

Article

Catalytic Conversion of Oil Shale over Fe or Ni Catalysts under Sub-Critical Water

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Abstract: Sub-critical water is an environment-friendly solvent. It is widely used for the extraction of various organic compounds. It can be used to dissolve and transport organic matter in oil shale. In this study, the conversion of oil shale was synergistically catalyzed by the addition of Fe or Ni to the Fe inherent in samples under sub-critical water conditions. Oil shale can be converted to gas, oil and residues of oil. Thermogravimetric (TG) analysis results presented that the weight loss of raw oil shale was up to 15.85%. After sub-critical water extraction, the weight loss rate of the residues was reduced to 8.41%. With the application of a metal catalyst, Fe or Ni, the weight loss of residues was further reduced to 7.43% and 6.57%, respectively. According to DTG curves, it was found that there were two weight-loss rate peaks. The decomposition process of kerogen in oil shale could be divided into two cracking processes. One is decomposed at a high velocity at around 420 °C, and another is decomposed at a low velocity at around 515 °C. Gas chromatography (GC) results of gas products indicated that Fe or Ni could contribute to producing normal alkanes, such as methane, ethane, propane, etc., which are produced by the hydrogenation of alkenes via hydrogen transfer during the conversion process of kerogen. Gas chromatography-mass spectrometry (GC-MS) was conducted to analyze the components of the liquid products. The results showed that *n*-alkanes, *iso*-alkane, oxygenated hydrocarbons and aromatic compounds were the major components of the kerogen cracking products. When Ni was introduced as a catalyst, the contents of aromatic compounds and oxygenated hydrocarbons in the liquid products were increased from 19.55% and 6.87% to 22.38% and 13.77%, respectively. This is due to the synergistic effect of the addition of Ni with the inherent Fe in oil shale under sub-critical water which ensures kerogen is more easily cracked to produce aromatic compounds and oxygenated hydrocarbons.

Keywords: oil shale; kerogen; sub-critical water; synergistic; catalytic cracking



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1. Introduction

With the increasing consumption of conventional fossil fuels, especially petroleum and natural gas, many countries have had to explore unconventional resources to increase energy supply [1,2]. Oil shale is a kind of rock rich in kerogen and is regarded as supplementary resource of petroleum [3,4]. The kerogen in oil shale is usually converted to oil and gas through downstream retorting technology. This technology depends on building large-scale installations on the surface to produce shale oil and gas in a high-temperature and oxygen-free environment [5–7]. The technology encounters significant challenges, such as energy consumption, pollution and residues disposal problems [8].

The in situ conversion technologies for oil shale have received widespread attention for oil shale exploration. At sub-surface levels, kerogen in oil shale is cracked under high-temperature conditions. The oil and gas produced by cracking are extracted to the surface, leaving the residues underground. Heat is supplied by sub-surface combustion or by introducing high-temperature gases or liquids to the oil shale [9–13]. In situ conversion technology not only avoids the disadvantages of the high cost of oil shale downstream retorting process and their greater environmental harm, but also can economically develop deep oil shale resources [14–16]. Jilin University has proposed an in situ conversion technology that utilizes sub-critical water (SCW) as the heat transfer medium and extracting agent for oil shale cracking [17].

SCW is compressed liquid water existing above its saturation vapor pressure ($p = 0.4\text{--}22.1$ MPa) and below or near the critical temperature ($T = 150\text{--}370$ °C) [18]. SCW is a new environmentally friendly solvent with acid/alkali catalytic functions and excellent extraction abilities. Hu [19] used non-isothermal and isothermal cracking technology to extract the organic compounds from Huadian oil shale by using SCW. Lewan [20,21] pioneered the application of hydrous pyrolysis to Woodford oil shale, and obtained products similar to natural crude oil. Jiang [22] found that SCW conditions not only improve the shale oil yield of Huadian oil shale by enhancing the free radical reactions, but also can increase the content of aliphatic hydrocarbons in shale oil by reducing the secondary cracking of the oil vapors. Muntaser [23] demonstrated that heavy oil could be upgraded to light oil in SCW without additional catalysts and hydrogen. The cleavage of C–N, C–S and C–C bonds significantly occurs in SCW conditions, which leads to intensified cracking reactions primarily through the decomposition and dealkylation of colloid and asphaltene. However, it takes a long time to extract organic compounds from oil shale in SCW, which may be attributed to the fact that the temperature of SCW is much lower than that of retorting [24–27]. Therefore, it is necessary to screen suitable catalysts to enhance the extraction efficiency of SCW.

