Article

Synergistic Catalysis of Reservoir Minerals and Exogenous Catalysts on Aquathermolysis of Heavy Oil

Yunlei Zang [1,2], Huaizhu Liu [3], Dong Chen [3], Shu Zhang [1], Shanjian Li [1] and Gang Chen [1,2,*]

1 Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oilfields, Xi'an Shiyou University, Xi'an 710065, China; 21211070913@stumail.xsyu.edu.cn (Y.Z.); 20212070889@stumail.xsyu.edu.cn (S.Z.)
2 Shaanxi University Engineering Research Center of Oil and Gas Field Chemistry, Xi'an Shiyou University, Xi'an 710065, China
3 Tangshan Jiyou Ruifeng Chemical Co., Ltd., Tangshan 063200, China; jxzx_chd@petrochina.com.cn (D.C.)
* Correspondence: gangchen@xsyu.edu.cn

Abstract: In this study, based on existing heavy oil extraction technology, combined with the mineral composition in a reservoir, the synergistic catalytic effect of reservoir minerals and exogenous catalysts under the reaction system of a hydrogen-rich environment not only reduces the viscosity of thick oil but also reduces the extraction cost and further improves the recovery rate of heavy oil. In this study, the impacts of different reservoir minerals and exogenous catalysts on the aquathermolysis of heavy oil were investigated. The research results showed that the sodium montmorillonite within the reservoir minerals exhibited an optimal catalytic effect, and the synergistic catalytic effect of sodium montmorillonite and catalyst C-Fe (catechol iron) resulted in a viscosity reduction rate of 60.47%. Furthermore, the efficiency of different alcohols as hydrogen donors was screened, among which ethanol had the best catalytic effect. Under the optimal reaction conditions, the viscosity reduction rate after the addition of ethanol was 75.25%. Infrared spectroscopy, elemental analysis, thermogravimetry, and differential scanning calorimetry were used to study the changes in heavy oil before and after hydrothermal cracking. Element analysis showed that the synergistic catalytic effect of sodium-based montmorillonite and catalyst C-Fe increased the hydrocarbon ratio from 0.116 to 0.117, and the content of S and N elements decreased. This fully confirms the catalytic effect of sodium-based montmorillonite and C-Fe catalyst for he hydrogenation reaction of the unsaturated carbon in heavy oil.

Keywords: reservoir minerals; heavy oil; catalytic aquathermolysis; synergistic

1. Introduction

The global demand for oil will rise by more than 40% by 2025. About 70% of the world's total oil reserves are made up of heavy oil, extra heavy oil, and bituminous heavy oil, all of which have geological reserves that are significantly bigger than those of regular crude oil [1]. China has reserves of more than 4 billion tons in more than 70 heavy oil fields. The majority of these heavy oil reservoirs are located in the Liaohe, Huanxiling, Xinjiang Karamay, and Shengli Oilfields. Conventional heavy oil is rich in compounds with high boiling points and viscosities, resulting in the poor fluidity of heavy oil, which poses great difficulties for heavy oil exploitation [2]. Common heavy oil viscosity reduction methods include thermal viscosity reduction, chemical viscosity reduction, microbial viscosity reduction, and dilute viscosity reduction. Among the various thermal viscosity reduction methods, steam stimulation (CSS), steam flooding (SF), steam-assisted gravity drainage (SAGD), and steam-injection-based combustion of oil layers are the primary techniques [3], but these technologies lead to high energy consumption and have a high environmental impact. Chemical viscosity reduction mainly includes emulsion dispersion viscosity reduction, oil-soluble viscosity reducer viscosity reduction, etc. [4,5],

which are highly selective but costly and complicated to operate. Microbial viscosity reduction technology is environmentally friendly and low cost, but the treatment time is long; dilution viscosity reduction technology is simple and the effect is immediate, but it is energy-dependent and may lead to the degradation in oil quality.

