



Review Paper

Development review and the prospect of oil shale in-situ catalysis conversion technology



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ARTICLE INFO

Article history:

Received 15 February 2023

Received in revised form

26 June 2023

Accepted 30 August 2023

Available online 1 September 2023

Edited by Jia-Jia Fei and Min Li

Keywords:

Oil shale

In-situ catalytic technology

Pyrolysis catalyst

Kerogen pyrolysis mechanism

ABSTRACT

As an unconventional resource, oil shale possesses abundant reserves and significant potential for industrial applications. The rational and efficient development of oil shale resources holds immense importance in reducing national energy demand. In-situ catalytic technology, characterized by its high efficiency, low pollution, and minimal energy consumption, represents a key direction for future oil shale development. This paper provides a comprehensive review of research progress in in-situ oil shale mining technology, oil shale pyrolysis catalysts, the pyrolysis mechanism of kerogen, and the compatibility of different heating processes and catalysts. Furthermore, the paper proposes future research directions and prospects for oil shale in-situ catalytic technology, including reservoir modification, high-efficiency catalyst synthesis, injection processes, and high-efficiency heating technology. These insights serve as valuable technical references for the advancement of oil shale in-situ catalytic technology. © 2023 The Authors. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co. Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In the face of the critical situation regarding oil and gas resources, finding diverse and suitable alternatives to replace the depleting reserves has become a crucial strategic concern for national energy development. Oil shale, a solid combustible organic sedimentary rock with high ash content and oil content exceeding 3.5%, can be obtained through low-temperature distillation, typically possessing a calorific value higher than 4.18 MJ/kg. It is categorized as an unconventional oil and gas resource (Hou et al., 2022; Hu et al., 2014). In China, the geological resources of oil shale have reached 719,937 million tons, including approximately 47,644 million tons of convertible shale oil, making it a significant strategic resource for China's energy security. Consequently, oil shale is considered a vital energy source for future oil and gas replacements (Aurela et al., 2021; Can et al., 2020; Kalu et al., 2022). China possesses the world's second-largest oil shale resources, with shale oil conversion equivalent to 62% of the country's conventional oil resources. Efficient and environmentally friendly utilization of oil shale resources has thus become an urgent issue.

According to statistics, China's oil shale reserves are abundant

and widely distributed, totaling 7.2×10^{11} tons. However, based on the exploration of oil shale quality and maturity, the oil content of Chinese oil shale is moderately high, with a small proportion of high maturity. Extracting oil shale is challenging, resulting in an annual production of only 7.8×10^5 tons in China (Hou et al., 2022; Fu et al., 2021). To expedite the application and transformation of oil shale, research efforts are underway both domestically and internationally. These efforts primarily focus on: (1) high-efficiency heating technology with composite heating, high-efficiency downhole heaters, and catalytic enhancement as the core components; (2) horizontal well guidance drilling technology with rotary guidance drilling and precision ranging as the central elements; and (3) composite reservoir modification technology with CO₂ dry fracturing, acid fracturing, and gas drive water sealing as the essential components.

Oil shale organic matter primarily consists of immature kerogen, which is a solid material that cannot be directly extracted. To obtain oil from oil shale, it needs to undergo low-temperature dry distillation (450–500 °C). Pyrolysis technology for oil shale conversion includes ex-situ and in-situ methods (He et al., 2022). Ex-situ methods involve extraction, grinding, screening, and pyrolysis of oil shale. This approach is typically used for mining shallow deposits, offering advantages such as low cost and high safety factors. However, ex-situ mining can only be conducted in open areas, leading to land occupation and severe ecological damage (Hu et al.,

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2022). The pyrolysis process of oil shale has low conversion efficiency, resulting in resource wastage. Moreover, incomplete pyrolytic conversion of casein in oil shale leads to unstable quality and high viscosity of shale oil. In-situ conversion mining technology for oil shale involves artificially heating the underground oil shale reservoir, cracking the solid casein inside the oil shale in-situ into oil and gas, and then extracting them through specific processes. This technology offers advantages such as environmental protection, a small footprint, low development cost, and the ability to extract deep oil shale resources, making it the future trend in the oil shale industry (Kang et al., 2022).

Although in-situ mining technology for oil shale has high efficiency and environmental benefits, it consumes a significant amount of energy with low energy utilization. Catalysts, which can regulate the reaction process and alter the energy required for chemical reactions, present a solution to the high energy consumption in in-situ oil shale conversion. Hence, in-situ oil shale catalytic technology is proposed. In this technology, catalysts are injected into the reservoir to fully interact with the oil shale, enabling pyrolysis reactions under the temperature and pressure conditions of the reservoir, thereby extracting oil and gas from the formation (Sun et al., 2019, 2021). It combines in-situ oil shale extraction technology with catalytic dry distillation technology. In recent years, scholars have shown significant interest in in-situ catalytic modification technology for oil shale due to its technical advantages and promising application prospects.

This paper provides a review of the current status of in-situ mining technology for oil shale, the mechanism of casein pyrolysis, and the research status of oil shale catalysts. It summarizes the compatibility of different heating methods and pyrolysis catalysts. Furthermore, it offers suggestions and perspectives on the application of in-situ catalytic technology for oil shale, focusing on oil shale catalyst development, reservoir fracturing technology, related injection technology, and efficient heating technology.

2. Oil shale in-situ mining technology

The technology for in-situ conversion of oil shale is based on hydraulic fracturing, whereby the fractured oil shale is subjected to heating through methods such as hot steam injection, electricity, combustion, and radiation (Liu, 2019). At elevated temperatures, the kerogen within the oil shale undergoes pyrolysis, resulting in the production of shale oil and hydrocarbon gases (Kang et al., 2020; Hou et al., 2022; Xie et al., 2021). The characteristics of both domestic and foreign oil shale in-situ conversion technologies are presented in Table 1 in this study.

The differences between shale reservoirs in China and foreign shale reservoirs have resulted in the adoption of different oil shale extraction technologies. Currently, abroad, the generally used technology is ICP (In-situ Conversion Process), whereas in China, NCW (Near-Critical Water) technology is employed. Among the most developed in-situ heating technologies for shale reservoirs is Shell's ICP technology. This technique involves drilling heating and production wells into shale formations and utilizing downhole electric heaters with small spacing to uniformly heat the formation through conduction, reaching temperatures suitable for shale fracturing. Depending on the well spacing and heating rate, it can take two to four years for the formation to reach the required temperatures for extracting shale oil and combustible gas from the production wells (Xie et al., 2021). ICP technology necessitates downhole electric heaters capable of withstanding high temperatures and having a long lifespan, as well as specific requirements for formation suitability. The product of oil content and oil shale thickness must meet the lower techno-economic limit. Given the deep burial, thin thickness, and low oil content of Chinese oil shale

reservoirs, ICP technology is applicable when short horizontal well technology is required. Currently, China is actively conducting field research on oil shale extraction technology. For instance, Jilin University has developed the Near-Critical Water Shale In-situ Conversion Technology (NCW method), which has shown promising results (Kang et al., 2020), as depicted in Fig. 1. The NCW method involves using a downhole heater to heat the injection water to near-critical water conditions (374 °C, 22.1 MPa) or a supercritical state. The near-critical water is then employed as a heat and mass transfer medium and extractant to penetrate, permeate, and swell the oil shale formation, while simultaneously fracturing the kerogen's organic matter within the oil shale. This process allows the generated oil and gas products to be extracted from the wellbore. Furthermore, near-critical water possesses advantages such as high activity, strong heat and mass transfer capabilities, and environmental friendliness. Therefore, it represents a green and energy-saving new technology for the subsurface in-situ transformation of oil shale.

3. Mechanism of kerogen pyrolysis

The main constituent of oil shale is kerogen, which is tightly bound with inorganic minerals and requires physical and chemical methods for separation from the oil shale. Kerogen is a highly complex organic polymer with an average molecular weight of several thousand daltons, and is insoluble in organic solvents. The conversion of kerogen is responsible for the production of fractured shale oil (Jagadisan and Heidari, 2022; Ma J. et al., 2022; Thana et al., 2022). Fig. 2 illustrates molecular simulations of kerogen from Estonia and China's Huadian region. The molecular model of kerogen in the figure reveals that the carbon content of Chinese shale kerogen is significantly lower, while the sulfur content is higher, as compared to foreign kerogen. Therefore, it is important to elucidate the pyrolysis mechanism of kerogen based on its unique characteristics.

Different in-situ oil shale extraction techniques employ various heating methods, but they all rely on the thermal cracking of organic matter within the oil shale to produce shale oil. Zhang et al. (2023) elucidated the molecular structure of kerogen through elemental analysis and ^{13}C nuclear magnetic resonance (^{13}C NMR), and developed four representative molecular models of kerogen. To further investigate the pyrolysis mechanism of kerogen, researchers utilized these average molecular structures to calculate and analyze reactive sites and pyrolysis behavior by constructing two-dimensional (2D) and three-dimensional (3D) reaction models of kerogen. As a result, they proposed a three-stage pyrolysis theory for kerogen (Qing et al., 2022; You et al., 2019; Zhang et al., 2021).