At present, there are few studies on the catalytic cracking of oil shale in water or organic solvents. Metecan [28] investigated the catalytic role of pyrite (FeS_2) in extracting organic compounds from Göynük oil shale using sub-critical or supercritical toluene. It was observed that pyrite can improve the conversion of organic matter in oil shale and the yield of shale oil, even when the extraction temperature is less than 400 °C, while reducing the average relative molecular weight of the shale oil. Kartal [29] investigated the effects of Fe_2O_3 , MoO_3 , $\text{Mo}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and zeolite on the cracking behavior of Niğde-Ulukışla oil shale in tetrahydronaphthalene. It was found that when a large amount of MoO_3 was added, the conversion rate of organic matter and the extraction rates of shale oil and gas could be effectively improved. Zhou [30] studied the effects of four catalysts, H_3PO_4 , Na_2CO_3 , NaOH and FeHZSM-5, on the cracking of Fushun oil shale in supercritical ethanol. The results showed that these four catalysts could improve the yield of shale oil, with FeHZSM-5 having the best effect. However, organic solvents are heavily polluting to the environment. Existing studies have shown that transition metals such as Fe, Co and Ni have a good catalytic effect on the cracking of kerogen in oil shale.

Due to the high siderite content in oil shale samples selected for this study, they are inherently rich in Fe. This paper focuses on the performance difference of catalyzing the conversion of kerogen into oil and gas under SCW conditions through the synergistic effect of the addition of Fe or Ni to the Fe inherent in the sample. The composition evolution characteristics of shale gas, shale oil, kerogen and residues with the different catalysts were investigated systematically. This study hopes to provide some theoretical support for the in situ catalytic conversion of oil shale to shale oil and shale gas under SCW conditions. For ease of expression, its inherent Fe and the additional Fe and Ni are denoted as Fe(i), Fe(a) and Ni(a), respectively.

2. Materials and Methods

2.1. Sampling Settings

Oil shale samples were collected from Fugu County, Yulin City, Shannxi Province, China (N 110°47'48", E 39°12'53"). The Fugu oil shale has a burial depth of 70–80 m. Oil shale reserves are approximately 10 million tons. A series of random samples were taken for elemental analysis and Fischer assay analysis, and the results are listed in Table 1. It can be seen from the table that these Fugu oil shale samples are inferior, as the Fischer assay oil yield is 6.06% but the H/C atomic ratio is about 0.08. This indicates that Fugu oil shale contains less kerogen. Oil shale was crushed to particles smaller than 20 mesh. Selecting small granules of oil shale instead of powdered oil shale for these experiments was more conducive to studying the migration process of organic products in the oil shale matrix and to researching the process of extracting oil shale in SCW. The experiments were repeated twice under the same conditions to diminish the experimental errors caused by sample heterogeneity.

Table 1. Elemental and Fischer assay analysis of Fugu oil shale.

Elemental Analysis (wt%, ad)		Fischer Assay Analysis (wt%)	
C	16.32	Shale oil	6.06
H	1.26	Gas	2.24
N	0.24	Water	8.19
S	0.27	Residues	83.51

The XRD analysis of Fugu oil shale is shown in Figure 1. The XRD showed the main components of the mineral matter including quartz, calcite, kaolinite, hydromica and siderite. The simplified standard XRD patterns for each mineral are plotted separately in Figure 1. It is worth mentioning that the oil shale samples selected in this study have a high content of siderite, meaning that they have a high element content of Fe(i). According to the existing research, Fe has a strong promotional effect on kerogen cracking [31].

