The Research on Application of Supercritical Carbon Dioxide in Petroleum Industry

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Abstract

This paper mainly introduces the supercritical carbon dioxide, it has the unique physical and chemical properties, possesses advantages of gas and liquid. This paper analysis the supercritical carbon dioxide using in the petroleum industry: including drilling, fracturing and displacement. It provides direction of the application and further development of supercritical CO_2 in petroleum industry.

Keywords

Supercritical CO_2; Petroleum Industry; Drilling; Fracturing; Displacement.

1. Introduction

In recent years, along with the study of physicochemical properties of supercritical carbon dioxide in depth, people gradually realized the importance of supercritical carbon dioxide technology research and application, the technology is developing rapidly and spreads in chemical, material, food, clothing and many other fields [1], especially in the oil industry.

The low viscosity of supercritical CO_2 gas with high density, high diffusion coefficient, and chemically inert, non-toxic and non-corrosive, besides, the critical state is easy to realize, so it is an excellent environmentally friendly solvent. By analyzing the unique physical properties of supercritical CO_2, the article introduces the application of supercritical CO_2 in petroleum industry.

2. The Overview of the Supercritical CO_2

When the temperature is higher than 31.1 DEG C, the pressure is greater than 7.38MPa, CO_2 will become a supercritical carbon dioxide (Supercritical Carbon Dioxide, referred to as SC-CO_2). Figure 1 is the temperature pressure phase diagram of CO_2, the critical point of SC-CO_2 is Tc=31.1 Deg. C, Pc=7.38MPa. Due to its low critical value, when injecting CO_2 in formation, it is easy to get the supercritical state in the wellbore. Usually, supercritical state are got in the wellbore at a depth of 750 meters [2].

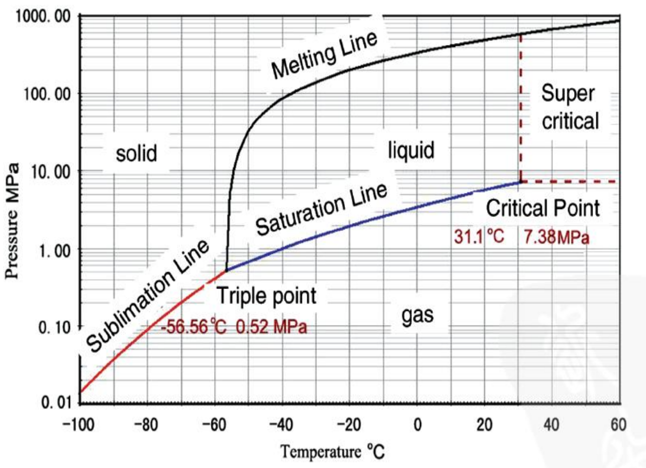

Fig. 1 The phase diagram of carbon dioxide (Al-Adwani, 2008)

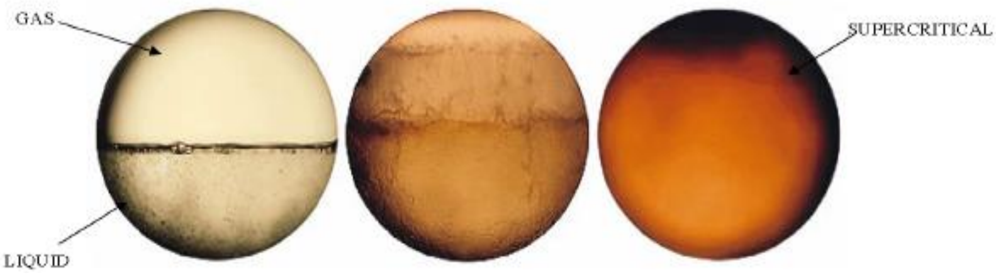

Fig. 2 The phase state change process of supercritical phase

As shown in Figure 2, the phase change process of supercritical carbon dioxide in the interface between gas and liquid phases gradually disappear and eventually become a single supercritical phase. Therefore, supercritical carbon dioxide is not only different from the gas, but also different from the liquid. The physicochemical properties of it are between the gas and liquid.