The first stage involves the breaking of chemical bonds, with weaker bonds being broken first, including $-\text{C}-\text{O}-$, $-\text{C}-\text{S}-$ connected $-\text{C}-\text{C}-$ bond bridges, and heteroatoms such as N and S within aromatic structures. In the second stage, the pyrolysis of broken kerogen fragments occurs, primarily involving the substitution of aromatic structures with hydrocarbons, long straight-chain hydrocarbons, and cyclic chain hydrocarbons, which possess greater stability compared to the first stage. The third stage involves the recombination of aromatic rings and the crosslinking of free radicals. Fig. 3 illustrates the kerogen pyrolysis model.

Based on ReaxFF molecular dynamics simulations, Zhao H. et al. (2022) discovered that water molecules may participate in chemical reactions during kerogen pyrolysis under super-heated steam conditions. These reactions include the decomposition of carbon and heavy shale oil, ring-opening reactions of heterocyclic compounds, transfer and exchange of OH radicals, and the formation of various products (e.g., hydrocarbons, alcohols, NH_3 , H_2S , and H_2) through the attack of free radicals or fragments. Zhang et al. (2022)

Table 1
Technical characteristics of oil shale in situ conversion.

Heating method	Technology	Unit	On-site trial	Advantages	Disadvantage	References
Heat of reaction	In-situ combustion heating	U.S. Bureau of Mining	Yes	Fast heating speed; energy high utilization	Complex control process	Feng et al. (2011); Bai (2015)
	TSA Technology	Jilin University	Yes			
Conduction heating	ICP Technology	Shell Corporation	Yes	Flexible heating method; the equipment is relatively simple; easy to control	Heat transfer is slow; long heating time	Jagodzińska et al. (2021) Symington et al. (2010) Kang et al. (2020)
	Electrofrac™	Exxon M. Corporation	/			
	GFC Technology	IEP Corporation	No			
	HVF Technology	Jilin University	No	Fast heating		
Convection heating	CRUSH Technology	Chevron Corporation	No	High heating efficiency; oil and gas products are easy to produce; cracking gas can be recycled	Great heat loss in the conveying process; the produced gas needs to be separated	Wang et al. (2013)
	CCR Technology	American Shale Oil Corporation	/			
	IVE Technology	Western Mountain Energy Corporation	No			
	MTI Technology	Taiyuan University of Technology	No			
	NCW Technology	Jilin University	No			
Radiant heating	RF/CF Technology	Raytheon Corporation	No	The heating area can be selected; high energy utilization	The technology is not mature; the radiated energy has a limited transmission range	Wang et al. (2013)
	LLNL Technology	Lawrence Livermore National Laboratory	No			
	Microwave Technology	Phoenix Wyoming Corporation	No			

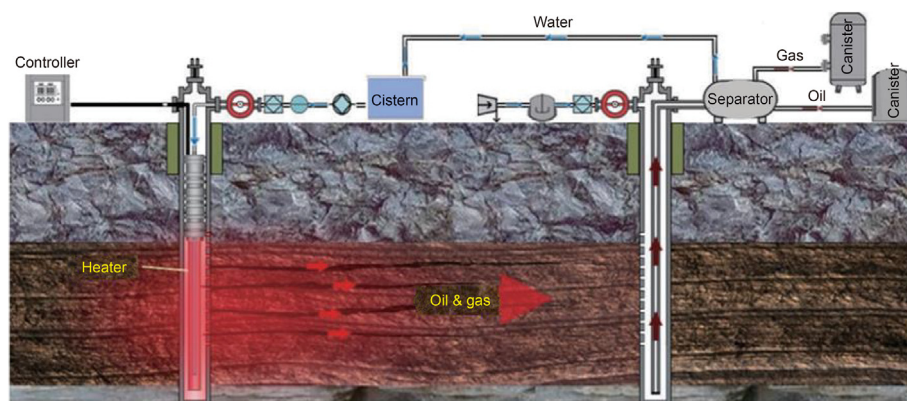


Fig. 1. NCW in situ mining technology (Sun et al., 2021).

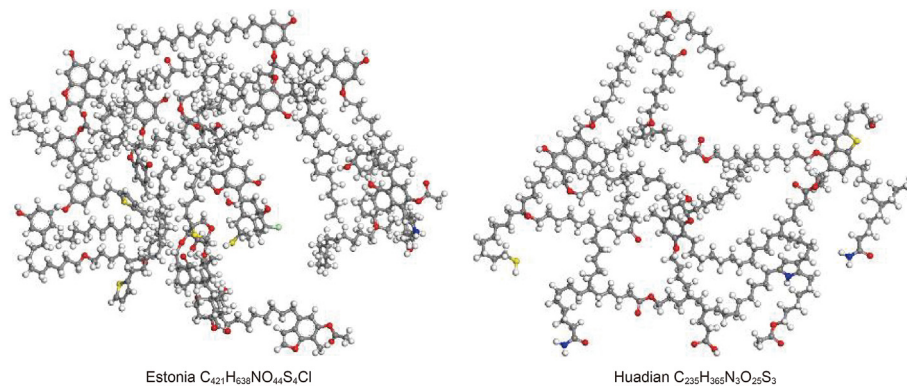


Fig. 2. Molecular structure of kerogen (You et al., 2019; Tian et al., 2022).

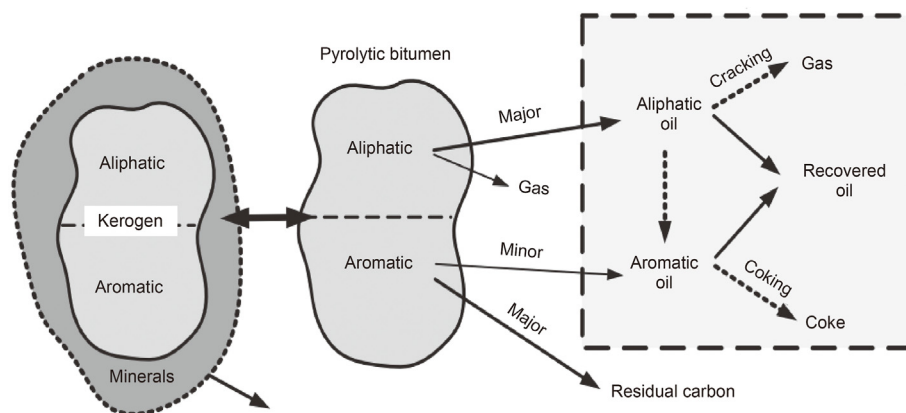


Fig. 3. Pyrolysis model of kerogen (Lai et al., 2017a, b).

analyzed over 500 unique kerogen model compounds in different chemical environments.

The results indicate that although the bond dissociation energy (BDE) values for each key bond type exhibit a wide range of values and overlap, the trend follows $C-S < C-N < C-O < C-C < C-H < C=C$. This trend can serve as a reference for the order of bond cleavage during kerogen pyrolysis. However, it should be noted that apart from the stability of free radical fragments, the BDE also relies on the chemical environment of the bond under investigation. Therefore, investigating different bonds within the kerogen macromolecular model can help unveil the sequence of bond cleavage during kerogen pyrolysis. The active sites of chemical bond cleavage in the three-stage theory of kerogen pyrolysis primarily depend on the stability of bonds within the kerogen structure. The proposed first-order broken chemical bond, based on bond energy, exhibits low BDE and predicts the reaction activity of kerogen from a thermodynamic perspective. However, during the actual pyrolysis process, kerogen pyrolysis involves complex free radical reactions, and considering only the position of broken bonds based on bond energy is incomplete (Liu et al., 2022). Instead, the fracture tendency and capability of each reaction site within the molecular structure should be analyzed. By calculating the electronic properties of the kerogen parent material's molecular structure model, information regarding the electron density distribution of the carbon skeleton and heteroatomic compounds, as well as the frontier orbital characteristics of the molecular model, can be obtained. This enables a discussion of the chemical reactivity of the kerogen parent material, ultimately revealing the true chemical reaction mechanism during the pyrolysis process.

4. Research and development of oil shale pyrolysis catalysts

During the pyrolysis process of oil shale, the low conversion efficiency of kerogen in oil shale can have a negative impact on the quality of shale oil, leading to oil instability and high viscosity. Therefore, various catalysts have been used in catalytic pyrolysis experiments to promote the conversion of kerogen and improve its efficiency, as depicted in Fig. 4. Currently, research on oil shale pyrolysis catalysts is still in the laboratory stage and mainly involves the use of metal salt, mineral, and molecular sieve catalysts. This review provides a summary and analysis of the progress made in the research and development of oil shale pyrolysis catalysts, and concludes by highlighting the future development direction of oil shale catalysts.

