

PAPER • OPEN ACCESS

An Overview of in-situ Development Technology of Oil Shale with Near and Sub-critical Water

To cite this article: Lan Wang and Zhiping Li 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **295** 042105

View the [article online](#) for updates and enhancements.

An Overview of in-situ Development Technology of Oil Shale with Near and Sub-critical Water

Lan Wang^{1,2,*}, Zhiping Li^{1,2}

¹School of Energy Resource, China University of Geosciences (Beijing), Beijing 100083, China

²Beijing Key Laboratory of Unconventional Natural Gas Geological Evaluation and Development Engineering, Beijing 100083, China

*Corresponding author: 13096362996@163.com

Abstract. With unconventional oil and gas reservoirs gradually becoming the global oil and gas hotspot resources, the development and research of unconventional reservoirs has also been paid more and more attention by researchers. Among them, oil shale has enormous reserves in the world and plays an important role in unconventional resources. The development of oil shale can be divided into surface distillation and in-situ development. The purpose of this paper is to systematically summarize and evaluate the application of critical water in the development of oil shale. This paper also tries to find out whether there is more study on its application in order to realize industrial production of oil shale by critical water extraction. At present, researchers in China have done a lot of researches about near and sub-critical water development on oil shale, especially teachers and graduates of Jilin University. In the past two decades, researchers have made rapid progress in extracting organic matter from oil shale by using sub-critical water and near critical water. Sub-critical water refers to water whose temperature is lower than 374 °C and pressure is between 14 and 22.1 MPa, while near-critical water refers to water whose temperature is between 150 and 374 °C while the pressure is between 0.4 and 22.1 MPa. Water in these two states has superior mass transfer performance, acid-base catalytic function and lower dielectric constant than normal water. Of course, the biggest advantages of sub-critical water and near-critical water are non-toxic and inexpensive, which is of great significance to environmental protection in the process of oil shale development. In order to study the feasibility of in-situ extraction of shale oil from near-critical water and sub-critical water for field application, a comprehensive survey was conducted.

1. Introduction

Oil shale reserves are huge all over the world, which can be converted into 400 billion tons of oil shale reserves. This is 5.4 times the proven reserves of crude oil in the world. China's oil shale resources amount to 11602×10^8 t, of which the buried depth of 500-1500m is 6813×10^8 t. At present, the above-ground retorting technology is the way of utilizing this part of resources in the world. In-situ production technology is an effective means to develop this part of resources. Today, energy restricts the development of national economy and science and technology, so the conversion and development of such unconventional oil and gas resources is particularly important.

At present, the main problems of surface retorting in China are as follows^[1]: First of all, surface retorting technology in China can't deal with powdery and small-grained oil shale, mainly referring to



oil shale particles less than 12 mm in diameter. Secondly, the industrial exhaust gas produced by surface retorting technology pollutes the environment seriously. Finally, surface retorting process is complex and costly. Although it has been industrialized, its economic benefit is not high.

The main technical difficulty of in-situ development technology is to keep the underground temperature. On the other hand, in-situ development also has some environmental pollution problems. Especially when the injected fluid contains volatile chemicals. Relatively speaking, the underground retorting technology has the advantages of simple process and low cost.

As early as 1995^[2], researchers at the University of Alberta in Canada studied the application of sub-critical water and near-critical water in oil shale development. The experimental results show that the oil recovery extracted from critical water is 75% higher than that obtained from traditional distillation. In addition, in the presence of CO₂, the sulfur element in the extract can be removed. This has greatly improved the environmental pollution in oil shale retorting^[3]. In 1996, students from Dalian University of Technology of China^[4] conducted a series of studies on sub-critical water extraction of organic matter from oil shale. Since then, Chinese researchers have been studying the extraction of organic matter from oil shale by sub-critical water and near-critical water, and many research results have been published until 2018. In recent years, Jilin University is the largest institution to study shale oil extracted from oil shale by critical water. Professor Wang Hongyan, School of Chemistry, Jilin University, has done a lot of research on organic matter extraction from oil shale by critical water.

2. Result and discussion

The results and discussion are mainly composed of three parts. The first part is related investigation and review of subcritical water and near-critical water extraction of oil shale. The second part is about the research and review of in-situ development of oil shale. Finally, the discussion section will give directions for further study in this research. It is hoped that through the cross-study and cooperative research of different disciplines, the research depth of in-situ production of oil shale by sub-critical water and near-critical water will be deepened.