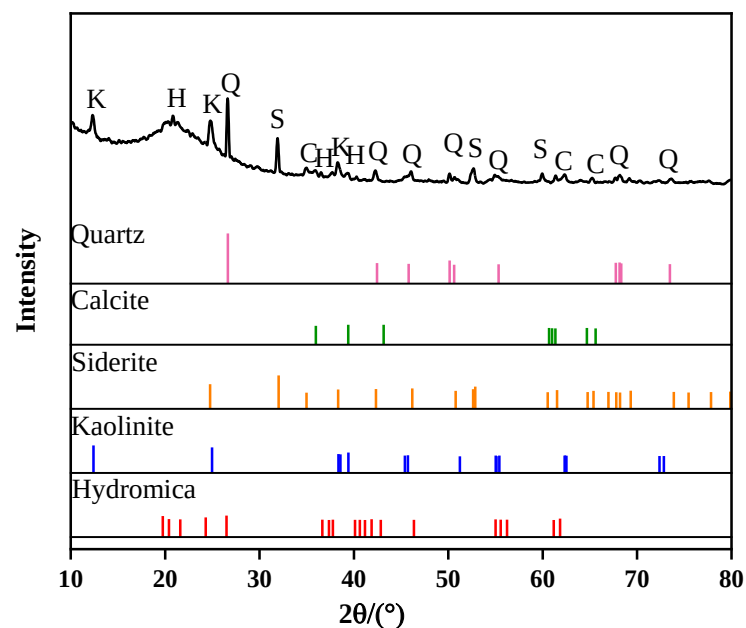


Figure 1. XRD pattern of raw oil shale.

2.2. Oil Shale Catalytic Conversion Experiments

Oil shale catalytic experiments were conducted in an autoclave. In each experiment, dry granular oil shale and distilled water or 0.01 mol/L Fe(a) solution or 0.01 mol/L Ni

(a) solution were loaded into the autoclave, and then the autoclave was sealed. The Fe(a) solution and Ni(a) solution were prepared from commercially available $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In preparation, 1 MPa N_2 was used to purge the air in the headspace of the autoclave three times, and then the N_2 was released to keep the system at atmospheric pressure. The autoclave was heated from room temperature to 340 °C and kept at the final temperature for 48 h. The experimental conditions such as time and temperature were selected after a series of preliminary experiments. When the temperature of the autoclave reached 340 °C, the internal pressure of the autoclave was 14.2 ± 0.3 MPa. Then, the internal pressure of the autoclave gradually increased to a maximum value of 14.8 ± 0.3 MPa with the reaction time. After the heating procedure was completed, the reactor was cooled down to room temperature. Finally, the gas products, liquid products and residues were collected in sequence for further analysis. The kerogen in the oil shale was cracked to produce bitumen. The bitumen transported from the oil shale matrix was called shale oil. Residual bitumen represents the unreleased bitumen remaining in the pores of the oil shale. The residual bitumen can be extracted from oil shale residue by dichloromethane at 60 °C. Shale oil and residual bitumen were dissolved and mixed, then analyzed as a liquid product. The residues were washed and dried.

2.3. Analytical Methods

The Fischer assay analysis and Element analysis were utilized to evaluate the quality characteristics of the oil shale. The Fischer assay analysis used equipment compliant with Chinese national standards, which are revised in line with the international ISO 647 standard [32]. The elemental analysis of the samples was performed using a vario PYRO cube elemental analyzer. Samples were burned at high temperatures, transforming the elements into gaseous forms for precise quantification. Oil shale was treated with a series of dilute hydrochloric acid and hydrofluoric acid to obtain kerogen. The kerogen was analyzed for carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content, adhering to the Chinese standard GB/T 19145-2022 [33].

The mineral compositions of the original oil shale and shale residue were characterized by X-ray diffractometer (XRD) (Bruker D8 ADVANCE (Billerica, MA, USA)) with Cu K α radiation at 60.0 kV and 60.0 mA. The 2 θ scan range was from 10° to 80°.

Agilent's 7890B GC (Agilent Technologies, Santa Clara, CA, USA) was used to detect the composition and content of the gas products. It was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The FID was used to detect the hydrocarbons (C_1 – C_4) using HP-AL/S columns (25 m $\times$ 0.32 mm $\times$ 8 μm) with helium as the carrier gas. CO_2 from the gas samples was determined using HayeSep A 80–100 mesh columns with helium as the carrier gas and the TCD.

Liquid products were assessed using Agilent's 7890A-5975N GC–MS. The chromatographic column was a HP-5MS (30 m $\times$ 0.32 mm $\times$ 0.25 μm) capillary column. The split ratio was set to 20:1, with helium at a constant flow mode of 2 mL/min, and the temperature was maintained at 300 °C. The initial temperature was 50 °C, and was then heated at a 10 °C/min temperature ramp to 200 °C, then heated at a 5 °C/min temperature ramp until a final temperature of 280 °C and held for 10 min. The database used for detection was the National Institute of Standards and Technology (NIST) (Version 2.02) Mass Spectra Libraries.

The thermogravimetric experiment on the solid residues was completed on a TG-DSC thermogravimetric analyzer (SDT Q600) under N_2 atmosphere with a heating rate of 20 °C/min from room temperature to 800 °C.

The above experiments were all repeated three times under the same conditions to ensure the accuracy of the results.