4.1. Transition-metal salts

Transition-metal salt catalysts are widely used in oil shale pyrolysis due to their ability to form complexes and break bonds (Pan et al., 2021; Jiang et al., 2015). Metal oxides such as Fe, Co, Zn, and Ni, as well as chlorides, have been found to improve the pyrolysis efficiency of oil shale, generate hydrogen-free radicals, and increase the yield of shale oil (Chen et al., 2022). As illustrated in Fig. 5, the study conducted by Song (2016) explores the catalytic thermal decomposition effects of different transition metal salts on oil shale. The findings reveal that these metal salts serve as effective catalysts, significantly reducing the pyrolysis temperatures across various thermal breakdown intervals of the oil shale. Notably, cobalt salts exhibit the most pronounced effect, decreasing the activation energy required for oil shale pyrolysis by approximately 20%. Jiang et al. (2020) investigated the coupling of montmorillonite and $CoCl_2 \cdot 6H_2O$ and found that it significantly affected the pyrolysis behavior, product distribution, and liquid fuel characteristics. The presence of $CoCl_2 \cdot 6H_2O$ and montmorillonite increased the decomposition temperature of kerogen and decreased the apparent activation energy, with the average apparent activation energy reduced by approximately 122.42 kJ/mol. Pan et al. (2006) studied the pyrolysis effect of inorganic salts in the formation of kerogen and found that most inorganic salts had catalytic effects, while only a small number of chlorinated salts inhibited the pyrolysis of kerogen. Kang et al. (2021) studied the reaction of Huadian oil shale in $FeCl_2$ solution at 350 °C and found that $FeCl_2$ played a crucial role in promoting the cracking of kerogen heteroatomic bonds and the transport of asphalt in shale matrix. Zhang et al. (2020) found that under the action of the Ni-Mo/ Al_2O_3 catalyst, 84.6% of sulfur was removed from shale oil at 380 °C, and the yield of modified oil was higher. Jiang et al. (2015) used a thermogravimetric analyzer to conduct thermogravimetric experiments on oil shale treated with different transition-metal salts as catalysts and natural catalysts. The results showed that all of these substances can promote the secondary cracking of shale oil. Metal salts can also catalyze the aromatization of aliphatic hydrocarbons to aromatics. The effects of metal salts on the deactivation energy of the three stages of oil shale pyrolysis were different, and the catalytic effects of different types of catalysts on oil shale were compared. For example, $MnSO_4 \cdot H_2O$ and $CoCl_2 \cdot 6H_2O$ can reduce the temperature of the first stage of oil shale pyrolysis. When 0.1 wt% $MnSO_4 \cdot H_2O$ and $CoCl_2 \cdot 6H_2O$ were added, the activation of the second stage of pyrolysis (430–520 °C) was reduced by 3.621 and 5.964 kJ/mol, respectively, and the oil yield was increased by 0.44% and 0.53%, respectively. In addition, $NiCl_2 \cdot 6H_2O$ reduced the activation energy

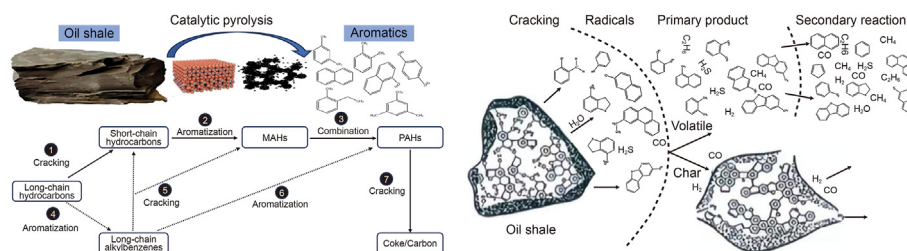


Fig. 4. Catalytic pyrolysis mechanism of oil shale (Jiang et al., 2015).

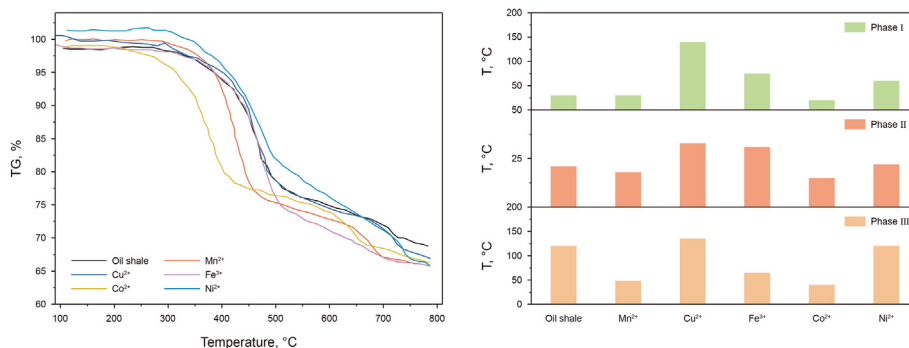


Fig. 5. Catalytic effect of different types of transition metal salts on oil shale (Song, 2016).

of oil shale pyrolysis and promoted the conversion. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and ZnCl_2 had little effect on the decomposition behavior of oil shale. Metal salts also promote the aromatization of aliphatic hydrocarbons into aromatics.

4.2. Natural minerals

As previously mentioned, oil shale is comprised of both organic and inorganic minerals. Inorganic minerals typically constitute 50%–85% of oil shale, primarily consisting of silicates, carbonates, quartz, and pyrite (Thiery et al., 2015; Yan et al., 2013). The presence of inorganic compounds tightly bound to organic matter increases the challenge of organic decomposition (Lu et al., 2019). Yan et al. (2022) investigated the influence of mineral content on the activation energy of oil shale pyrolysis. They treated the oil shale with hydrochloric acid (HCl) and hydrofluoric acid (HF) to obtain kerogen, and conducted thermogravimetric analysis using a thermogravimetric analyzer. The results demonstrated that inorganic minerals in oil shale can exert a catalytic effect on pyrolysis. Wang et al. (2014) and Alstadt et al. (2012) examined the impact of minerals on the volatile yield and composition of oil shale. Their findings revealed that hydrofluoric acid elution of oil shale enhances the pyrolysis conversion of organic matter, while hydrochloric acid elution reduces the pyrolysis conversion. Nitric acid elution, however, has no effect. Pyrolysis of acid-treated shale indicated that carbonate minerals exhibit a catalytic effect on organic pyrolysis, while silicate minerals have an inhibitory effect, with the inhibition effect surpassing catalysis. Furthermore, experimental results confirmed that different alkali metal carbonates have varying catalytic effects on oil shale. Magnesium carbonate (MgCO_3) demonstrated outstanding catalytic effects on organic matter during the initial stage of pyrolysis compared to other alkali metal carbonates (Pan et al., 2009; Kang et al., 2020). In order to gain a better understanding of the interaction between organic matter and minerals during oil shale pyrolysis, Huadian oil shale was treated with a mixture of hydrochloric acid and

hydrofluoric acid. The results indicated that mineral compounds have minimal impact on the decomposition of organic matter but do influence volatile reactions. Calcium carbonate (CaCO_3), kaolinite, and titanium dioxide (TiO_2) exhibited negligible effects on volatile reactions, while potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and manganese carbonate (MnCO_3) promoted volatile reactions.

Hu et al. (2014) conducted a study on the co-pyrolysis behavior of kerogen and montmorillonite. The results revealed that montmorillonite exhibited significant catalytic activity during the pyrolysis of kerogen, leading to enhanced shale oil formation and reduced residue yield. Consequently, montmorillonite can be regarded as a promising natural catalyst. Additionally, it was observed that the presence of kaolin facilitated the conversion of kerogen into low molecular weight shale oil, while calcite hindered the formation of shale oil. Li et al. (2022) and Yan et al. (2013) discovered that pyrite promoted the pyrolytic transformation of oil shale. When 8% pyrite was added, the yield of pyrolytic oil and gas from oil shale increased by 4.5% and 3.3% respectively. Lai et al. (2017) investigated the catalytic pyrolysis of shale ash on oil shale and observed that as the pyrolysis temperature increased from 465 to 525 °C, the utilization of shale ash significantly increased the content of light oil by 10.24%, reduced the content of heteroatomic compounds, and facilitated the transformation of aliphatic hydrocarbons to aromatic hydrocarbons.

4.3. Molecular sieves

Molecular sieves, as a novel catalyst with a unique pore structure, have gained widespread application in the chemical process industry. Currently, the commonly utilized molecular sieves include SAPO-11 molecular sieve, aluminum phosphate molecular sieve, ZSM-5 molecular sieve, TS molecular sieve, MCM molecular sieve, SBA molecular sieve, among others (Zhang et al., 2017). Molecular sieves possess several advantages such as a uniform pore size, large specific surface area, and stable structure, making them

highly effective in catalyzing oil shale (Huang et al., 2020). Fig. 6 depicts the catalytic mechanism of the SAPO-11 molecular sieve. The presence of acidic sites within the SAPO-11 framework facilitates the catalytic cracking and isomerization of hydrocarbon molecules. These acidic sites donate the requisite protons for such reactions, resulting in the cleavage of carbon-carbon bonds and the reorganization of the hydrocarbon molecular structure.