2.1. Extraction of Oil Shale by Sub-critical and near critical Water

Sub-critical water is more widely used in oil shale extraction because of its wider definition and experimental conditions than near critical water. At present, the researchers who use sub-critical water and near-critical water to extract oil shale are mainly teachers and students of Jilin University. In their research process, they mainly focus on indoor chemical experiments^[5]. This kind of experiment usually needs high temperature and pressure reactor (Fig.1) as the experimental generator. Continuous extraction was carried out for several hours in sub-critical water and near-critical water. Then, the extracts were analyzed by component analysis. Finally, sufficient experimental data were obtained for the analysis and demonstration of the results. The overall experimental schematic diagram is shown in Fig.2. Sunhua Deng (2011) carried out a sub-critical water extraction experiment of organic matter from Huadian oil shale. The effects of temperature and pressure on hydrocarbon extraction were analyzed experimentally. Oil shale was extracted under pressure of 15 MPa for 2.5h at 260 Centigrade, and the extraction rate reached 7 %. It can be seen that the sub-critical water has a high oil recovery in the experiment. At the same time, the change of temperature and pressure will have a greater impact on oil recovery and experimental results. These two factors are also the main factors affecting the properties of the sub-critical water state. The team also carried out thermogravimetric analysis of the extraction experiment. The results show that at lower temperatures, sub-critical water can crack kerogen into smaller hydrocarbons. Sunhua Deng (2012) analyzed the extracts from oil shale organic matter extraction by subcritical water by gas chromatography-mass spectrometry. On the other hand, the pyrolysis process was also analyzed by GC-MS. Through experiments and analysis, it was found that the content of long-chain alkanes in subcritical water extracts was higher than that in anhydrous pyrolysis. Olefin extracts can be converted to alkanes in subcritical water.



Figure 1. CJF1 stainless steel high temperature and pressure reactor

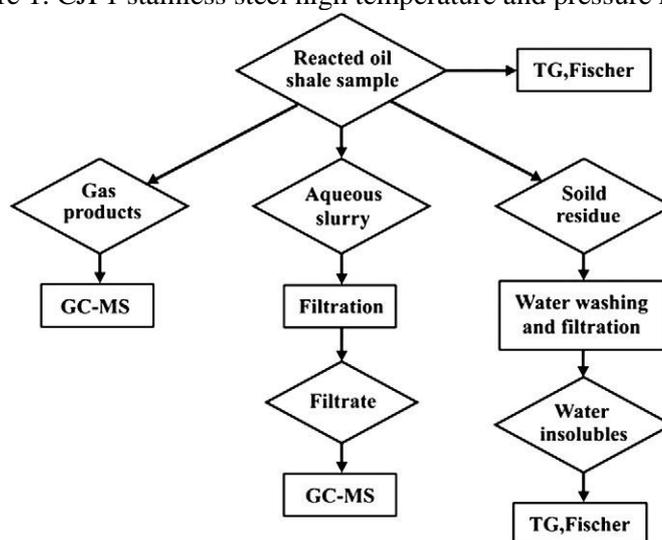


Figure 2. Flow chart of extraction experiment and analysis and detection

In the latest research of Professor Wang Hongyan's students^[6], the simulation experiment of extracting organic matter from oil shale by near critical water was carried out. The experimental results mainly analyzed the influence of asphaltene content, comprehensive temperature field and porosity on the oil yield of organic matter in oil shale. It also analyzed the extract products. At the academic seminar in 2015, Wang Hongyan and her students published the research results on the extraction process of oil shale by near critical water. The results show that near critical water extraction experiments in different areas have achieved a high extraction effect. The maximum oil recovery of Huadian oil shale can reach 18.1% in 70 hours, which is higher than the oil content obtained by Fisher test. Previously, in 2014, Wang and his team used a high temperature and pressure reactor to study the extraction effect of near critical water on large-scale oil shale blocks. The effects of extraction conditions of near critical water, texture and size of oil shale samples on the extraction of organic matter from oil shale by near critical water were investigated. The composition of near critical water extract and the change of matrix properties of oil shale during extraction were analyzed. The feasibility of extracting organic matter from massive oil shale by near critical water method is proved, which provides experimental basis and theoretical basis for in situ extraction of underground oil shale by near critical water method.

In fact, on the extraction of organic matter from oil shale, the first researchers used chemical organic matter for extraction. In the subsequent study, considering the cost and the possible pollution caused by chemical agents, more environmentally friendly water was chosen as extractant, which not only controlled the production cost but also caused very low pollution to the environment. Jameel S et al^[7] made use of conventional HCl-HF method to extract marine oil shale in their research in 2019.