Catalytic modification and viscosity reduction is a typical combination of thermal viscosity reduction and chemical viscosity reduction, a heavy oil modification and viscosity reduction technology. By injecting the catalyst into a heavy oil reservoir, the combined effect of high temperature and the catalyst removes the impurities in the heavy oil and cracks the heavy constituents into light constituents, which reduces the apparent viscosity of the heavy oil [6,7]. In addition, the structure of gums and asphaltenes contains many functional groups that can form hydrogen bonds, and the hydrothermal cracking reaction causes a hydrogenation reaction, cracking reaction, and ring-opening reaction [8,9]. When the catalyst and hydrogen donor ethanol are added, the metal ions fully act on the S atoms to catalyze the acid polymerization and hydrogas shift reactions, resulting in the formation of free radicals by breaking the C-S bonds. In order to improve the recovery rate of heavy oil, the majority of research efforts have been directed towards developing crude oil fluidity improvers [10–13] and heavy oil aquathermolysis catalysts [14,15]. Currently, transition metal catalysts are mainly categorized into water-soluble catalysts and oil-soluble catalysts [16]. Water-soluble catalysts are some of the commonly used chemicals in the petroleum industry. Maity et al. [17] used the metals Ru and Fe as catalysts in asphaltene reforming experiments with desulfurization effects of 21% and 18%, respectively. The results showed that the first-row transition metals and AL^{3+} ions have high catalytic activity for thiophene and tetrahydrothiophene, and these metals convert large molecules into small molecules by breaking the C-S bond. Zhong et al. [18] studied the changes in viscosity and average molecular weight of heavy oil in the presence of eight metal ions, such as Fe^{2+}, Co^{2+}, Ni^{2+}, and so on, and the results showed that the metal ions all have certain viscosity-reducing effects on heavy oil. Clark et al. [19,20] investigated the application of several catalysts in hydrothermal cracking reactions, pointing out that transition metal salts can break C-S bonds in heavy oil components, accelerate the removal of organic sulfur in heavy oil, and generate light hydrocarbons, CO_2, H_2, and H_2S, resulting in an irreversible decrease in the viscosity of heavy oil. Subsequently, a large number of applied studies have been carried out at home and abroad [21,22]. Among them, Chen et al. synthesized a series of catalysts with transition metal ions as the center, and these catalysts had a good catalytic viscosity reduction effect. Oil-soluble catalysts can more fully contact with the oil phase, but the implementation conditions of this technology are harsh, and the extraction cost is high. Zhao et al. [23] succeeded in reducing the viscosity of Liaohe thick oil by more than 90% using nickel- and cobalt-based catalysts as well as petroleum sulfonates as emulsifiers at a lower temperature of 180 °C. Muneer et al. [24] used oil-soluble transition-metal catalysts (Fe, Co, Ni) to catalyze hydrothermal decomposition of heavy oil during steam injection. The catalytic performance of these catalysts is good at 300 °C, and they can be used to improve the quality of thick oil and reduce the viscosity of thick oil, among which Ni has the best catalytic performance.

As shown in the oil production profile in Figure 1, heavy oil has the most contact with minerals in the reservoir [25,26]. Minerals have great potential to participate in chemical reactions during the injection of high-temperature steam into the reservoir. So far, there has been no research on the aquathermolysis reaction that is catalyzed by foreign catalysts and in situ minerals. In this work, we explored the possibility of heavy oil aquathermolysis synergistically catalyzed through the application of exogenous catalysts in conjunction with in situ minerals. The synergistic catalytic effect of different reservoir minerals and exogenous catalysts and the effect of the addition of ethanol on aquathermolysis were studied under optimum reaction conditions. The compositional changes in the heavy oil before and after the reaction were characterized using elemental analysis, DSC, and TGA.
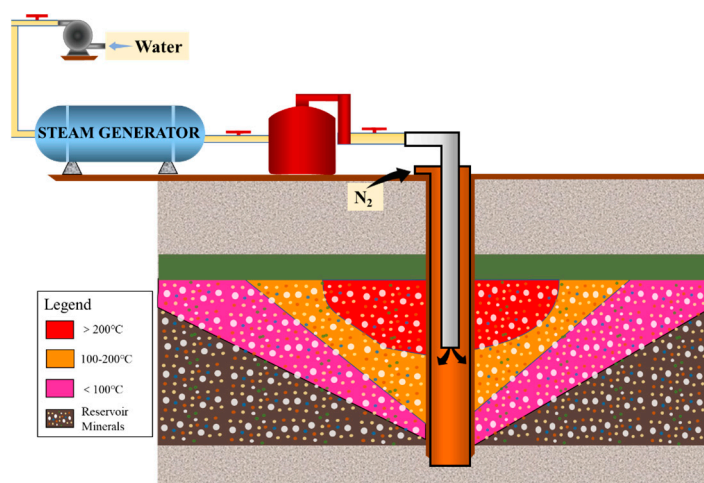
Figure 1. Schematic diagram of oil field recovery.

2. Materials and Methods

2.1. Materials

Commercially available chemical reagents of analytical grade were utilized in this experiment without undergoing additional purification processes prior to their usage. The reservoir minerals used in the experiment were all uniformly pulverized powders, which could be used directly. The crude oil samples utilized in this study were sourced from the Nanyang Oilfield in Henan, China. Oil sample properties are shown in Table 1.

Table 1. The physical parameters of heavy oil.

Pour Point/°C	Asphaltene, %	Saturated HC, %	Aromatic HC, %	Resin, %
20.0	23.44	31.16	28.73	16.67

2.2. Synthesis of the Catalyst

A certain mass of catechol was dissolved in ethanol, and an iron chloride aqueous solution was prepared according to the molar ratio of iron chloride to catechol of 1:2. The iron chloride aqueous solution was slowly dropped into catechol ethanol solution, mixed evenly, stirred at 70 °C for 4 h, and dried to obtain a catechol iron (C−Fe) catalyst. The preparation of C−Fe is shown in Figure 2.
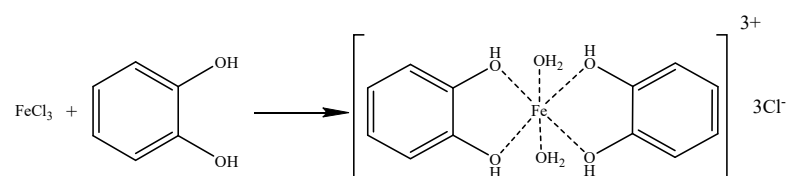

Figure 2. Catalyst synthesis and structures.