Kaur and Kumar Chopra (2023) discovered that MCM-41 exhibits catalytic properties in the pyrolysis of oil shale and is extensively employed in hydrocarbon conversion processes such as aromatic dealkylation, cracking, and hydrocracking. MCM-41 also demonstrates unique cracking selectivity, leading to increased shale oil production. Park et al. (2021) employed gas chromatography-mass spectrometry to investigate the catalytic pyrolysis of acidic zeolite mixed with black pine wood (BPW) and Cook oil shale (KOS). The findings indicate that in non-catalytic pyrolysis, the production of oxygen compounds and light hydrocarbons primarily originates from BPW and KOS. However, during catalytic pyrolysis, these substances are transformed into aromatic hydrocarbons on acidic zeolites. BPW and KOS can yield up to 56% aromatic hydrocarbons during the pyrolysis process. Heracleous et al. (2019) examined the impact of ZSM-5 zeolite catalyst on pyrolysis temperature, residence time, and catalyst regeneration on the yield and composition of shale oil. The results indicate that the addition of the catalyst increases the content of gas products and shale semi-coke while reducing the yield of shale oil. This promotes the conversion of long-chain alkanes and olefins into low-molecular-weight, short-chain alkenes, and significantly reduces the total nitrogen and sulfur content in the catalytic oil. The catalyst can be recycled, and regeneration up to five times has minimal effect on the catalytic pyrolysis performance. Fan et al. (2023) investigated the influence of Al-SBA-15 molecular sieve catalyst on pyrolysis temperature and the reduction of pyrolysis activation energy. The results reveal that the activation energy for organic matter conversion in shale decreases from 113.80 to 37.28 kJ/mol with the addition of the catalyst. Consequently, the transformation temperature of shale oil decreases, the reaction rate increases, and the energy consumption for in-situ upgrading diminishes.

5. Uniformity of catalyst and heating mode

Shale oil is subjected to various heating methods, necessitating the compatibility between catalysts and heating techniques. For instance, electric heating involves filling fractures with conductive proppants to create an electric heater. Heat is then transferred to the oil shale through these electrically conductive proppants via heating wells, resulting in the conversion of kerogen into shale oil and combustible gas, which are subsequently recovered from production wells (Kyung et al., 2017). Therefore, the catalyst should not compromise the conductivity of the proppants used in convection heating, which is crucial for the formation of shale oil and combustible gas carried by low-temperature steam. Ideally, the catalyst should enhance proppant conductivity while ensuring its catalytic effectiveness. Metal salts and certain metal oxides are examples of such catalysts. In convection heating technology, high-temperature steam (400–700 °C) is injected into the oil shale formation through heat injection wells, leading to the cracking of kerogen and the release of oil and gas, which are then extracted to the surface through production wells for separation (Hou et al., 2022). In this case, there should be minimal interaction between the catalyst and high-temperature steam to prevent catalyst poisoning and deactivation. Alternatively, high-temperature steam can be used to inject the catalyst into the formation. Thus, for the use of convection heating technology, the catalyst should possess characteristics such as small size, high-temperature resistance, and low reactivity with high-temperature steam. Molecular sieve catalysts are an example of such catalysts. The implementation of radiative heating technology involves placing a radio-frequency emitter in the oil shale layer to heat it, followed by the injection of supercritical CO₂ as a carrier. This process transports the oil and gas generated from the oil shale to the production well for recovery (Liu et al., 2009). In this case, the catalyst is required not only to enhance the radio-frequency heating effect but also to improve catalytic cracking. Fe₃O₄ is an example of such a catalyst. Reaction heating technology involves improving the permeability of the formation through fracturing or explosion after surface drilling, followed by heating the oil shale to crack and burn it, and

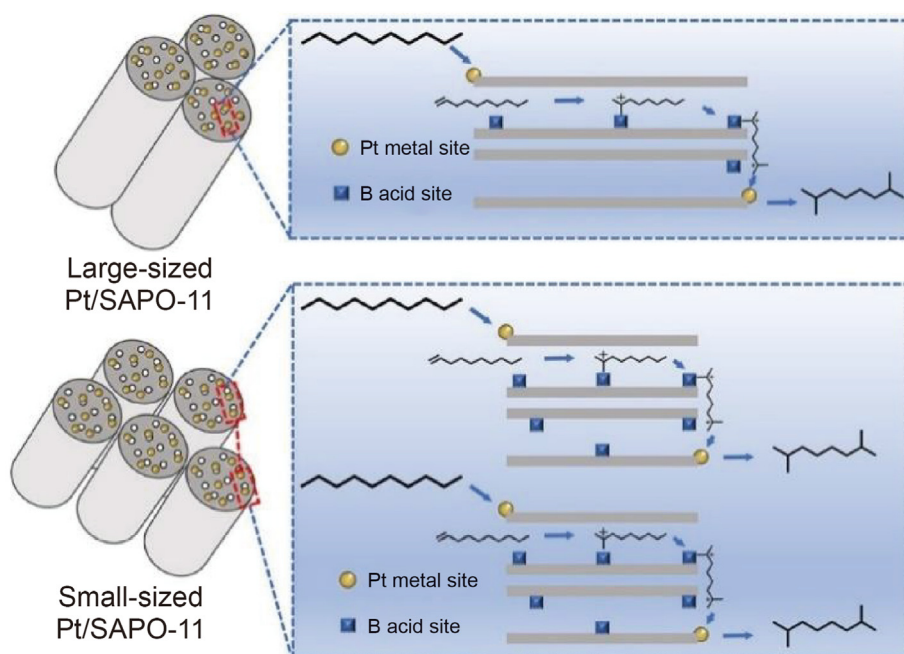


Fig. 6. Simulation diagram of catalytic mechanism of SAPO-11 class molecular sieve (Wang et al., 2022).

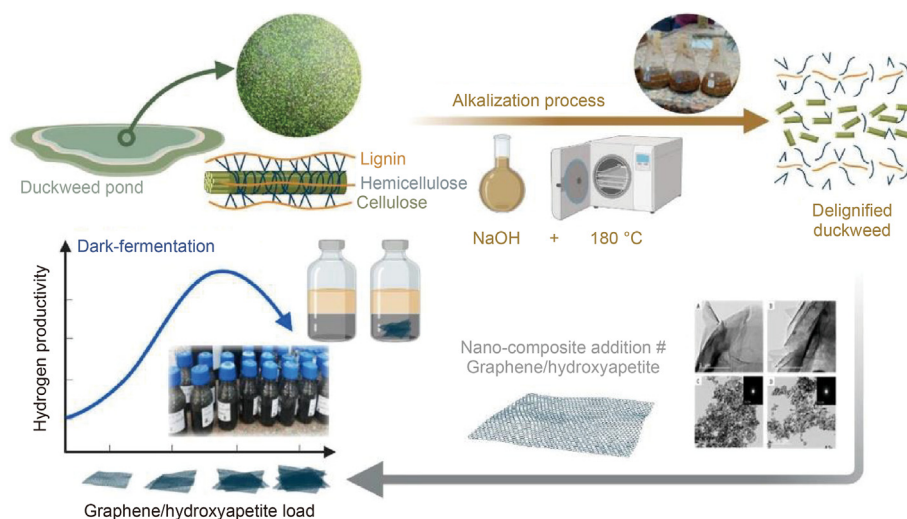


Fig. 7. Composite nano-catalyst to improve the catalytic effect (Tawfik et al., 2022).

ultimately extracting shale oil and gas from the production well (Wang et al., 2013). This technology does not impose stringent catalyst requirements; rather, it necessitates a catalyst with good catalytic effectiveness that can be easily injected into the formation.

6. Research prospect of in situ catalysis technology under oil shale

Currently, in China, the in-situ catalytic technology for oil shale extraction is still in the research stage, lacking fundamental theoretical research, technological research, and field application. Building upon previous research findings, future efforts should focus on enhancing the understanding of the mechanism behind kerogen thermal transformation and investigating new catalysts suitable for in-situ oil shale conversion, as well as exploring related injection processes. This paper presents the prospects of in-situ catalytic technology for oil shale in the future, encompassing four key aspects: catalyst development, reservoir reconstruction technology, catalyst injection technology, and high-efficiency heating technology.

6.1. Development of new catalysts

Experiments have demonstrated that the utilization of catalysts can effectively reduce the cracking temperature of kerogen, enhance in-situ conversion efficiency, and improve oil quality. This approach serves as an effective means to reduce production costs and increase oil recovery. Currently, research on oil shale pyrolysis catalysts remains primarily in the laboratory stage, both domestically and internationally, with limited investigation into their applicability and effectiveness in the in-situ conversion process. Consequently, there is a pressing need to develop catalysts that are facile to employ and exhibit high efficiency. The catalytic process of oil shale involves the coexistence of catalytic cracking reactions and thermal cracking reactions, representing a scenario where both positive carbon ion mechanisms and free radical mechanisms are at play. As a result, it is imperative that the pyrolysis catalysts possess acid catalytic properties (Li D. et al., 2021).