Table 1 shows the supercritical carbon dioxide has advantages of both gas and liquid, the density is close to the liquid and has strong dissolving ability. What's more, viscosity and diffusion coefficient are similar to gas (Han, 2005), and the surface tension is zero [3], so it is easy to enter other channels larger than the supercritical carbon dioxide molecule. Its heat and mass transfer performance are good, and easy to penetrate the surrounding porous medium, with other material incomparable advantages in oil and gas development.

Table 1. Comparison of supercritical, gas phase and liquid phase properties of CO_2 (according to Peng Yingli et al., 2005)

Fluid	Density ρ/(g/cm^3)	Viscosity μ/(mPa s)	Diffusion Coefficient D/(cm^2/s)	Thermal conductivity k
Gaseous	$(0.6\sim2.0)\times10^{-3}$	10^{-2}	0.1~0.4	$(5\sim30)\times10^{-3}$
Super critical state	0.2~0.9	0.03~0.1	0.7×10^{-3}	$(30\sim70)\times10^{-3}$
Liquid state	0.6~1.6	0.2~3.0	$(0.2\sim3)\times10^{-5}$	$(70\sim250)\times10^{-3}$

In addition, critical opalescence and significant fluctuations for physical parameters are based in supercritical carbon dioxide at the critical point. The change of the disturbance in the vicinity of the critical point, small temperature and pressure will cause the parameters. Therefore, supercritical CO_2 is widely used in chemical industry, printing and dyeing, extraction and other industries. It also has broad prospects for development in the petroleum industry.

3. The application of supercritical CO_2 in petroleum industry

3.1 The application of supercritical carbon dioxide in drilling

Supercritical CO_2 drilling is a new type of drilling method which uses supercritical CO_2 fluid as drilling fluid. It uses high pressure to pump cryogenic liquid CO_2 in drill pipes, the liquid CO_2 downs to a certain depth to the supercritical state, and auxiliary rock breaking for supercritical CO_2 jet to achieve drilling rapidly [4]. Supercritical CO_2 drilling is better than conventional drilling with fast drilling speed, low threshold pressure for rock breaking, hole cleaning ability, reservoir pollution. In recent years, domestic and foreign experts and scholars have conducted exploratory research on supercritical CO_2 drilling, and made a series of progress.

In the supercritical CO_2 jet rock breaking, Kolle J J et al [5] made jet rock breaking laboratory experiment with SC-CO_2 and jet assisted drilling field test in 2000, the results of the study showed that in Manchester Caicos shale in the SC-CO_2 jet drilling speed was 3.3 times of water jet, and the required ratio SE (SE, special energy, which is the ratio of the required hydraulic, mechanical energy for rock breaking and flaking rock volume [6]) for rock breaking is only 20% of which in hydraulic drilling.

In 2002, Tempress technological company proposed SC-CO_2 coiled tubing drilling scheme, and carried out exploratory experiments about it, founding that SC-CO_2 could improve the ROP. In 2005, Louisiana State University studied the field test of using supercritical carbon dioxide as drilling fluid, found that the bottom conditions were conducive to supercritical carbon dioxide, and proved the feasibility of supercritical carbon dioxide as deep under-balanced drilling fluid.

On the basis of theoretical research, domestic scholars in the study of supercritical carbon dioxide drilling are also prominent. Professor Zhengsong Qiu of China University of Petroleum developed the simulated experiment device about SC-CO_2 drilling fluid circulation, studied the flow characteristics of the supercritical CO_2 drilling fluid, and revealed the change law of carrying rock capacity. In 2012, Du Yukun, Wang Ruihe etc.[7], according to the properties of supercritical carbon dioxide and the condition of drilling and completion, developed the first domestic set of SC-CO2 test device in drilling and completion [8]. The device could simulate the actual underground working conditions, and do rock breaking test by use of supercritical CO_2 jet. The results showed that SC-CO_2 had a significant advantage, and the influence of environmental temperature on the bottom of the rock breaking effect was remarkable.

In 2012, Wang Haizhu, Li Gensheng et al.[9], pointed out that the advantages of supercritical CO_2 drilling, namely low threshold pressure, high rock breaking speed, and it could effectively protect the oil and gas reservoir and increase oil and gas well production and recovery. They also pointed out that the supercritical CO_2 would promote the development of coiled tubing borehole, micro borehole drilling, horizontal wells with extremely short radius and radiate horizontal wells in the future.