They compared the experimental results with NaOH-HF extraction results. Similar to other oil shale extraction methods, gas chromatography and total ion chromatography were used to analyze the extracts. The extracts obtained by the two methods are similar, but the content of iron ions in solid residues is quite different. Since most regions and countries limit the use of HF, this method may be limited to laboratory experiments. Jin Y et al^[8] (2018) used N, N-dimethyl form amide (DMF) as refining solvent to separate diesel fractions from Xinjiang Baoming oil shale. Thirty-three phenolic compounds were identified in the final concentrated product, mainly phenol, alkyl phenol, thymol, naphthol and alkyl naphthol.

It can be seen that other organic solvents also have a good effect on oil shale extraction, and the changes of physical parameters of oil shale samples during extraction can be analyzed according to experiments. The extraction effects of different extractants are different. If these extractants can be used for in-situ development, the compatibility of extractants with oil shale reservoirs and the evaluation of extraction effects need to be further studied. In addition, through the study of temperature, pressure and extraction time, field process design can be better carried out.

According to the previous experimental studies, the physical properties of oil shale in different areas are different, so the extraction effect is also different. At present, there is no systematic method suitable for general oil shale under normal conditions. Because of the intense pyrolysis process, some physical properties of oil shale itself have not been considered before extraction experiments. On the other hand, the ultimate goal of subcritical water and near-critical water extraction experiments is to apply to in-situ development of oil shale. At present, there are few studies on this aspect. The problems to be solved in situ development of oil shale include the variation of temperature field, heating range and the infiltration of liquid water underground. In the process of in-situ development, the change of temperature will affect the change of permeability and porosity of rock itself. The change of these two data is an important factor affecting the migration of products. Because of the limitations of laboratory experiments, the research in this field can only rely on numerical simulation. Tiikma et al^[9]. (2015) compared the effects of four different solvent conditions on oil shale extraction at the same temperature and pressure. Al-Gharabli^[10] (2015) studied oil shale by microwave radiation and tested the extraction ability of several different solvents at different temperatures. Khraisha et al^[11]. (2015) used batch autoclave to extract Jordanian oil shale by supercritical fluid extraction. By changing the mixing time, types of extractants, temperature and pressure, the influence of these factors on the extraction effect was analyzed.

According to the current literature and research results, the experiments of extracting organic matter from oil shale by sub-critical water and near-critical water are only carried out indoors. The main research method is to carry out chemical experiments, and to analyze the products and experimental process. Similar to ground distillation, product analysis experiments are usually carried out by GC-MS analysis. The whole experiment was evaluated by thermogravimetric analysis of the experimental process.

2.2. In-situ Development

In-situ production technology is an effective means to develop this part of resources. China's oil shale in-situ production technology is in the experimental stage. Through the study of thermal decomposition, thermal fracture and permeability variation of oil shale, a mathematical model is established to discuss the feasibility of in-situ development of oil shale.

In this section, the research progress of numerical simulation of in-situ development of oil shale is investigated in depth. In order to further study the influence factors and characteristics of this technology, it can be better combined with indoor experiments.

Zhijun Liu et al^[12] (2018) studied the evolution mechanism of pore structure during in-situ development of oil shale. The results show that temperature is an important factor causing the change of pore structure. Hydrostatic pressure will not change the evolution law of pore structure, but it has a significant inhibitory effect on pore development. Maes J et al^[13] (2017) established a mathematical model for in-situ conversion of heavy oil and oil shale. The model quantitatively analyzed the ratio of

chemical reaction rate to heat conduction rate in the conversion process. With regard to the numerical simulation of in-situ transformation of oil shale, in 2016, Chinese researcher Han H et al^[14] also established relevant models, which mainly simulated the in-situ transformation of continental oil shale in Northeast China. Shufeng Pei et al^[15] (2018) proposed a novel nitrogen injection-assisted in-situ conversion process, which can improve formation heating rate and oil shale recovery rate. Through investigation, it is known that in-situ development of oil shale is similar to thermal recovery of heavy oil, and it needs to raise the temperature of target area before development. However, compared with heavy oil, oil shale has a longer heating period, which is due to the higher temperature required for in-situ development of oil shale. Generally, the heating time of oil shale set by numerical simulation is calculated on an annual basis, which can be as long as five or six years. This leads to the problem of estimating the economic cost. More importantly, the long-term heating temperature field changes will be more complex, and the freezing wall must be carried out in the target area.