In the future, catalysts will emerge as the primary focus of catalytic pyrolysis of oil shale. Firstly, abundant nano-catalysts will be developed. Nano-catalysts can readily penetrate the reservoir, while their surface active sites provide the necessary conditions to significantly enhance reaction efficiency, control reaction rates, and

even enable previously unattainable reactions (Davoodi et al., 2022; Simão et al., 2022), as depicted in Fig. 7. Secondly, building upon existing knowledge, supported catalysts incorporating molecular sieves, biomass, montmorillonite, and Al_2O_3 as supports will be developed. The active component and support comprise the loaded catalyst, wherein the dispersion of the active component is improved upon loading the support. This approach allows for reduced catalyst dosage, effective mitigation of active component aggregation through the pore structure of the support, and synergistic effects between the catalyst carrier and active component in specific reactions. These exceptional characteristics have led to a rapid increase in research interest in supported catalysts. Thirdly, to enhance the applicability and effectiveness of the in-situ conversion process, it is crucial to independently research and develop water-soluble, micro/nano-sized effective catalysts that can be easily transported. Moreover, a feasible in-situ catalyst injection process should be developed (Fig. 7).

6.2. Reservoir fracturing technology

Oil shale in-situ catalysis technology primarily involves thermal catalysis, thus the construction of fracture networks in oil shale reservoirs should facilitate heat transfer while minimizing heat loss. Shale reservoirs are characterized by their continuous distribution, low porosity, ultra-low permeability, and high brittleness (Kang et al., 2022; Ma T. et al., 2022; Tang et al., 2022). The distribution of organic matter within oil shale directly impacts the mode, speed, and efficiency of shale gas and oil extraction (Zamiri et al., 2022). The extraction of oil and gas derived from kerogen transformation relies on pore and fracture networks, and the development of these networks determines the difficulty of oil and gas exploitation (Yuan et al., 2021; Huang et al., 2022). The connectivity between pores and fractures in oil shale is a crucial factor in the effectiveness of in-situ oil conversion technology. Therefore, reservoir transformation is an essential step in the in-situ conversion of oil shale. Additionally, the connectivity between pores and fractures also determines the feasibility of catalyst injection into the formation.

Currently, fracturing technology is a viable method for transforming oil shale reservoirs to meet the technical requirements of in-situ conversion and controllable exploitation. Multi-process fracturing technology is employed to achieve accurate volume reservoir transformation, considering the multi-section thin layer

distribution of oil shale deposits. Fracturing strength is designed based on mineral deposit storage conditions and the heating range of in-situ conversion technology. Real-time monitoring and control of the expansion direction of dominant fractures ensure optimal economic benefit development through fracturing. It is crucial to improve the compatibility of fracturing fluid, ensuring the flow channel for oil and gas output in oil shale reservoirs with strong water sensitivity and clay mineral expansion during pyrolysis production (Liang et al., 2017; Qun et al., 2019; Zhao et al., 2019; Chen et al., 2021).

Shale gas well fracturing typically involves large-scale operations with a significant amount of sand and low sand ratios. Horizontal well completion and multi-segment cluster perforation, along with drill-type bridge plug sealing segmented fracturing, have become key technologies for modifying shale gas reservoirs (Sun et al., 2011). The industry is currently exploring high-precision fracturing technology and fabric seam optimization technology guided by big data and artificial intelligence. However, further research is required to develop fracturing technologies that truly meet the demands of the field. Quantico Energy Company in the United States has utilized artificial intelligence technology to closely integrate static models with geophysical interpretations and quality control of data, resulting in a high-precision prediction model for fracturing design. This model has been successfully applied to over 100 wells in the Permian Basin and the Bakken Oilfield, showcasing increased production by 10%–40% and effective reduction of overall fracturing operation costs (Fig. 8) (Jiang et al., 2022).

In the future, improvements to existing fracturing technologies are necessary. To meet the technical requirements of in-situ transformation and controlled production of oil shale, multi-process fracturing technology should be employed to achieve reservoir transformation. The development of intermediate and low-maturity shale resources also necessitates the combination of volume fracturing of horizontal wells and in-situ conversion technology (Huang et al., 2022; Sun et al., 2022). Close-cutting fracturing of horizontal wells, CO₂ dry fracturing, acidification fracturing, and in-situ transformation technology should be comprehensively applied to monitor and control the expansion direction of dominant fractures in real-time, enabling economic and efficient development (Clarkson et al., 2016; Song et al., 2014; Wang et al., 2022; Zhao F. et al., 2022; Ren et al., 2021).

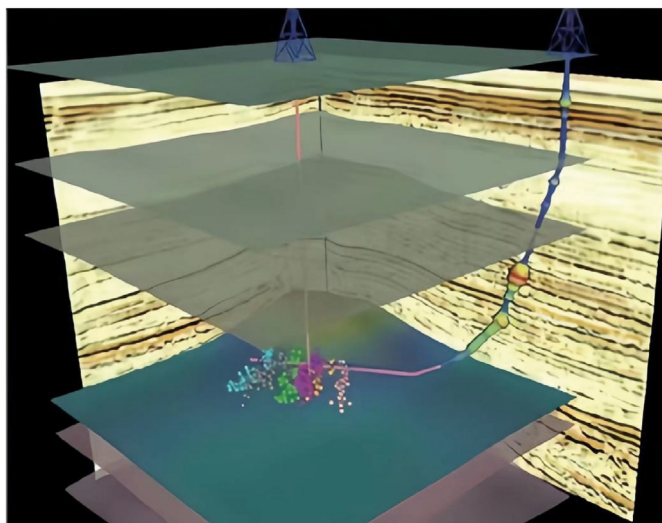


Fig. 8. High-precision intelligent fracturing schematic (Jiang et al., 2022).

6.3. Relevant injection processes

Due to the continuous distribution, low porosity, and ultra-low permeability of shale reservoirs, injecting catalysts presents a challenge. As shown in Fig. 9, Guo et al. (2016) proposed that catalysts can be injected into the formation by utilizing fluid-carrying nanocatalysts. In the technology of oil shale in-situ catalysis, the injection of a catalyst directly determines the catalytic effect. Some catalysts, such as water-soluble or liquid catalysts, can be injected into the formation along with the fracturing fluid. For solid catalysts, nano-type catalysts can be prepared using suitable methods, allowing the nanoparticle catalysts to be distributed through the porous medium. The injected catalyst can form a catalytic bed around the injection well, spreading over a large range and aging for an extended period (Wang et al., 2020). Gas carrying methods, such as CO₂ injection, can also be utilized to deliver catalysts into the formation. Furthermore, Zhao et al. (2021) conducted molecular dynamics simulations to study the CO₂-kerogen interaction dominated by countercurrent diffusion. They found that the interaction between kerogen and CO₂ is stronger than the interaction between kerogen and hydrocarbons, resulting in a spontaneous countercurrent diffusion process. This efficient extraction of hydrocarbons from kerogen improves the recovery of shale oil (Li H. et al., 2021) and also indicates the significant potential for CO₂ storage in shale formations (Zhou et al., 2022). Related injection processes vary according to the injection pipeline, including injection wells, Direct Push, pumping well groups, and groundwater circulation wells. Injection types can be gravity injection or pressurized injection. Injection depths can be single-depth injection wells or multi-depth injection wells. Depending on the specific project, different combinations of methods are required (Wu et al., 2021; Yang, 2019). For different blocks of oil shale, joint indoor experiments and field experimental studies are necessary to determine the optimal catalyst injection dosage based on the block conditions. It is crucial to fully consider the characteristics of the formation structure, determine the appropriate depth and location of the catalyst injection well, and ensure thorough mixing of the catalyst with the oil shale in the formation. However, the injection of catalysts may introduce other safety hazards, such as formation pollution, corrosion of mining equipment, and damage to gathering and transportation pipelines. Therefore, before adopting oil shale in-situ catalytic modification technology, it is essential to thoroughly identify, analyze, and evaluate the risk factors associated with the mining process and formulate relevant improvement measures and protective methods.

6.4. Efficient heating technology

Oil shale in-situ catalysis is essentially a thermal catalysis process, and efficient heating technology is a crucial aspect of shale oil extraction. Currently, the primary heating methods employed in situ mining technology include reaction heating, conduction heating, convection heating, and radiation heating. Regardless of the heating method used, significant energy loss occurs. The Shell ICP technology is a relatively mature in-situ heat generation technology for oil shale, which employs a single physical heat transfer method but suffers from low thermal efficiency and high cost. Similarly, alternative heating techniques may be integrated, such as the synergistic application of surface and subsurface heating, multi-stage physicochemical composite heating, and autogenous heat-driven chain pyrolysis utilizing in-situ composite thermal fluid heating technology. This integration aims to create complementary heating strategies that bolster efficiency, augment resource utilization, and substantially diminish the costs associated with in-situ development. However, it should be noted that not