2.3. Characterization of the Complex

A Fourier transform infrared spectrometer, was used with the pressed-disk technique, and the spectral range of the measurement process was $400-4000$ cm^{-1}.

2.4. Aquathermolysis of Heavy Oil

In a high-temperature and high–pressure reactor, the oil sample was combined with certain amounts of water, reservoir minerals, exogenous catalysts, and hydrogen donor. The reaction took place at 200 °C for 4 h, and the working pressure was $0.2-0.3$ mpa.

2.5. Product Evaluation

The viscosity of heavy oils was measured in accordance with ASTM D97-96. The viscosity reduction rate, denoted as $\Delta\eta\%$, was determined using the formula $((\eta 0 - \eta)/\eta 0) \times 100$, where $\eta 0$ and η (mPa·s) represent the viscosities of the oil prior to and subsequent to the reaction [27,28]. Furthermore, the analysis of heavy oil components was carried out in accordance with the China Petroleum Industry Standard SY/T 5119-2016. An elementar vario EL cube was used to determine the elemental compositions (C, H, N, and S) of the original oil and the improved oil. The distribution of carbon in crude oil at various temperatures was assessed via thermogravimetric analysis. Under a nitrogenous environment, the oil samples were heated at a rate of 10 °C/min from 30 °C to 550 °C. According to SY/T 0545−2012, the wax precipitation point of the heavy oil was tested. Using Mettler−Toledo DSC822e DSC (Mettler Toledo Limited, Shanghai, China) equipment, the different scanning calorimetry (DSC) analyses of heavy oil were all performed within a temperature range of −25 to 50 °C, a flow rate of 50 mL/min, and a nitrogen environment.

3. Results and Discussion

3.1. Characterization of the Catalyst

Figure 3 displays the infrared spectra of the catalyst and ligand. The absorption peaks of the ligand at 1616 cm^{-1}, 1517 cm^{-1}, and 1469 cm^{-1} are the absorption peaks of the benzene ring. The corresponding absorption peaks at 1616 cm^{-1}, 1483 cm^{-1}, and 1430 cm^{-1} in the catalyst are also the absorption peaks of the benzene ring. The stretching vibration peak of −OH in the ligand catechol is around 3457 cm^{-1}, and the peak is strong and sharp. After the association with the iron ion is completed, where the stretching vibration peak position of the hydroxyl group is at 3222 cm^{-1}, and the peak width is strong, the infrared absorption position shifts. It shows that the −OH of the ligand coordinated with metal ions, and the ligand formed a stable complex.
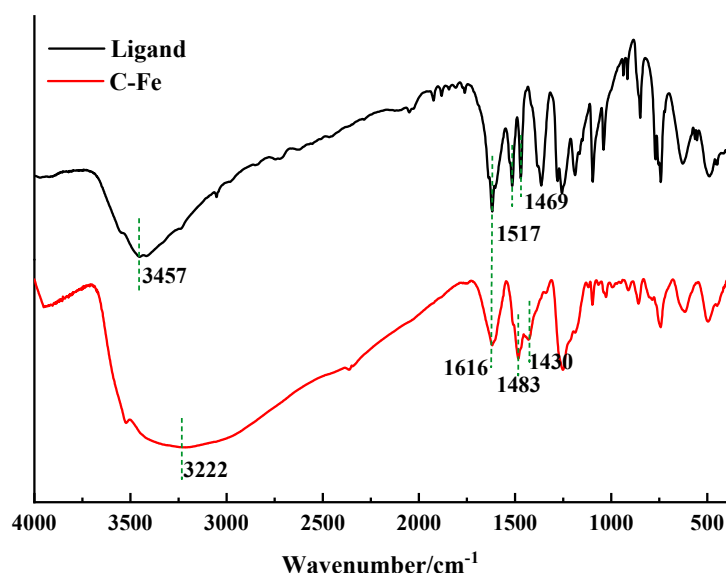

Figure 3. Infrared spectra of the ligand catechol and the C−Fe complex.

3.2. Effect of Reaction Temperature on Aquathermolysis

We aimed to investigate the viscosity–temperature properties of the oil samples after a hydrothermal cracking reaction at different reaction temperatures. As shown in Figure 4, the oil samples already had a good viscosity reduction effect at low temperature, and the higher the temperature, the better the viscosity reduction effect. The viscosity reduction rate of the oil samples reached its maximum at 200 °C. Due to the increase in temperature, the energy given to the system became larger, which caused the chemical bonds of the recombinant components in the oil samples to break, resulting in a viscosity decrease.