In 2014, Zhu Zhongxi et al. [10], proposed the concept of gas circle drilling by using supercritical CO_2, this technology uses ground gas recycling equipment and separate and filtrate the returned gas rock carrying from the wellhead, and then compressed the gas into underground. This technology will greatly reduce the cost of drilling.

3.2 The application of supercritical carbon dioxide in fracturing

In 2004, Shen Zhonghou proposed using supercritical carbon dioxide to replace water as fracturing fluid, for the supercritical state density is close to water, the viscosity is low, and the surface tension is close to zero, which can solve the problems caused by hydraulic fracturing.

In 2009, J K Daniel and others [11] through the study of the total organic carbon (TOC), inorganic minerals and pore structure on the CO_2 and CH_4 adsorption, found that the shale adsorption capacity of CO_2 was significantly higher than CH_4.

In 2011, Wang Haizhu et al.[12], proposed using supercritical carbon dioxide to exploit shale gas. Through reservoirs fractured by SC-CO_2, it produces more micro fractures, which contributes to shale's gas production; the most important is the adsorption strength of CO2 with shale is higher than CH4, so CO_2 can replace the CH_4 adhered to shale. Improving the yield and production rate at the same time realizes the permanent storage of CO_2.

In 2013, Cheng Yuxiong, Li Gensheng et al.[13] summed up the advantages of supercritical carbon dioxide fracturing fluid in oil and gas production areas, and put forward the coiled tubing fracturing process of supercritical CO_2 jet. In 2014, they formed fracturing wellbore flow model of SC-CO_2 injection, made the calculation and analysis, and studied how to control the phase of wellbore fluid in the reservoir with abnormal low geothermal gradient. The results showed that in the process of fracturing by supercritical CO_2 jet, controlling wellbore temperature is the critical point for supercritical CO_2 injection to control fracturing phase. They also used the method of computational fluid dynamics to simulate flow fields in pore in the injection fracturing process of supercritical CO2[14], compared and analyzed the super the critical CO2 ejector effect of the fracturing and hydraulic jet fracturing. Due to lower viscosity of supercritical CO_2, when nozzle pressure drop is at

30MPa, 20MPa, 10MPa, the internal pore pressure of supercritical CO_2 jet is higher than the same conditions of the water jet, which shows that the effect of supercritical CO_2 jet is better.

In 2015, Guo Jianchun, Zeng Ji[15] had established coupling model with unsteady temperature and pressure of supercritical carbon dioxide fracturing in wellbore. The bore temperature, pressure and physical parameters of CO_2 fluid influence each other. Appropriate regulation of the injection temperature and injection rate contributing to bottom hole temperature, can make CO_2 reach supercritical state in the bottom hole, and high friction and the low viscosity of CO_2 restrict lifting displacement and sand ratio.

Compared with hydraulic fracturing, supercritical carbon dioxide fracturing saves water resources has no reverse discharging and no pollution, can dissolve some pollutants near bore zones. Because of low viscosity and high diffusion coefficient of SC-CO_2, so it is good in mass transfer to easily enter into the reservoir and formats complex fracture networks by jet fracturing. Therefore, supercritical carbon dioxide fracturing technology in reservoir reconstruction of the oil industry has wide application foreground.

3.3 The application of supercritical carbon dioxide in displacement

In 2006, Li Mengtao, Shan Wenwen et al.[16] launched a single experimental study on the mechanism of supercritical carbon dioxide miscible flooding. Research shows that the supercritical carbon dioxide could lower the tension of the interface of involved oil and water, and the content of carbon dioxide in carbon component of oil could reach the highest value in the miscible region. Water is bad effect of mixing when inject water and gas alternately.

In 2011, Dr. Wang Guanhua performed a foaming experiment about supercritical carbon dioxide, and found that foam became gray white emulsion. He combined the PVT experiment of CO_2 foam, introduced the concept of water solubility of CO_2, and developed the theory of state equation of CO_2 foam finally. Through microscopic displacement experiment, he also studied on the micro flow and oil displacement rule of supercritical carbon foam dioxide.