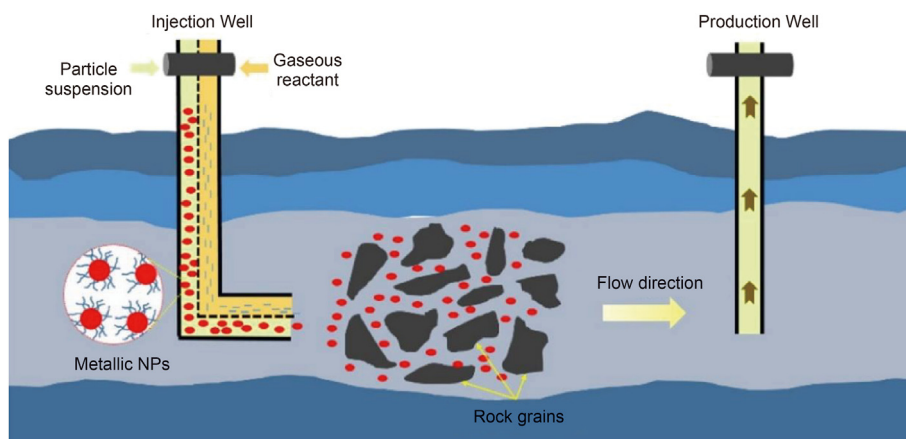


Fig. 9. Simulation of nano-catalyst injection into the formation (Guo et al., 2016).

every combination of two or more single intensification techniques can produce better heat transfer enhancement than a single intensification technique. For example, studies have shown that the average Nussler number of spiral coils with inner fins is lower than that of ordinary spiral coils. To confirm the effectiveness of enhanced heat transfer and obtain the best-enhanced heat transfer, it must be tested in practice. In the future, wind, solar, hydro, geothermal, and even nuclear energy will be applied to the in-situ conversion process of oil shale to improve heating efficiency and reduce energy loss. The development of oil shale resources using renewable energy sources is crucial for environmental safety, cost control, and carbon neutrality.

7. Conclusions

Oil shale resources exhibit three prominent characteristics: extensive geological reserves, challenging development technology, and significant development potential. The current underground in-situ conversion mining technology faces drawbacks such as low energy utilization and high energy consumption, and is still distant from commercial application. In-situ catalytic technology for oil shale involves injecting a catalyst into the reservoir to ensure complete contact with the oil shale formation. Subsequently, under the influence of temperature and pressure conditions within the reservoir, a pyrolysis reaction takes place, enabling the extraction of oil and gas from the formation. This technology represents one of the future directions for shale oil extraction. The implementation of oil shale in-situ catalytic technology is complex and demanding, necessitating revolutionary advancements in theory, technology, and equipment. Efficient heating technology, catalyst injection technology, composite reservoir modification technology, and catalyst development all require extensive research. Of utmost importance is the identification of water-soluble and micro-nano effective catalysts that are conducive to independent research and development, as well as the establishment of a viable in-situ catalyst injection process. The integrated development model encompassing industrialization, environmental sustainability, informatization, and intelligence is the primary approach for future in-situ conversion and extraction of oil shale. The objectives of commercial oil shale development are low cost, high yield, and minimal pollution. Achieving these goals necessitates a comprehensive approach that integrates resources, technology, economy, and society, requiring systematic research to obtain a comprehensive solution.

Declaration of competing interest

All authors disclosed no relevant relationships.

Acknowledgments

This study was financially supported by the National Natural Science Foundation of China (52174047) and Sinopec Project (P21063-3).

References

- Alstadt, K.N., Katti, D.R., Katti, K.S., 2012. An in situ FTIR step-scan photoacoustic investigation of kerogen and minerals in oil shale. *Spectrochim. Acta Mol. Biomol. Spectrosc.* 89, 105–113. <https://doi.org/10.1016/j.saa.2011.10.078>.
- Aurela, M., Mylläri, F., Konist, A., et al., 2021. Chemical and physical characterization of oil shale combustion emissions in Estonia. *Atmos. Environ.* X, 12, 445–461. <https://doi.org/10.1016/j.aeaoa.2021.100139>.
- Bai, F.T., 2015. *Theoretical and Laboratory Experimental Study on Local Chemical Pyrolysis of Oil Shale*. Jilin University, p. 128 (in Chinese).
- Chen, Z., Liu, H.L., Li, Y.J., 2021. Present situation and development suggestion of shale oil reservoir reconstruction technology at home and abroad. *Petroleum Drilling Techniques* 49 (4), 1–7 (in Chinese).
- Chen, Z., Liu, H.L., Li, Y.J., 2022. Research progress of fracturing volume and scale monitoring methods for shale reservoirs. *Liaoning Chem. Indust.* 51 (5), 662–666 (in Chinese).
- Can, R.Y., Mai, U., Mustafa, C.U., et al., 2020. CO₂ mineralization by burnt oil shale and cement bypass dust: effect of operating temperature and pre-treatment. *J. Therm. Anal. Calorim.* 142, 991–999. <https://doi.org/10.1007/s10973-020-09349-9>.
- Chen, B., Li, Y., Yuan, M., et al., 2022. Study of the Co-pyrolysis characteristics of oil shale with wheat straw based on the hierarchical collection. *Energy* 239, 122144. <https://doi.org/10.1016/j.energy.2021.122144>.
- Clarkson, C.R., Haghshenas, B., Ghanizadeh, A., et al., 2016. Nanopores to megafactures: current challenges and methods for shale gas reservoir and hydraulic fracture characterization. *J. Nat. Gas Sci. Eng.* 31, 612–657. <https://doi.org/10.1016/j.jngse.2016.01.041>.
- Davoodi, S., Al-Shargabi, M., Wood, D.A., et al., 2022. Experimental and field applications of nanotechnology for enhanced oil recovery purposes: a review. *Fuel* 324, 124669. <https://doi.org/10.1016/j.fuel.2022.124669>.
- Fang, C.H., Zheng, D.W., Liu, D.X., 2009. Development direction and trend of in-situ exploitation technology of oil shale. *Energy Tech. Manag.* 78 (2), 78–80 (in Chinese).
- Fu, C., Ding, H., Chen, W.M., 2021. Distribution and comprehensive utilization of symbiotic resources between oil shale and coal in China. *Coal Quality Tech.* 36 (3), 1–13 (in Chinese).
- Feng, X.W., Chen, C., Chen, D.Y., 2011. New progress in in-situ exploitation technology of oil shale. *China Mining Indust.* 20 (6), 84–87 (in Chinese).
- Fan, Y., Han, Y., Zhu, J., et al., 2023. Production optimization of refined bio-oil through plasma coupling catalysis and composite zeolite effect of Al-SBA-15/HZSM-5. *Fuel* 347, 128494. <https://doi.org/10.1016/j.fuel.2023.128494>.
- Guo, K., Li, H., Yu, Z., 2016. In-situ heavy and extra-heavy oil recovery: a review. *Fuel* 185, 886–902. <https://doi.org/10.1016/j.fuel.2016.08.047>.
- Heracleous, E., Pachatouridou, E., Hernández-Giménez, A.M., et al., 2019. Characterization of deactivated and regenerated zeolite ZSM-5-based catalyst extrudates used in catalytic pyrolysis of biomass. *J. Catal.* 380, 108–122. <https://doi.org/10.1016/j.jcat.2019.04.011>.