When the temperature was too high, the hydrothermal cracking reaction polymerization reaction dominated, and coking occurred at the bottom of the reactor. Therefore, 200 °C was selected as the optimum reaction temperature.
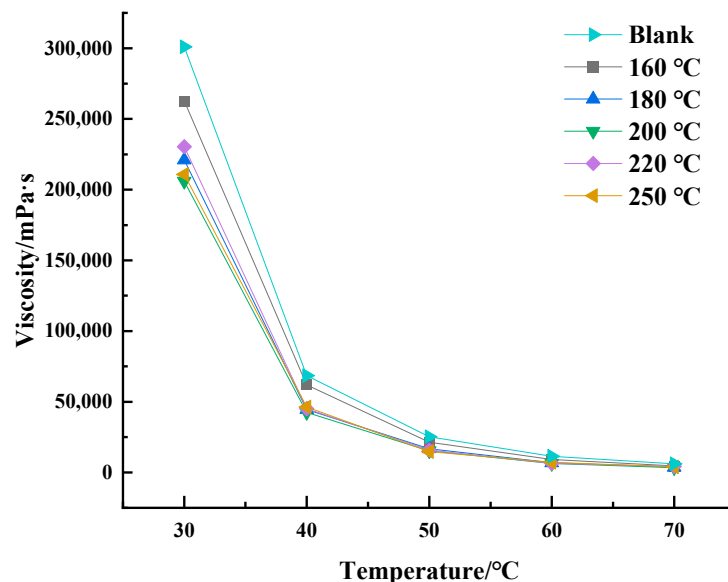

Figure 4. Effect of different reaction temperatures on the viscosity of oil samples.

3.3. Effect of Reaction Time on Aquathermolysis

After determining the reaction temperature at which the oil samples were subjected to a hydrothermal cracking reaction, we continued to examine the effect of different reaction times on the viscosity–temperature properties of the oil samples after hydrothermal cracking. As shown in Figure 5, the viscosity of the oil samples decreased with increasing reaction time, and the hydrothermal cracking reaction had the best viscosity-reducing effect on the oil samples when it reached 4 h. The viscosity of the oil samples gradually recovered as the reaction time increased, which indicated that the hydrothermal cracking reaction was essentially completed at 4 h. Therefore, the reaction duration was determined to be 4 h.
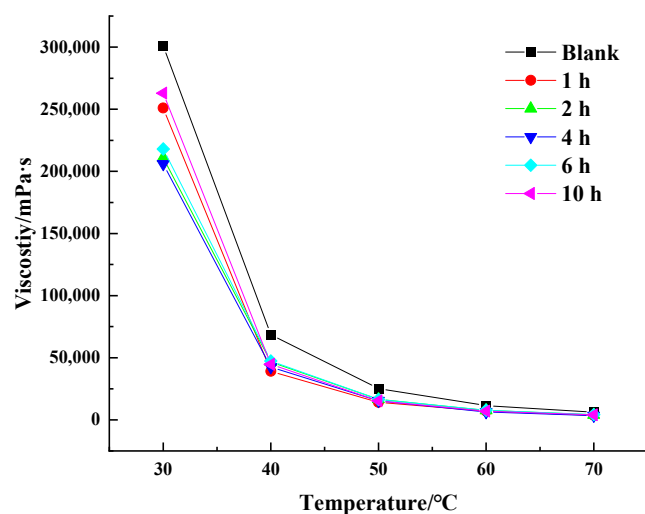

Figure 5. Effect of different reaction times on the viscosity of oil samples.

3.4. Effect of Water

Figure 6 clearly illustrates the substantial impact of the water-to-oil mass ratio on viscosity. The viscosity of heavy oil falls dramatically with an increase in the water to oil mass ratio when the water-to-oil ratio is between 0 and 0.3. For water-to-oil ratios between

0.3 and 0.5, the viscosity of heavy oil shows a positive correlation with the corresponding water-to-oil mass ratio. This phenomenon can be attributed to the occurrence of the reaction of a water–gas shift (WGSR) [29] between the heavy oil and water. This is due to the fact that in the hydrothermal cracking reaction, the main role of water is to give the active hydrogen needed for the reaction system, and as the amount of water is increased, the amount of active hydrogen that can be provided by water increases, resulting in the hydrothermal cracking reaction being carried out more thoroughly and inhibiting the polymerization of free radicals. When the amount of water is too large, it plays a certain role in diluting the free radicals produced in the reaction process, resulting in an increase in the viscosity of the oil samples. Simultaneously, considering the dilution of catalyst in subsequent catalytic reactions due to the increase in the water amount [30], the subsequent experiments adopted a water-to-oil mass ratio of 0.3 as the reaction condition.
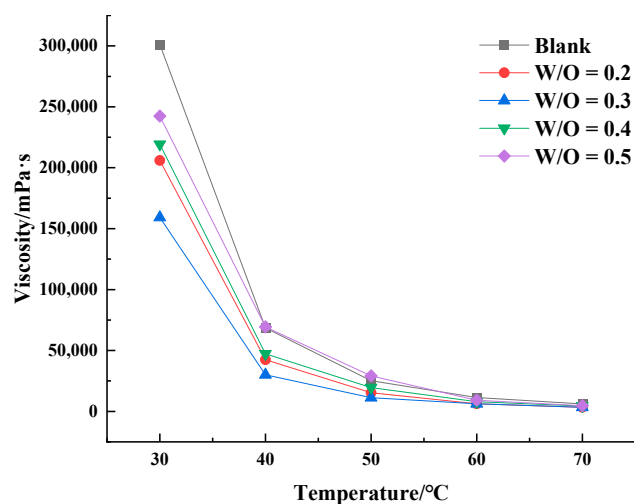

Figure 6. Effects of different water additions on aquathermolysis.