2.4. Data Treatment

Due to the presence of interlayer water in oil shale, the TG experiment was mainly focused on evaporation of water before 200 °C. Therefore, the weight of the oil shale at a

sample temperature of 200 °C is recorded as 100% for the TG data treatment. The weight loss rate is calculated as follows: $\text{wt}\% = (W_{(200\text{ }^{\circ}\text{C})} - W_{(600\text{ }^{\circ}\text{C})})/W_{(200\text{ }^{\circ}\text{C})}$.

For GC-MS, some small peaks can be seen in the spectrum. These are not the focus of this article, so these small peaks are ignored. The sum of the peak areas corresponding to the compounds of focus is recorded as 100%, and the proportion of the peaks' area is the same as the proportion of the compounds in the liquid product.

The average weight loss rate of each group of experiments was calculated from the TG data. Data of the most closely matched average were selected for charting.

For the GC and GC-MS data, the results of the components in each parallel experiment are averaged and displayed in the figures and tables in the following section.

3. Results and Discussion

3.1. Characterization of Solid Residues

3.1.1. TG and DTG of Raw Oil Shale and Residues

TG analysis of raw oil shale and oil shale residues was performed to evaluate the catalytic cracking of oil shale over the different catalysts under SCW. TG and DTG curves from the TG analysis are presented in Figures 2 and 3. During the initial stage between 200 °C and 400 °C, a small amount of weight loss occurred, mainly due to the volatilization of the light organics or decomposition of bicarbonate in the oil shale. A very obvious rapid decrease of mass appeared in the temperature range of 400–600 °C, which was the loss of mass caused by the cracking of the kerogen in the oil shale. The less weight loss, the less organic matter in the oil shale residues after the reaction. Calculation of the weight loss rates of the oil shale residues at 200–600 °C are listed in Table 2. The results showed that the weight loss of oil shale was up to 15.85% because of the cracking of kerogen in raw oil shale. When oil shale was cracked without any catalysts under SCW conditions, kerogen was partially converted to oil and gas and the weight loss of the shale residue was decreased to 8.41%. Then, Fe(a) and Ni(a) catalysts were introduced to the reaction process, and the weight loss of shale residues was further reduced to 7.43% and 6.57%, respectively. The results also indicated that 8.42% and 9.28% of the organic matter in oil shale had been extracted by SCW-Fe(i)-Fe(a) and SCW-Fe(i)-Ni(a); the extraction rates were 53.12% and 58.55%, respectively.

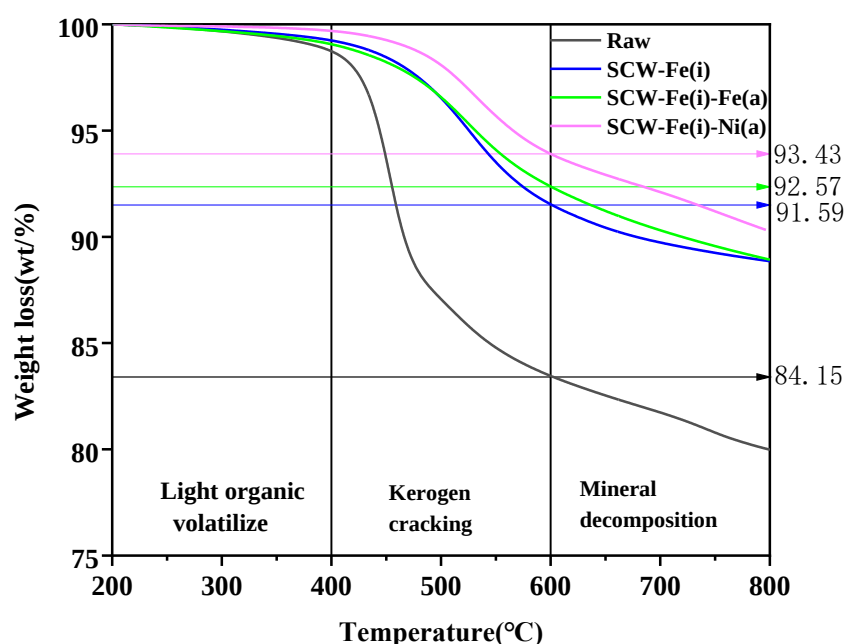


Figure 2. TG curves of raw oil shale and residues.