- doi.org/10.1016/j.jcat.2019.10.019.
- Hu, M., Cheng, Z., Zhang, M., et al., 2014. Effect of calcite, kaolinite, gypsum, and montmorillonite on Huadian Oil Shale kerogen pyrolysis. *Energy Fuels* 28 (3), 1860–1867. <https://doi.org/10.1021/ef4024417>.
- Hu, S.Y., Sun, Z.X., Li, Q.Y., et al., 2022. Environmental impacts of oil shale exploitation and research progress. *Environ. Protection Oil Gas Field*. 32 (4), 44–49 (in Chinese).
- Huang, J.L., Liu, D.H., Shang, Y.F., 2022. Current situation and development trend of intelligent fracturing technology at home and abroad. *Petroleum Drilling Techniques* 50 (3), 1–9 (in Chinese).
- Hou, L.H., Luo, X., Lin, S.H., et al., 2022. Assessment of recoverable oil and gas resources by in-situ conversion of shale—case study of extracting the Chang 73 shale in the Ordos Basin. *Petrol. Sci.* 19 (2), 441–458. <https://doi.org/10.1016/j.petsci.2021.10.015>.
- He, L., Ma, Y., Yue, C., et al., 2022. Microwave pyrolysis of oil shale for high-quality oil and gas production. *J. Therm. Anal. Calorim.* 147 (16), 9083–9093. <https://doi.org/10.1007/s10973-021-11169-4>.
- Huang, J.F., Liu, H., Wei, K., et al., 2020. Adsorption properties of zeolite molecular sieve and its application in flue gas emission reduction. *Contemp. Chem. Ind.* 49 (3), 544–548 (in Chinese).
- Jagadisan, A., Heidari, Z., 2022. Molecular dynamic simulation of the impact of thermal maturity and reservoir temperature on the contact angle and wettability of kerogen. *Fuel* 309, 122039. <https://doi.org/10.1016/j.fuel.2021.122039>.
- Jagodzińska, K., Garcia-Lopez, C., Yang, W., et al., 2021. Characterisation of excavated landfill waste fractions to evaluate the energy recovery potential using Py-GC/MS and ICP techniques. *Resour. Conserv. Recycl.* 168, 105446. <https://doi.org/10.1016/j.resconrec.2021.105446>.
- Jiang, H.F., Song, L.H., Cheng, Z.Q., et al., 2015. Influence of pyrolysis condition and transition metal salt on the product yield and characterization via Huadian oil shale pyrolysis. *J. Anal. Appl. Pyrol.* 112, 533–541. <https://doi.org/10.1016/j.jaap.2015.01.020>.
- Jiang, H.F., Hong, W.P., Zhang, Y., et al., 2020. Behavior, kinetic and product characteristics of the pyrolysis of oil shale catalyzed by cobalt-montmorillonite catalyst. *Fuel* 269, 117468. <https://doi.org/10.1016/j.fuel.2020.117468>.
- Jiang, W., Pin, H., Fang, M.G., et al., 2022. Effect of sorption-induced deformation on methane flow in kerogen slit pores. *Fuel* 325, 124886. <https://doi.org/10.1016/j.fuel.2022.124886>.
- Kalu, I.E., Jossou, E., Arthur, E.K., et al., 2022. Characterization and mechanical property measurements by instrumented indentation testing of Niger Delta Oil Shale cuttings. *Int. J. Eng. Res. Afr.* 6482, 89–100. <https://doi.org/10.4028/p-2m9z7g>.
- Kang, S., Sun, Y., Deng, S., et al., 2021. Extraction of huadian oil shale in subcritical FeCl₂ solution. *Fuel Process. Technol.* 211, 106571. <https://doi.org/10.1016/j.fuproc.2020.106571>.
- Kang, W., Zhou, B., Issakhov, M., et al., 2022. Advances in enhanced oil recovery technologies for low permeability reservoirs. *Petrol. Sci.* 19 (4), 1622–1640. <https://doi.org/10.1016/j.petsci.2022.06.010>.
- Kaur, P., Kumar Chopra, H., 2023. MCM-41 supported S-alkyl/aryl-substituted 2-mercaptobenzothiazolium-based ionic liquids: synthesis, characterization, and application in the fuel desulfurization. *Fuel* 332, 126009. <https://doi.org/10.1016/j.fuel.2022.126009>.
- Kyung, J.L., George, J.M., Christine, A.E., 2017. Numerical simulation of diverse thermal in situ upgrading processes for the hydrocarbon production from kerogen in oil shale reservoirs. *Energy Explor. Exploit.* 35 (3), 315–337. <https://doi.org/10.1177/0144598716689354>.
- Kang, Z.Q., Zhao, Y.S., Yang, D., 2020. Review of oil shale in-situ conversion technology. *Appl. Energy* 269, 115121. <https://doi.org/10.1016/j.apenergy.2020.115121>.
- Liu, D.X., Wang, H.Y., Zheng, D.W., 2009. Advances in in-situ exploitation of oil shale in the world. *Nat. Gas. Ind.* 5 (5), 128–132 (in Chinese).
- Liang, W., Liu, S.M., Cheng, Y.P., et al., 2017. Reservoir reconstruction technologies for coalbed methane recovery in deep and multiple seams. *International Journal of Mining Science and Technology* 27 (2), 277–284. <https://doi.org/10.1016/j.ijmst.2017.01.026>.
- Liu, Z.Y., 2019. Coupled Numerical Simulation of In-Situ Oil Shale Exploitation, vol. 105. Jilin University, pp. 125–133 (in Chinese).
- Lu, Z.H., Zhao, X.S., Liu, Z.Y., et al., 2019. Mutual influences between organic matter and minerals during oil shale pyrolysis. *Energy Fuels* 33 (3), 1850–1858. <https://doi.org/10.1021/acs.energyfuels.8b03703>.
- Lai, D., Zhan, J., Tian, Y., et al., 2017a. Mechanism of kerogen pyrolysis in terms of chemical structure transformation. *Fuel* 199, 504–511. <https://doi.org/10.1016/j.fuel.2017.03.013>.
- Lai, D., Zhang, G., Xu, G., 2017b. Characterization of oil shale pyrolysis by solid heat carrier in moving bed with internals. *Fuel Process. Technol.* 158, 191–198. <https://doi.org/10.1016/j.fuproc.2017.01.005>.
- Li, D., Pan, H., Di, X.J., et al., 2021. Progress in catalytic pyrolysis of oil shale. *Scanning* 2021, 867–876. <https://doi.org/10.1155/2021/6759176>.
- Li, H., Yang, Z., Li, R., et al., 2021. Mechanism of CO₂ enhanced oil recovery in shale reservoirs. *Petrol. Sci.* 18 (6), 1788–1796. <https://doi.org/10.1016/j.petsci.2021.09.040>.
- Li, K., Zhao, Z., Lu, H., et al., 2022. Effects of inherent pyrite on hydrocarbon generation by thermal pyrolysis: an example of low maturity type-II kerogen from Alum shale formation, Sweden. *Fuel* 312, 122865. <https://doi.org/10.1016/j.fuel.2021.122865>.
- Liu, K., Jin, Z., Zeng, L., et al., 2022. Microstructural analysis of organic matter in shale by SAXS and WAXS methods. *Petrol. Sci.* 19 (3), 979–989. <https://doi.org/10.1016/j.petsci.2022.01.012>.
- Ma, J., Kang, D., Wang, X., et al., 2022. Defining kerogen maturity from orbital hybridization by machine learning. *Fuel* 310, 122250. <https://doi.org/10.1016/j.fuel.2021.122250>.
- Ma, T., Luo, H., Huang, K., et al., 2022. Hierarchical health risk assessment and influence factors of an ecological post-restoration oil shale mining area based on metal bioavailability. *Sci. Total Environ.* 821, 153480. <https://doi.org/10.1016/j.scitotenv.2022.153480>.
- Pan, L.W., Dai, F.Q., Pei, S.H., 2021. Influence of particle size and temperature on the yield and composition of products from the pyrolysis of Jimsar (China) oil shale. *J. Anal. Appl. Pyrol.* 157, 105211. <https://doi.org/10.1016/j.jaap.2021.105211>.
- Pan, C., Geng, A., Zhong, N., et al., 2009. Kerogen pyrolysis in the presence and absence of water and minerals: amounts and compositions of bitumen and liquid hydrocarbons. *Fuel* 88, 909–919. <https://doi.org/10.1016/j.fuel.2008.11.024>.
- Park, Y., Siddiqui, M.Z., Karagöz, S., et al., 2021. In-situ catalytic co-pyrolysis of kokersite oil shale with black pine wood over acid zeolites. *J. Anal. Appl. Pyrol.* 155, 105050. <https://doi.org/10.1016/j.jaap.2021.105050>.
- Pan, C.C., Geng, A.S., Zhong, N.M., 2006. Effects of mineral and water on hydrocarbon generation by kerogen pyrolysis – III. Formation and thermal evolution of steroidal hopanes (alkenes). *Acta Geol. Sin.* 3, 446–453 (in Chinese).
- Qing, W., Wang, X.M., Pan, S., et al., 2022. Study on the structure, pyrolysis kinetics, gas release, reaction mechanism, and pathways of Fushun oil shale and kerogen in China. *Fuel Processing Technology* 225, 107085. <https://doi.org/10.1016/j.fuproc.2021.107085>.
- Qun, L., Baoshan, G., Bo, C., et al., 2019. Technological progress and prospects of reservoir stimulation. *Petrol. Explor. Dev.* 46 (3), 19–27. [https://doi.org/10.1016/S1876-3804\(19\)60040-6](https://doi.org/10.1016/S1876-3804(19)60040-6).
- Ren, J.W., Zhang, X.M., Wang, X.J., 2021. Optimization of close fracturing parameters for horizontal wells in tight sandstone reservoirs. *Fault-Block Oil Gas Field* 28 (6), 859–864 (in Chinese).
- Simão, A., Domínguez-Álvarez, E., Yuan, C., et al., 2022. On the use of metallic nanoparticulated catalysts for in-situ oil upgrading. *Fuel* 313, 122677. <https://doi.org/10.1016/j.fuel.2021.122677>.
- Song, Z., Su, W., Yang, Y., et al., 2014. An experimental study on the CO₂/sand dry-fracture process. *Nat. Gas. Ind. B.* 1 (2), 192–196. <https://doi.org/10.1016/j.ngib.2014.11.011>.
- Song, L.H., 2016. Catalytic Effects of Transition Metal Salts on Pyrolysis of Oil Shale. Jilin University, p. 138 (in Chinese).
- Sun, H.C., Tang, D.Z., Jiang, T.X., 2011. Fracturing technology of shale gas reservoir. *Petrol. Geol. Recovery Efficiency*. 18 (4), 90–93 (in Chinese).
- Sun, Q.H., Wang, W.D., Su, Y.L., et al., 2022. Production characteristics of micro-pore oil during imbibition of fracturing fluid in shale reservoir. *J. Cent. S. Univ.* 78 (6), 1–12 (in Chinese).
- Sun, X., Xue, L.F., Wang, Y.Y., 2019. Numerical simulation and well location discussion of hydrocarbon generation process in situ exploitation of oil shale. *World Geol.* 38 (3), 759–766 (in Chinese).
- Sun, Y.H., Guo, W., Deng, S.H., 2021. In-situ conversion and drilling technology of oil shale and its development trend. *Drilling Eng.* 48 (1), 57–67 (in Chinese).
- Symington, W., Olgaard, D., Otten, G., et al., 2010. ExxonMobil's electrofrac process for in situ oil shale conversion. *ACS (Am. Chem. Soc.) Symp. Ser.* 1032, 185–216. <https://doi.org/10.1021/bk-2010-1032.ch010>.
- Tang, H., Zhao, Y., Kang, Z., et al., 2022. Investigation on the fracture-pore evolution and percolation characteristics of oil shale under different temperatures. *Energies* 15 (10), 3572. <https://doi.org/10.3390/en15103572>.
- Tawfik, A., Tan, X., Elsamadony, M., et al., 2022. Graphene/hydroxyapatite nanocomposite for enhancement of hydrogen productivity from delignified duckweed. *Fuel* 330, 125537. <https://doi.org/10.1016/j.fuel.2022.125537>.
- Thana, A.N.A.A., Mustapha, K.A., Idris, M., 2022. Source rock pyrolysis and bulk kinetic modelling of Miocene sedimentary sequences in southeastern Sabah, Malaysia: the variability of thermal maturity to oil-gas producing kerogen. *J. Petrol. Sci. Eng.* 208, 109513. <https://doi.org/10.1016/j.petrol.2021.109513>.
- Thiéry, V., Bourdot, A., Bulteel, D., 2015. Characterization of raw and burnt oil shale from Dotternhausen: petrographical and mineralogical evolution with temperature. *Mater. Char.* 106, 442–451. <https://doi.org/10.1016/j.matchar.2015.06.022>.
- Tian, Z., Chen, B., Qiu, X., et al., 2022. Study of quantum chemistry calculation simulation for the effect of electric field on the kerogen molecular decomposition. *Fuel* 318, 123584. <https://doi.org/10.1016/j.fuel.2022.123584>.
- Wang, Q., Wan, X.M., Pan, S., 2022. Study on the structure, pyrolysis kinetics, gas release, reaction mechanism, and pathways of Fushun oil shale and kerogen in China. *Fuel Process. Technol.* 225, 107058. <https://doi.org/10.1016/j.fuproc.2021.107058>.
- Wang, X., Wen, C., Fan, Y., 2022. Synthesis of hierarchical SAPO-11-based catalysts with Al-based metal-organic framework derivative as mesopore to improve n-decane branched isomerization. *Petrol. Sci.* 19 (6), 3171–3181. <https://doi.org/10.1016/j.petsci.2022.06.003>.
- Wang, Y., Shang, Q., Wang, H., 2022. The leakoff in acid fracturing kinetics control mechanism. *Energy Rep.* 8, 46–52. <https://doi.org/10.1016/j.egy.2022.03.059>.
- Wang, Y.P., Wang, Y.W., Meng, X.L., 2013. In-situ exploitation of oil shale in the United States and its implications. *Petrol. Drilling Product. Tech.* 35 (6), 55–59 (in Chinese).
- Wang, M., Li, M., Li, J., et al., 2020. Porous aluminosilicates catalysts for low and medium matured shale oil in situ upgrading. *Energy Sci. Eng.* 8 (8), 2859–2867.