3.5. Effect of Reservoir Minerals on Aquathermolysis

Six minerals were selected to carry out the aquathermolysis reaction under the reaction conditions determined above. As evidenced by the analysis in Figure 7, clay minerals typically have a distinct catalytic reduction effect. Strong adsorption, cation exchange capacity (CEC), and strong acid centers of the clay may be responsible for this phenomenon. The viscosity comparison performed at 30 °C demonstrated that sodium montmorillonite exhibited the most significant reduction in viscosity, reaching up to 41.53%. This was followed by kaolin, showing a viscosity reduction rate of 40.10%, and ferrous sulfide, with a viscosity reduction rate of 40.00%. The findings indicate that minerals exhibit a notable influence on aquathermolysis.

3.6. The Effect of Hydrogen Donors on the Aquathermolysis of Heavy Oil

The type of alcohol has a non-negligible effect on the hydrothermal cracking of heavy oil. Different types of hydrogen donors all contributed to viscosity reduction, as shown in the analysis in Figure 8. Among them, isopropanol had the best hydrocracking impact in heavy oil, but its viscosity reduction effect under the dilution effect was less than ideal. Currently, isopropanol is commercially available at USD 1030 per ton and ethanol at USD 895 per ton, which is significantly costlier than ethanol. Therefore, in subsequent experiments, ethanol was selected as the hydrogen donor to reduce the viscosity. As the ethanol-to-oil ratio increased, Figure 9 shows that the viscosity of heavy oil significantly decreased. The subsequent studies used an ethanol-to-oil mass ratio of 0.3 as the reaction condition due to the dilution impact of the catalyst in the subsequent catalytic reaction caused by the rise in ethanol concentration.
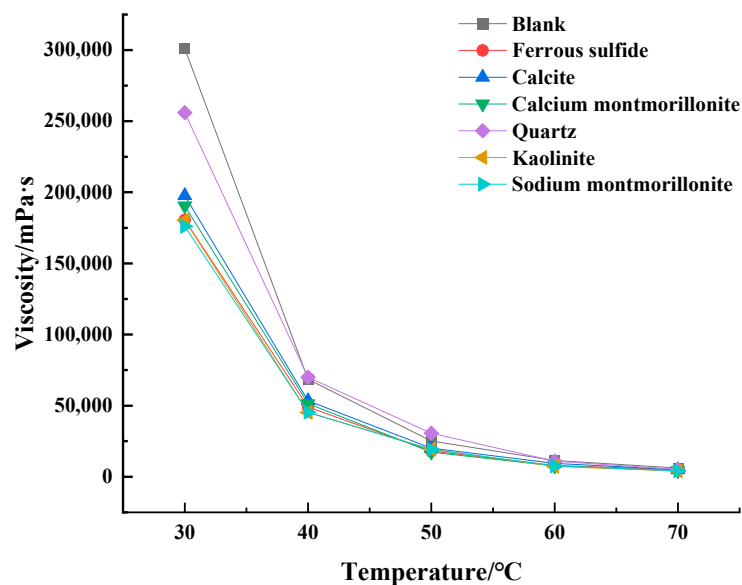
Figure 7. Influence of aquathermolysis of heavy oil with different minerals.
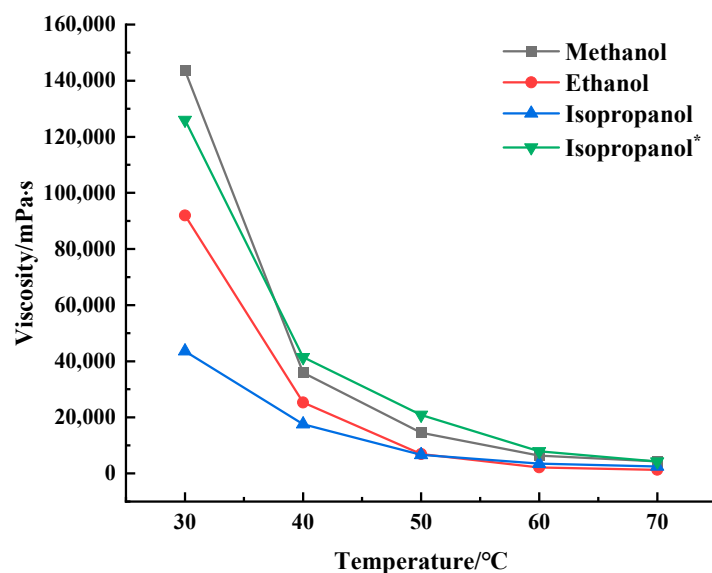

Figure 8. Influence of hydrogen donor on aquathermolysis reaction of heavy oil (isopropanol-hydrogen donor; isopropanol *—A diluent solvent at room temperature).