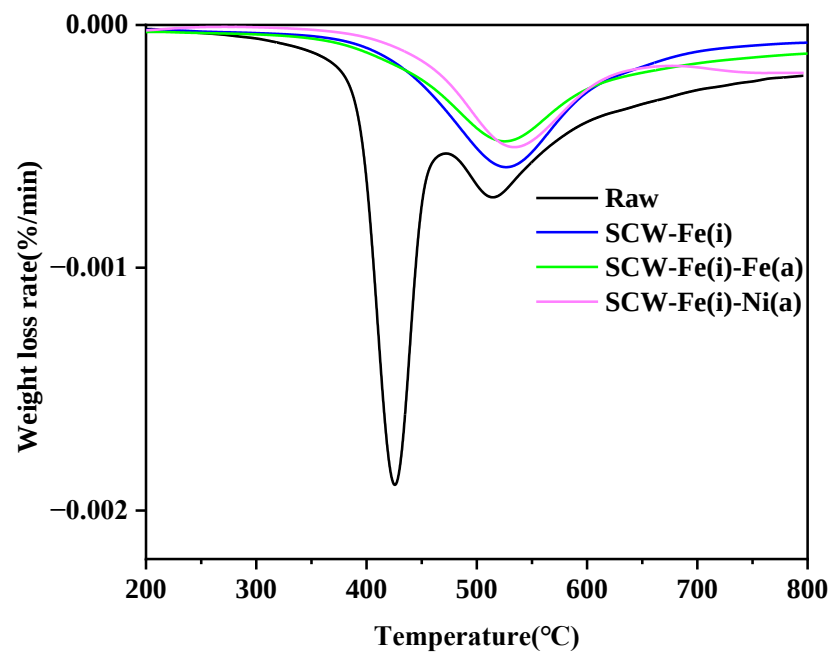


Figure 3. DTG curves of raw oil shale and residues.

Table 2. Weight loss of residues at 200–600 °C.

	Raw	SCW-Fe(i)	SCW-Fe(i)-Fe(a)	SCW-Fe(i)-Ni(a)
Weight loss/%	15.85	8.41	7.43	6.57

Combined with the DTG curve, it was found that there were two weight-loss rate peaks, corresponding to the two temperatures of the maximum mass loss rate of the oil shale. Therefore, the decomposition process of kerogen in oil shale could be divided into two cracking processes, inferring that the oil shale samples contained two types of kerogen components with different maturities. One is decomposed at approximately 420 °C with a high velocity, while another is decomposed at around 515 °C with a low velocity. It is indicated that the former is easy to be converted to oil and gas without any additional catalyst under SCW conditions, while the transformation of the latter is difficult and needs the promotion of catalysts and higher temperatures.

3.1.2. XRD of Raw Oil Shale and Residues

XRD patterns from the XRD analysis of oil shale before and after the experiments are shown in Figure 4. The comparison results showed that the peak of siderite disappeared after the reaction under SCW conditions, indicating that the siderite was fully decomposed and converted to hematite. It had a catalytic effect on the cracking of kerogen and formation of oil and gas substances [34]. When Fe(a) or Ni(a) was introduced, the peaks of intensity of hematite were increased. The hematite could synergize with the Fe(a) or Ni(a) catalyst, especially for Ni(a), to promote the cracking of kerogen in oil shale. At the same time, due to the decomposition of some minerals (e.g., bicarbonate), the relative content of other minerals increased and their corresponding XRD peak intensities (e.g., quartz) increased.

3.2. Characterization of Gas Products

The GC analysis results of the gas products from SCW-Fe(i), SCW-Fe(i)-Fe(a) and SCW-Fe(i)-Ni(a) are shown in Figure 5.