- <https://doi.org/10.1002/ese3.704>.
- Wang, L., Zhao, Y.S., Yang, D., 2020. Microscopic characteristics of in situ pyrolysis of oil shale by water injection steam. *Chin. J. Rock Mech. Eng.* 39 (8), 1634–1647 (in Chinese).
- Wang, Q., Sui, Y., Chi, M.S., 2014. Effects of minerals on the release of volatile noncondensate gas from oil shale. *Chem. Indust. Progress* 33 (10), 2613–2618 (in Chinese).
- Wu, Q.R., Wen, M.N., Li, G.L., et al., 2021. Enhanced mercury control but increased bromine and sulfur trioxides emissions after using bromine injection technology based on full-scale experiment. *Fuel* 285, 119130. <https://doi.org/10.1016/j.fuel.2020.119130>.
- Xie, H.P., Liu, T., Gao, M.Z., 2021. Research on in-situ condition preserved coring and testing systems. *Petrol. Sci.* 18 (6), 1840–1859. <https://doi.org/10.1016/j.petsci.2021.11.003>.
- Yang, C.X., 2019. Research on injection technology of the second type of oil reservoir with proportional regulation. *Chem. Eng. Equipm.* 56 (2), 80–82 (in Chinese).
- Yang, Y., 2014. Theoretical and Experimental Study on In-Situ Pyrolysis of Oil Shale by High-Pressure Power Frequency Electric Heating. Jilin University, p. 138 (in Chinese).
- Yan, J.W., Jiang, X.M., Han, X.X., 2013. A TG–FTIR investigation to the catalytic effect of mineral matrix in oil shale on the pyrolysis and combustion of kerogen. *Fuel* 104, 307–317. <https://doi.org/10.1016/j.fuel.2012.10.024>.
- Yan, Y., Gao, H., Sui, Y., et al., 2022. The catalytic effect of inner minerals on the combustion of oil shale char: characteristics and mechanism. *Fuel Process. Technol.* 236, 107426. <https://doi.org/10.1016/j.fuproc.2022.107426>.
- Yang, Y., Wang, Z.Y., Zheng, S.B., 2021. Secondary exfoliation of electrolytic graphene oxide by ultrasound assisted microwave technique. *Nanomaterials* 12 (1), 68. <https://doi.org/10.3390/nano12010068>.
- You, Y., Wang, X., Han, X., et al., 2019. Kerogen pyrolysis model based on its chemical structure for predicting product evolution. *Fuel* 246, 149–159. <https://doi.org/10.1016/j.fuel.2019.02.075>.
- Yuan, Y., Rezaee, R., Yu, H., et al., 2021. Compositional controls on nanopore structure in different shale lithofacies: a comparison with pure clays and isolated kerogens. *Fuel* 303, 121079. <https://doi.org/10.1016/j.fuel.2021.121079>.
- Zhao, X.Y., Wang, C.F., Wang, Z.W., et al., 2019. Postfracturing permeability prediction for CBM well with the analysis of fracturing pressure decline. *Energy Sci. Eng.* 7 (6), 3111–3123. <https://doi.org/10.1002/ese3.483>.
- Zamiri, M.S., Guo, J., Marica, F., et al., 2022. Characterization of kerogen in shale core plugs using T^{*}-based magnetic resonance methods. *Fuel* 324, 124573. <https://doi.org/10.1016/j.fuel.2022.124573>.
- Zhang, B., Zhong, Z., Chen, P., et al., 2017. Microwave-assisted catalytic fast copyrolysis of Ageratina adenophora and kerogen with CaO and ZSM-5. *J. Anal. Appl. Pyrol.* 127, 246–257. <https://doi.org/10.1016/j.jaap.2017.07.027>.
- Zhang, C., Yao, Y., Elsworth, D., et al., 2021. Microstructure characterization of kerogen in mature shale: molecular investigation of micropore development. *J. Nat. Gas Sci. Eng.* 95, 104239. <https://doi.org/10.1016/j.jngse.2021.104239>.
- Zhang, D., Cao, H., Lei, Y., et al., 2023. A study on molecular structural evolution of type II kerogen in a gold tube thermal system: insights from solid-state ¹³C NMR. *Fuel* 331, 125898. <https://doi.org/10.1016/j.fuel.2022.125898>.
- Zhang, H., Ahmed, M., Zhan, J., 2022. Recent advances in molecular simulation of oil shale kerogen. *Fuel* 316, 123392. <https://doi.org/10.1016/j.fuel.2022.123392>.
- Zhang, M., Wang, C., Wang, K., et al., 2020. Gentle hydrotreatment of shale oil in fixed bed over Ni-Mo/Al₂O₃ for upgrading. *Fuel* 281, 118495. <https://doi.org/10.1016/j.fuel.2020.118495>.
- Zhao, F., Li, B., Zhang, L., et al., 2022. The mechanism of superheated steam affecting the quality of in-situ pyrolysates of oil shale kerogen: Part A-saturation of pyrolytic organics. *Fuel* 323, 124331. <https://doi.org/10.1016/j.fuel.2022.124331>.
- Zhao, H., Xiong, Y., Zhen, H., et al., 2022. Experimental investigation on the fracture propagation of three-stage acid fracturing of tight sandstone gas reservoir. *J. Petrol. Sci. Eng.* 211, 110143. <https://doi.org/10.1016/j.petrol.2022.110143>.
- Zhao, X., Sang, Q., Li, Y., et al., 2021. CO₂-kerogen interaction dominated CO₂-oil counter-current diffusion and its effect on ad-/absorbed oil recovery and CO₂ sequestration in shale. *Fuel* 294, 120500. <https://doi.org/10.1016/j.fuel.2021.120500>.
- Zhou, D., Zhang, G., Huang, Z., et al., 2022. Effects of supercritical CO₂ on viscoelastic properties of shales. *Petrol. Sci.* 19 (5), 2199–2209. <https://doi.org/10.1016/j.petsci.2022.05.018>.