3.7. Analysis of the Viscosity of Heavy Oil Catalyzed by Various Catalysts

Figure 10 indicates that in the synergistic catalysis of minerals and C-Fe, the synergistic viscosity reduction effect of C-Fe and sodium montmorillonite was the best. The viscosity was reduced by 60.47% at 30 °C in comparison with the blank oil sample. Compared with the viscosity after aquathermolysis, the viscosity decreased by 42.23%. Therefore, the reaction system of sodium montmorillonite and C-Fe was selected for the subsequent experiment.
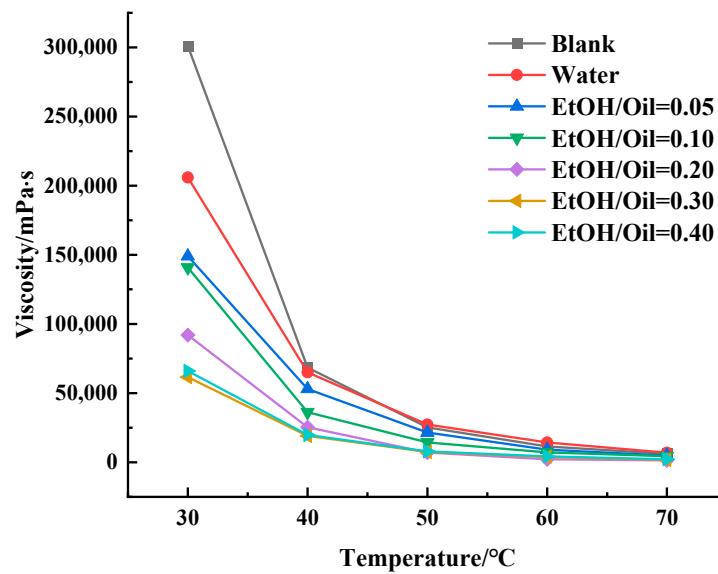
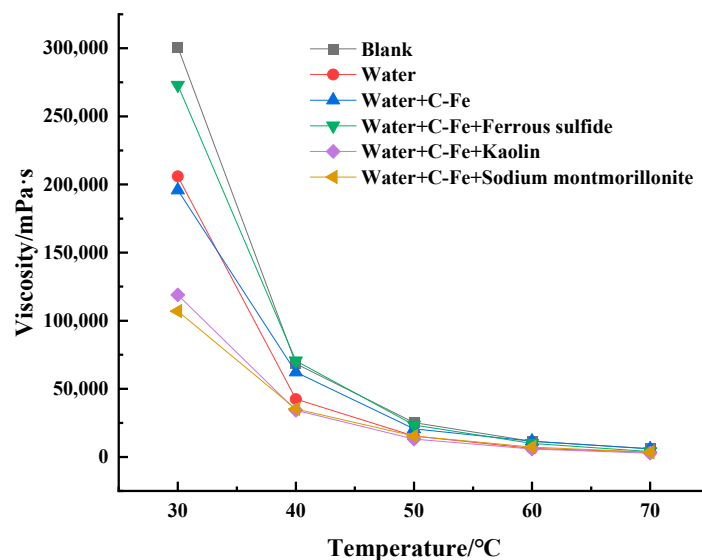**Figure 9.** Effect of ethanol dosage on the aquathermolysis.

Figure 10. Influence of synergistic catalysis between reservoir minerals and catalyst on heavy oil viscosity.

Figure 11 shows that the catalytic aquathermolysis reaction between heavy oil and water exhibited a certain viscosity reduction rate of up to 31.56%. Compared with the oil–water reaction, the addition of water and C-Fe to the heavy oil resulted in an increase of 3.32% in the viscosity reduction rate. After adding water and sodium montmorillonite to the oil, the viscosity reduction rate was increased by 9.97% compared with that of the oil–water reaction. Although the catalytic impact of the two together was not immediately apparent, it had a certain viscosity reduction catalytic effect on the aquathermolysis of the heavy oil. After adding water, C-Fe, and sodium montmorillonite to the heavy oil, the viscosity reduction rate was 18.94% higher than that of the oil–water sodium montmorillonite, indicating that the exogenous catalyst and clay have a synergistic catalytic effect on the aquathermolysis of heavy oil. The viscosity reduction rate of the heavy oil after the addition of water, C-Fe, sodium montmorillonite, and ethanol was 14.78% greater than that after the addition of oil–water, C-Fe, and sodium montmorillonite, demonstrating that ethanol has a superior hydrogen supply impact during the catalytic aquathermolysis of heavy oil.
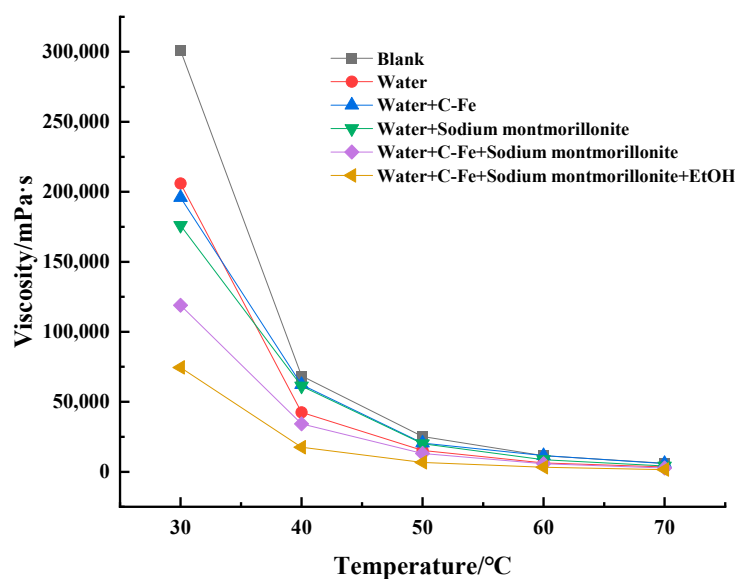
Figure 11. Performance of oil samples in reducing viscosity under various reaction circumstances.