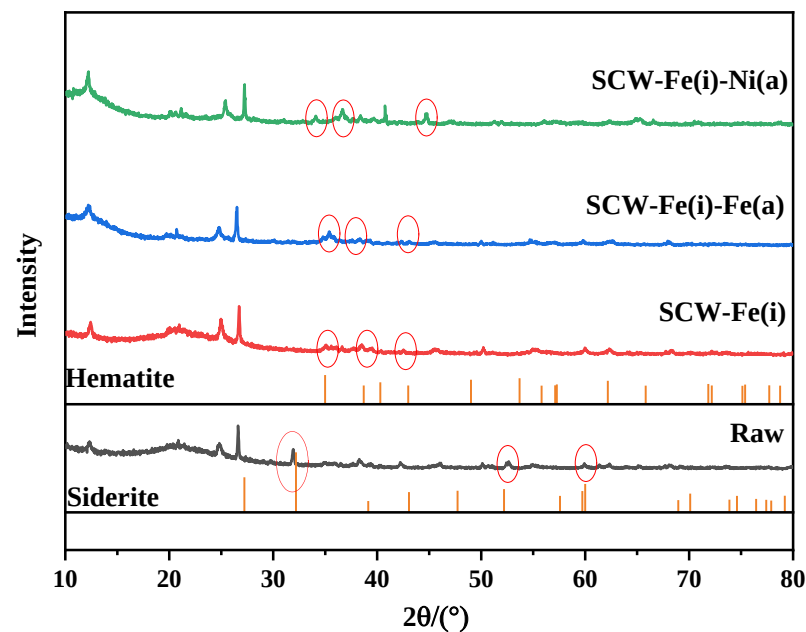


Figure 4. XRD patterns of raw oil shale and residues.

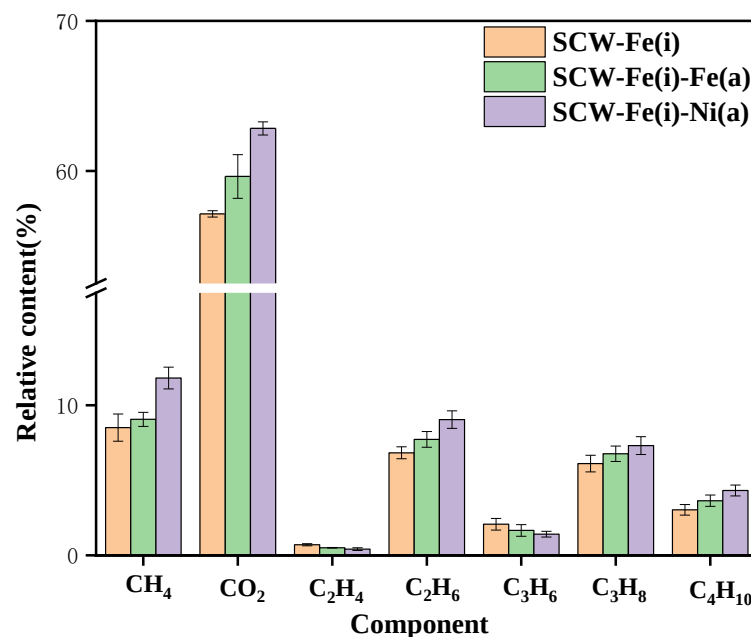


Figure 5. Content change of gas products.

As presented in the histogram, CO₂ is the highest content in all of the gas products. It is derived from the decomposition of bicarbonate in oil shale and the decarboxylation of carboxyl in kerogen. Most of the hydrocarbons are produced by the cracking of kerogen, and a small number are produced by the secondary cracking of intermediate products. When Fe(a) or Ni(a) was introduced, the relative percentage of CO₂ increased from 57.07% to 59.60% and 62.81%, respectively. The reason may be that the catalyst could promote the cracking of kerogen to produce more CO₂ or that the catalyst induced the decomposition of bicarbonate minerals to release CO₂. With the addition of catalysts, especially Ni, the *n*-alkanes content increased significantly and the *n*-alkanes content of the smaller carbon numbers increased more, but the *n*-alkenes content also decreased, and the *n*-alkenes content of the larger carbon numbers decreased more. This indicated that the synergistic effect of the addition of Fe(a) or Ni(a) with the inherent Fe(i) in oil shale has a tendency

to promote hydrocarbon macromolecules to be cracked into small molecules, and the produced *n*-alkane gases from C₁–C₄ are products of secondary hydrogenation of *n*-alkenes by hydrogen transfer from other organics in kerogen [35]. Compared with the composition of gas products from the retorting of oil shale, it was found that the content of CH₄ in the gas products of oil shale cracking is significantly increased under SCW conditions. This is due to the activity of SCW in catalyzing the cracking of methyl side-chains, thereby promoting the generation of CH₄. The content of *n*-alkenes in the gas products of oil shale cracking is significantly reduced under SCW conditions [36]. It can be deduced that a “high-temperature hydrogen-rich pyrolysis environment” promotes the hydrogenation of *n*-alkenes. This means that the H in the hydrogen transfer process comes not only from organic matter, but also from SCW. As can be seen in Figure 5, the catalytic activity of Ni(a) for the cracking of kerogen in oil shale is higher than that of Fe(a) under SCW conditions. In other words, the synergistic effect of Ni(a) with Fe(i) is stronger than that of Fe(a) with Fe(i). It can catalyze cracking to produce more organic matter that can provide H. This leads to more hydrogenation of *n*-alkenes in the gas products of SCW-Ni to form *n*-alkanes.