2.3. Discussion

The purpose of studying subcritical water and near-critical water is to apply it to in-situ development of oil shale. Therefore, in addition to chemical research, seepage and rock structure research is particularly important. In order to make in-situ development of oil shale with near-critical water and sub-critical water feasible, in addition to numerical simulation of in-situ development, more detailed research on development process and characteristics is needed. It mainly includes the law of production decline, injection process design and economic cost evaluation. This further increases the economic cost of development.

3. Conclusion

This paper summarizes the development history and main research results of oil shale technology with subcritical water and near-critical water. Based on the investigation of in-situ development technology of oil shale, the feasibility of in-situ development technology of oil shale with sub-critical water and near-critical water is discussed and analyzed. Finally, a complete review report has been formed, which provides some theoretical guidance for the in-situ development of oil shale economy and environmental protection.

In view of the fact that the development of oil shale by sub-critical water and near-critical water is mainly in China, other countries with abundant oil shale resources have seldom been studied. Oil shale reserves are mostly located outside China. Therefore, it will be very helpful for foreign researchers to review the relevant research in China. Through in-depth research and exchanges among researchers all over the world, the development of oil shale technology with sub-critical water and near-critical water will surely make greater progress. It can promote the application of this technology in the mine as soon as possible.

Acknowledgments

The completion of this paper cannot be separated from the careful guidance of my instructor and the research results made by the researchers of Jilin University. The paper database provided by China University of Geosciences (Beijing) is of great help to the completion of the article. Here, I would like to express my sincerest thanks to all of you and institutions.

References

- [1] Liu QQ.(2015) Thermo physical properties of oil shale particles and retorting experiments in rotary kiln[D].
- [2] Ogunsola O M and Berkowitz N.(1995) Extraction of oil shales with sub- and near-critical water [J]. Fuel Processing Technology 45(2):95-107.
- [3] Parkins. (1959) SYNTHESIS OF THERMALLY STABLE INORGANIC AND SEMI-INORGANIC BASE FLUIDS[J].Fuel,68 (10) :1234-1242,1959
- [4] Jun Zhang. (1996). Study on Supercritical Water Extraction of Huadian Oil Shale [D].

- [5] Deng S, Wang Z and Gu Q, et al. (2011). Extracting hydrocarbons from Huadian oil shale by sub-critical water[J]. *Fuel Processing Technology*, 92(5):1062-1067.
- [6] Wang Z J. (2014). Near-critical water simulation extraction and product analysis of oil shale in different areas[D]. Jilin University,
- [7] Aljariri Alhesan J S, Amer M W, Marshall M , et al.(2019). A comparison of the NaOH-HCl and HCl-HF methods of extracting kerogen from two different marine oil shales[J]. *Fuel*, 236:880-889.
- [8] Jin Y, Han D Y, Cao Z B, et al. (2018). EXTRACTION AND SPECTROSCOPY ANALYSIS OF BASIC NITROGEN AND PHENOLIC COMPOUNDS OF THE SHALE OIL OF BAOMING OIL SHALE, CHINA[J]. *Oil Shale*, 35(2).
- [9] LAINE T,ILLE J,HANS L,et al.(2015). Extraction of Oil From Jordanian Attarat[J].*Oil Shale*, 32(3):218-239.
- [10] SAMER I,MOHAMMED A G,AZZAM O J,et al. (2015). Microwave assisted Solvent Extraction of Shale Oil From Jordanian Oil Shale[J].*Oil Shale*, 32(3):240-251.
- [11] Jamil Al Asfar. (2016). Thermal Cracking Combined with Supercritical Fluid Extraction of Jordanian Oil Shale [J]. *Energy Sources Part A Recovery Utilization and Environmental Effects*, 38(issue : 8):pages : 1148-1155.
- [12] Liu Z J, Yang D, Hu Y Q, et al. (2018). Influence of In Situ Pyrolysis on the Evolution of Pore Structure of Oil Shale[J]. *ENERGIES*, 11(4):112-124
- [13] Maes J , Muggeridge A H , Jackson M D , et al. (2017). Scaling analysis of the In-Situ Upgrading of heavy oil and oil shale[J]. *Fuel*, 195:299-313.
- [14] Han, H, Zhong, N N, Huang, C X, et al, (2016). NUMERICAL SIMULATION OF IN SITU CONVERSION OF CONTINENTAL OIL SHALE IN NORTHEAST CHINA[J]. *Oil Shale* ,33(1):45-57
- [15] Shu F P , Yan Y W , Liang Z , et al. (2018). An innovative nitrogen injection assisted in-situ conversion process for oil shale recovery: Mechanism and reservoir simulation study[J]. *Journal of Petroleum Science and Engineering*:S0920410518306466-.