique has been developed and utilized to determine the minimum miscible pressure of crude oil with gas. [8, 9]By means of the measurement of equilibrium IFT between crude oil and gas as the pressure increases, we can receive that the equilibrium interfacial tension in isotherms decreases as the pressure is increased and it has a linear relation. [10] We can obtain an estimation of MMP by extrapolating the equilibrium IFT as pressure increases, when the equilibrium IFT is zero. The equilibrium interfacial tension was measured using IFT DSA 100 equipment. Figure 1 show the schematic diagram of the experimental setup for IFT measurement between the liquid and CO<sub>2</sub> samples. In this paper we study the effect of isopropanol on (CO<sub>2</sub>+ hexadecane) interfacial tension at supercritical state. Besides, the effect of isopropanol concentration on the MMP have been studied.



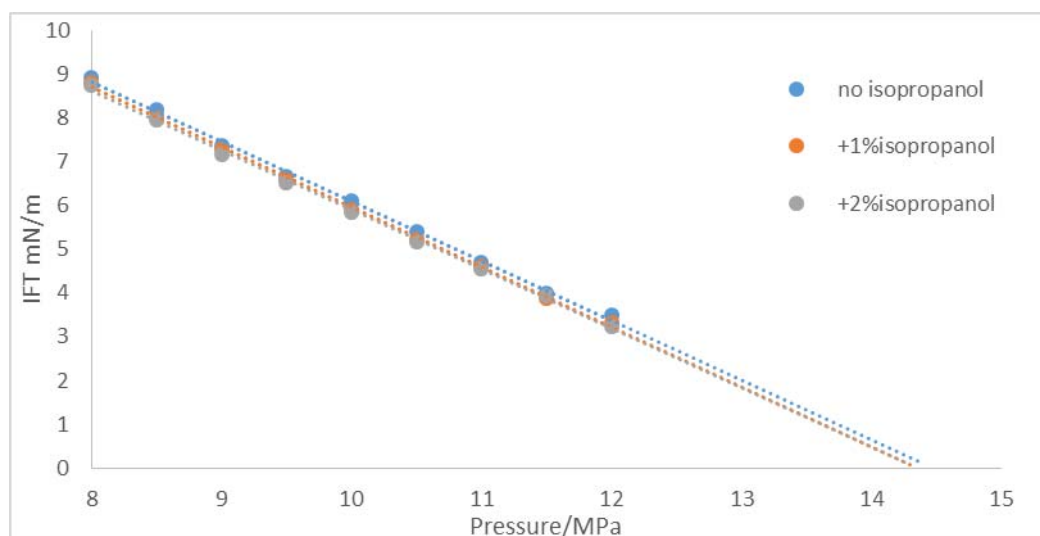
**Figure 2.** Schematic of the experimental apparatus used to measure interfacial tension: 1, view cell; 2, pressure generator; 3, pressure manometer; 4, bulk tank; 5, drop tank.

#### 3.2. Result analysis

The IFTs for each CO<sub>2</sub> + isopropanol system under supercritical pressures and 70°C are shown in Figs.2. It can be seen that the IFT of CO<sub>2</sub> and isopropanol decreases almost linearly with increasing pressure of the systems. Meanwhile, for each condition of isopropanol concentration, the minimum miscible pressure was determined by vanishing interfacial tension method.

When the isopropanol concentration is 0, 1%, 2%, respectively, the lowest reverberation pressure is 14.47MPa, 14.35MPa, 14.34MPa. The addition of isopropanol reduced the interfacial tension between CO<sub>2</sub> and hexadecane. Although the interfacial tension reduction is small, but for the entire fluid reservoir, this change may increase many economic benefits. This provides a way for future study of interfacial tension. Also we can continue to further study other co-solvents to continue to observe the effect.

The density of hexadecane in the experiment was treated as constant.



**Figure 3.** The IFTs between hexadecane and supercritical CO<sub>2</sub>

#### 4. Conclusion

In the supercritical CO<sub>2</sub> huff-n-puff experiment of shale oil, the recovery of shale oil increases significantly with the increase of isopropanol concentration. Therefore, it is feasible to further improve the recovery of shale oil by adding isopropanol to carbon dioxide. Also, it is found that the MMP between supercritical carbon dioxide and alkane decreases little with the increase of isopropanol concentration. So the MMP is not the main influencing factor of isopropanol. More influencing factors need to be further studied.

#### Acknowledgments

We gratefully acknowledge financial support from the National Science and Technology Major Project (2017ZX05049-006).

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