3.3. Characterization of Liquid Products

The compositions of the liquid products and residual bitumen were measured and identified by the GC–MS analyzer. Figure 6 shows the total ion chromatograms of the liquid products. The main components are *n*-alkanes in the liquid phase products, and other relatively abundant components are *iso*-alkanes, oxygenated hydrocarbons and aromatic compounds. The major components are marked by different symbols and the carbon atom number of individual *n*-alkanes is interval marked in Figure 6. In addition, the liquid products also contain a small number of naphthenes, fatty acids, *n*-alkenes and heteroatomic compounds.

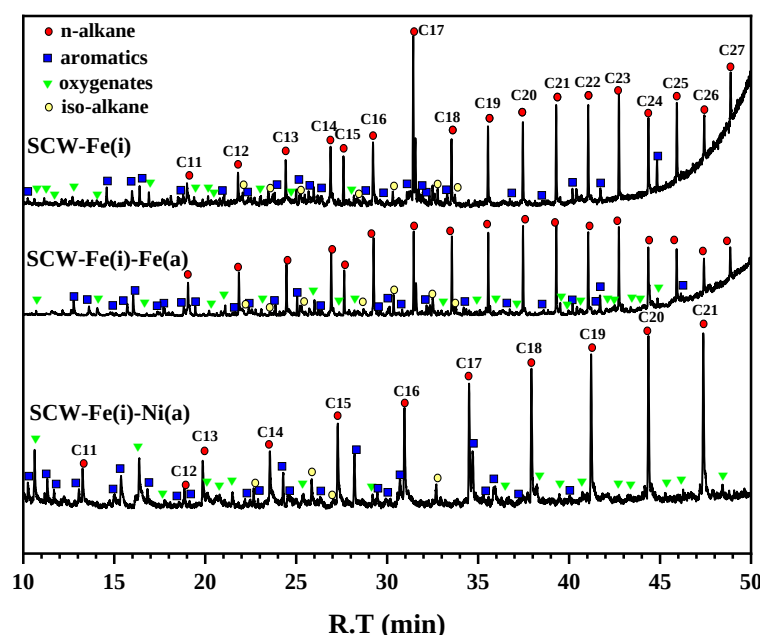


Figure 6. The GC-MS spectrum of liquid products.

n-alkanes are the dominant component in the liquid products, as shown in the chromatograms in Figure 6. The distribution of *n*-alkanes is complete and appears as the single-peak type. This is similar to the results in existing studies [9,26,27]. *n*-alkanes are mainly formed by the cleavage of the alkyl chains of aromatic compounds, bitumen and long-chain aliphatic hydrocarbons. Aromatic compounds are mainly formed by the thermal decomposition of asphaltenes in kerogen, which are mainly composed of many aromatic rings and alkane rings, and these aromatic rings contain many alkyl side chains. As a result

of the acid/alkali catalysis of SCW, the side chain cleavage of the aromatic rings in bitumen forms aromatic compounds and alkyl compounds. Oxygenated hydrocarbons are mainly produced by a series of reactions in SCW of organic compounds produced by kerogen cracking. For example, the ethers and esters produced by kerogen cracking are easily hydrolyzed in SCW to form alcohols and carboxylic acids. The alkenes produced by kerogen cracking after a hydration reaction with water form alcoholic compounds. However, these alcoholic compounds are highly unstable in SCW and are easily oxidized to ketone compounds. The alkane carbon number distribution of *n*-alkanes in the liquid products of SCW-Fe(i) or SCW-Fe(i)-Fe(a) is from C₁₁ to C₂₇ without any missing carbon numbers, whereas the alkane carbon number distribution of *n*-alkanes from the SCW-Fe(i)-Ni(a) process is from C₁₁ to C₂₁. It is indicated that the synergy of Fe(i) and Ni(a) can promote the cracking of kerogen and the secondary cracking of macromolecular long-chain alkanes and intermediate products into small alkanes during the catalytic conversion of oil shale under SCW.