For the unconventional reservoir flooding, in 2010, Yang Tao [17] analyzed coal seam injection of supercritical carbon dioxide, and did extraction experiment about the coal seam and micro CT test of coal samples before and after extraction. The experiment proved supercritical carbon dioxide to improve the feasibility of low permeability seam. In 2013, Li Gensheng proposed that shale gas or coal seam gas could be displaced strongly with SC-CO_2, CO_2 could replace CH_4 adsorbed on rock, while drive the free CH_4 into the wellbore. It couldn't only improve the recovery rate, but also storage CO_2 permanently. In 2014, Liang Weiguo et al. [18] developed the device of supercritical CO_2 flooding displaced CH_4 in coal seam, and carried out tests in different penetration conditions and the displacements. It provides technical support for the development of supercritical carbon dioxide flooding.

Applications of supercritical CO_2 in driving, on the one hand, can reduce the interfacial tension, and improve the recovery rate; on the other hand, in the development of unconventional reservoir, low viscosity and good properties of mass transfer of supercritical carbon dioxide, contribute to the supercritical CO_2 displacing the free state CH_4 in reservoir, thus strengthening the exploitation of unconventional reservoirs.

4. Conclusion

Due to the unique physical and chemical properties of supercritical CO_2, supercritical CO_2 has shown great advantages in drilling, fracturing and displacement replacement, which are mainly reflected in the following aspects:

(1) In supercritical CO_2 drilling, high density and low viscosity of supercritical CO_2 can effectively reduce the threshold pressure, increase drilling speed, and can keep the unbalanced state of underground, and can realize the fast complex well slim hole drilling combined with coiled tubing

technology, cause no pollution in reservoir. As a result, the costs of shale gas development will be effectively reduced.

(2) Supercritical CO_2 jet fracturing has great advantages in shale reservoir reconstruction, it can effectively reduce the threshold pressure, the good properties of mass transfer can make crack extend and connect reservoir natural fractures to format complex networks, and relieves the reservoir pollution for good solubility. Besides, reservoir transformation effect is better in water-based fracturing fluid, and it needn't flow back to reduce working procedure.

(3) Supercritical carbon dioxide flooding in the application of the CH_4, the competitive adsorption realizes the advantages of using supercritical CO2 to replace methane in the shale, and helps to store CO_2 underground, which has important significance for green energy saving and emission reduction.

With the continuous development of in-depth study on the basic theory of supercritical carbon dioxide and application technology, its application prospect in petroleum industry is very attractive. But many applications mainly focus on the feasibility study, and the studies of related theories and research field are not enough. At present, the application of supercritical carbon dioxide in the petroleum industry mainly has the following issues:

(1) In the presence of formation water, the use of supercritical carbon dioxide drilling can cause serious corrosion. If drilling in the formation of water, serious corrosion will be caused on all the pipeline, equipment and well bore.

(2) In the field application of supercritical carbon dioxide fluid, the Joule Thomson effect should be considered, and temperature dropping in the nozzle easily produces hydrate blockage.

(3) Carbon dioxide as a green solvent, from an environmentally friendly point of view, carbon dioxide can be recycled after compression.

(4) SC-CO_2 drilling requires high pressured equipment, including the pump injecting liquid carbon dioxide, high pressured coiled tubing and special jet drill.

5. Outlooks

At present, the application of supercritical carbon dioxide in the oil industry mostly in the mechanism research, laboratory experiment is difficult to be carried out, and it is difficult to promote the field application of supercritical carbon dioxide in put forward. So, put the following suggestions on the development of supercritical carbon dioxide in the oil industry:

(1) Deeply research on the technology equipment of supercritical carbon dioxide. Due to the operating conditions of the equipment are difficult to control, its automation degree can be improved in order to more accurately control the condition parameters;

(2) Further strengthen the basic theory research. For the phase equilibrium's determination of the super critical zone, and the mechanism of reservoir, seepage mechanism and so on, a lot of research work is still needed;

(3) Systematize the application of supercritical carbon dioxide in the petroleum industry, and strengthen the optimization of process parameter, the research of production scale expansion, in order to develop a suitable for industrialization and industrial production process.

In order to promote the application of supercritical CO_2 in petroleum industry, further development of theoretical and experimental research about supercritical CO2 drilling, fracturing and displacement on replacement should be carried out and increase the manufacture of relevant tools. Considering the source of carbon dioxide and innovation of technology, under the condition of laboratory experiment and field application should be combined to effectively promote the development of supercritical carbon dioxide in petroleum industry.

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