3.8. Determination of SARA before and after Reaction

The results in Table 2 show that when the hydrothermal cracking reaction was completed, the saturated and aromatic hydrocarbon fractions contained in the oil samples increased, and the asphaltene and colloidal fractions decreased, which also indicates that most of the large molecules in the recombined fractions of the oil samples underwent ring-opening and hydrogenation reactions. The addition of the composite catalyst promoted the conversion of the recombined components in the oil samples, consumed more free radicals, reduced the occurrence of copolymerization reactions, and increased the content of light components, thus improving the viscosity reduction efficiency.

Table 2. Oil sample SARA analysis before and after the reaction.

Oil Sample	Saturates, %	Aromatics, %	Asphaltenes, %	Resins, %
Blank	23.44	31.16	28.73	16.67
After reaction with C-Fe and sodium montmorillonite	30.28	36.20	25.98	7.54
After reaction with C-Fe and sodium montmorillonite and EtOH	33.15	37.74	23.19	5.92

3.9. Elemental Analysis (EA)

An analysis was conducted on the variation in the element content in the heavy oil before and after the aquathermolysis reaction. Table 3 presents the results of this study. The findings demonstrate that the concentrations of carbon, nitrogen, and sulfur reduced during pure aquathermolysis, while the amounts of hydrogen marginally rose. This suggests that water contributes hydrogen to the heavy oil aquathermolysis process, increasing the saturation of macromolecules in heavy oil. The synergistic effect of sodium montmorillonite and the catalyst leads to the increase in hydrogen content, the decrease in sulfur content, and the increase in H/C ratio. The data obtained affirms the synergistic effect of sodium clay and the catalyst on the hydrogenation process of unsaturated carbon in heavy oil. After the addition of ethanol, the elemental analysis revealed a higher hydrogen content and increased nitrogen, sulfur, and H/C ratio. It showed that ethanol has a stronger ability to provide protons for the reaction, promoting the generation of small molecules and the breaking of C-N, C-S, and other bonds in the oil samples to produce more heteroatomic compounds. More importantly, it can also promote the conversion of more asphaltenes,

gums, and other recombinant components into light components, thus improving the oil quality.

Table 3. Oil sample elemental content before and after the reaction.

Oil Sample	Elemental Content/%				C/H
	C	**H**	**N**	**S**	
Blank	86.20	10.02	1.88	0.65	0.116
After the aquathermolysis	85.90	10.04	1.41	0.56	0.116
After reaction with C-Fe and sodium montmorillonite	86.19	10.10	1.58	0.44	0.117
After reaction with C-Fe and sodium montmorillonite and EtOH	83.99	10.29	1.30	0.44	0.122

3.10. Thermogravimetric Analysis (TGA)

Figure 12 shows the TGA curves, while Table 4 presents the corresponding mass loss of the heavy oil before and after the reaction. After aquathermolysis catalyzed by sodium clay and a catalyst, it was observed that the weight loss rate of the oil with a boiling point less than 150 °C and more than 450 °C decreased, while the weight loss rate of the oil with a boiling point between 350 and 450 °C increased. The weight loss rate of light oil with a boiling point less than 150 °C increased after the aquathermolysis was catalyzed by sodium montmorillonite, catalyst, and an ethanol promoter. In addition, at a temperature above 350 °C, a significant reduction in mass loss was observed [31,32], which confirms that the addition of a composite catalyst promotes the conversion of asphaltenes, resins, and other heavy components to light components during the reaction process, leading to the increase in the light component content of oil samples, and then the viscosity of oil samples decreases.
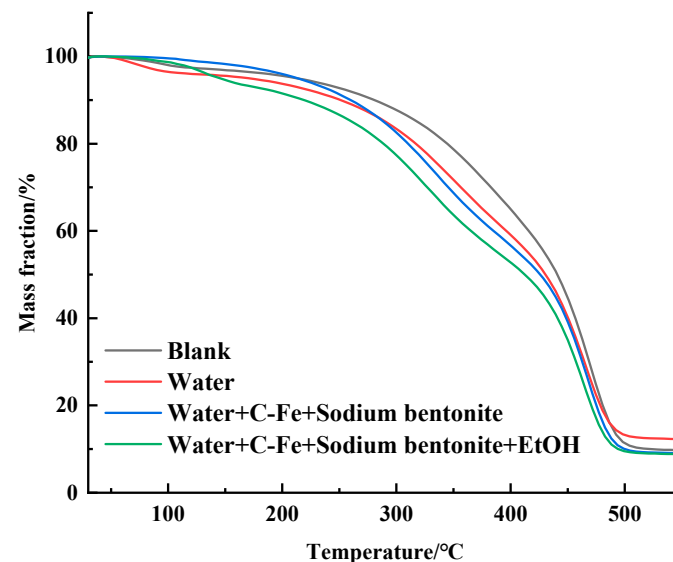

Figure 12. The TGA curves of the heavy oil before and after aquathermolysis.