Figure 7 presents the major components of these liquid products calculated by GC–MS peak area normalization. It is obvious from the histogram that the content of the major components of the liquid products of SCW-Fe(i) or SCW-Fe(i)-Fe(a) were basically unchanged. As the XRD results showed, siderite is converted to hematite under SCW conditions. It can catalyze the cracking of kerogen to produce oil and gas substances under SCW conditions [9]. GC–MS results indicated that Fe(a) only increases the amount of Fe in the catalytic system and does not synergistically catalyze the conversion of oil shale into liquid products with F(i). When Ni(a) was introduced, the contents of *n*-alkane and *iso*-alkanes in the liquid products were decreased from 68.58% and 4.80% to 60.04% and 3.81%, and the contents of aromatic compounds and oxygenated hydrocarbons in the liquid products were increased from 19.55% and 6.87% to 22.38% and 13.77%, respectively. Due to the synergistic effect of Ni(a) with Fe(i), kerogen is more easily cracked to produce aromatic compounds and oxygenated hydrocarbons. Ni(a) accelerates the dissociation of SCW, which plays a certain catalytic role in the hydrolysis and hydration of other organic compounds. It promotes the formation of aromatic compounds and oxygenated hydrocarbons. Furthermore, the hydrogen dissociates in the SCW effectively inhibit the condensation of aromatic compounds, enhancing the formation of fragments of aromatic compounds [37]. The production of these aromatic compounds and oxygenated hydrocarbons led to a decrease in the relative percentage of *n*-alkanes.

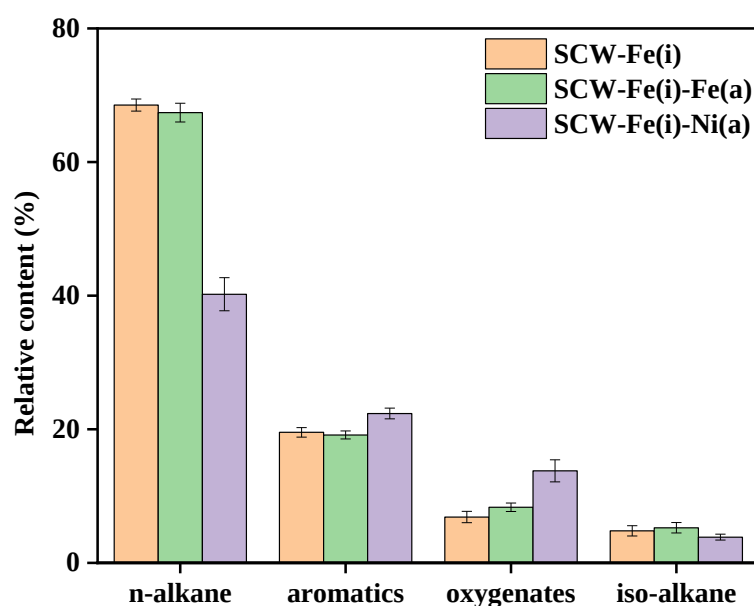


Figure 7. The relative content of major components in the liquid products.

4. Conclusions

In this study, the synergistic catalytic performance of Fe(i) and Fe(a) or Ni(a) in oil shale conversion to oil and gas under SCW conditions and the crack and release behaviors of organic compounds in oil shale during treatment with SCW-Fe(i), SCW-Fe(i)-Fe(a) and SCW-Fe(i)-Ni(a) were investigated. The results indicated that 53.12% and 58.55% of the organic matter in oil shale was extracted by SCW-Fe(i)-Fe(a) and SCW-Fe(i)-Ni(a), respectively.

The results of GC indicated that the synergistic effect of Ni(a) with Fe(i) is stronger than that of Fe(a) with Fe(i). It promotes the cracking of kerogen and produces more organic compounds that are provided by H, such that more hydrogenation of *n*-alkenes in the gas products of SCW-Ni takes place, forming *n*-alkanes.

The results of GC-MS showed that kerogen is more easily cracked to produce aromatic compounds and oxygenated hydrocarbons due to the synergistic effect of Ni(a) with Fe(i). The contents of aromatic compounds and oxygenated hydrocarbons in liquid products were increased from 19.55% and 6.87% to 22.38% and 13.77%, respectively. This was because the dissociation of SCW was accelerated by Ni(a), which plays a certain catalytic role in the hydrolysis and hydration of other organic compounds. Moreover, the hydrogen dissociates in the SCW effectively inhibited the condensation aromatic compounds, enhancing the formation of fragments of aromatic compounds. Overall, the synergistic catalytic conversion of oil shale by Ni(a) and Fe(i) under SCW conditions is a suitable method for engineering implementation. However, it should be noted that there are a series of issues to be considered, such as how to ensure contact between the catalyst and the organic matter, and how to control the amount of catalyst.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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Conflicts of Interest: Authors Chang Che, Junwen Wu and Zhibing Shen were employed by the company SINOPEC. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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