Table 4. Weight loss rate of oil samples after different reaction systems.

Reaction System	Weight Loss Ratio/%			
	0–150 °C	**150–350 °C**	**350–450 °C**	**>450 °C**
Blank	3.10	18.36	34.82	43.72
Water	4.42	24.05	31.90	39.63
Water + C-Fe + sodium montmorillonite	1.83	29.35	29.77	39.05
Water + C-Fe + sodium montmorillonite + EtOH	5.33	30.82	28.94	34.91

3.11. Differential Scanning Calorimetry Analysis (DSC)

Figure 13 illustrates the findings from a DSC study of the wax formation process of crude oil under various reaction conditions. Compared with the blank oil sample, the wax precipitation point after aquathermolysis increased from 43.00 °C to 43.07 °C. After the synergistic catalytic cracking of C-Fe and sodium montmorillonite, the wax precipitation point of the oil sample increased from 43.00 °C to 43.71 °C, and the wax precipitation point increased to 45.07 °C after the addition of ethanol. The aforementioned study shows that resins in the heavy oil are broken down and transformed into asphaltenes, which serve as the primary nucleus of the wax precipitation and hasten the formation of wax crystals, raising the wax precipitation point.
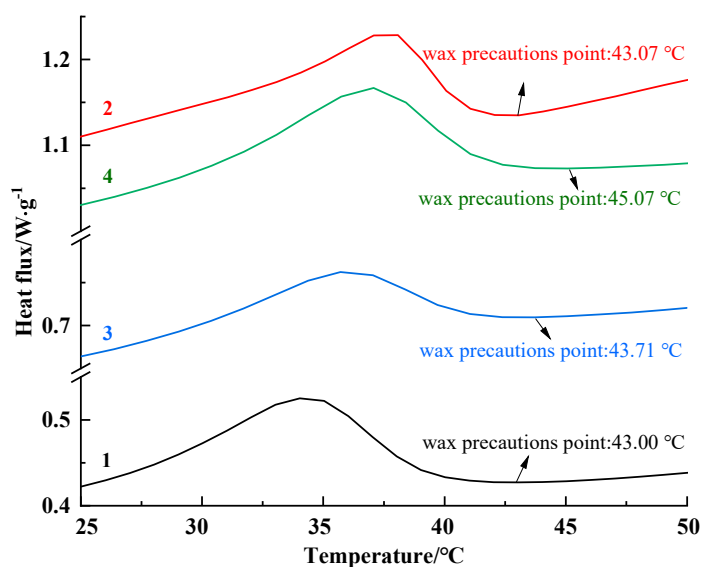

Figure 13. The DSC curves of the heavy oil before and after aquathermolysis. (1—blank; 2—water; 3—water + C-Fe + sodium montmorillonite; 4—water + C-Fe + sodium montmorillonite + ethanol).

3.12. Mechanism

Due to the layered structure of clay, there are numerous cations in its octahedral voids and numerous broken bonds on the surface of clay minerals, which have strong adsorption effects on organic macromolecules. The synergistic dual catalytic mechanism of exogenous catalysts and clay minerals is shown in Figures 14 and 15, which can be mainly described in the following stages: (1) The exogenous catalyst acts on the heteroatoms in the heavy components, destroying the hydrogen bonds between the molecules of some high-carbon hydrocarbon compounds, which results in the rupture of C-S, C=O, C-N bonds, etc. (2) The transition metal in the exogenous catalyst is easily exchanged with the sodium ion in the sodium montmorillonite, thus becoming the active center in the reaction. The presence of abundant vacant orbitals enables transition metals to readily engage with the electron-rich species present in heavy oil, thereby significantly enhancing the catalytic efficiency of the aquathermolysis decomposition in heavy oil [33,34]. (3) Due to the existence of Lewis acid on the surface of montmorillonite, high-carbon hydrocarbon compounds provide it with an electron, and simultaneously generate free radicals. The free radicals rearrange to promote the cleavage of C-C bonds and the formation of short-chain alkanes [35]. Clay minerals act as Bronsted acids to provide protons (H^+) for the organic matter adsorbed by it. Protons (H^+) are generated through the dissociation of the adsorbed water and interlayer water molecules that are bound to exchangeable cations. The primary reaction pathway for these protons involves the formation of transition-state carbocations [36,37]. (4) Upon the adsorption of water molecules onto the surface of clay minerals, the Lewis acid exhibits a high electron affinity, facilitating the sharing of an electron pair with the hydroxyl group in water. Consequently, the hydroxyl group becomes firmly adsorbed onto

the surface of the Lewis acid, while the remaining H^+ is readily released. This converts the Lewis acid into a Bronsted acid. When clay minerals are dehydrated, Bronsted acid sites are gradually converted into Lewis acids due to the lack of protons [38]. In this reaction system, montmorillonite activates the reactant water/steam, reduces the reaction activation energy, accelerates the breaking speed of some hydrogen bonds between the molecules of high-carbon hydrocarbon compounds, and improves the effectiveness of reducing the viscosity of heavy oil.
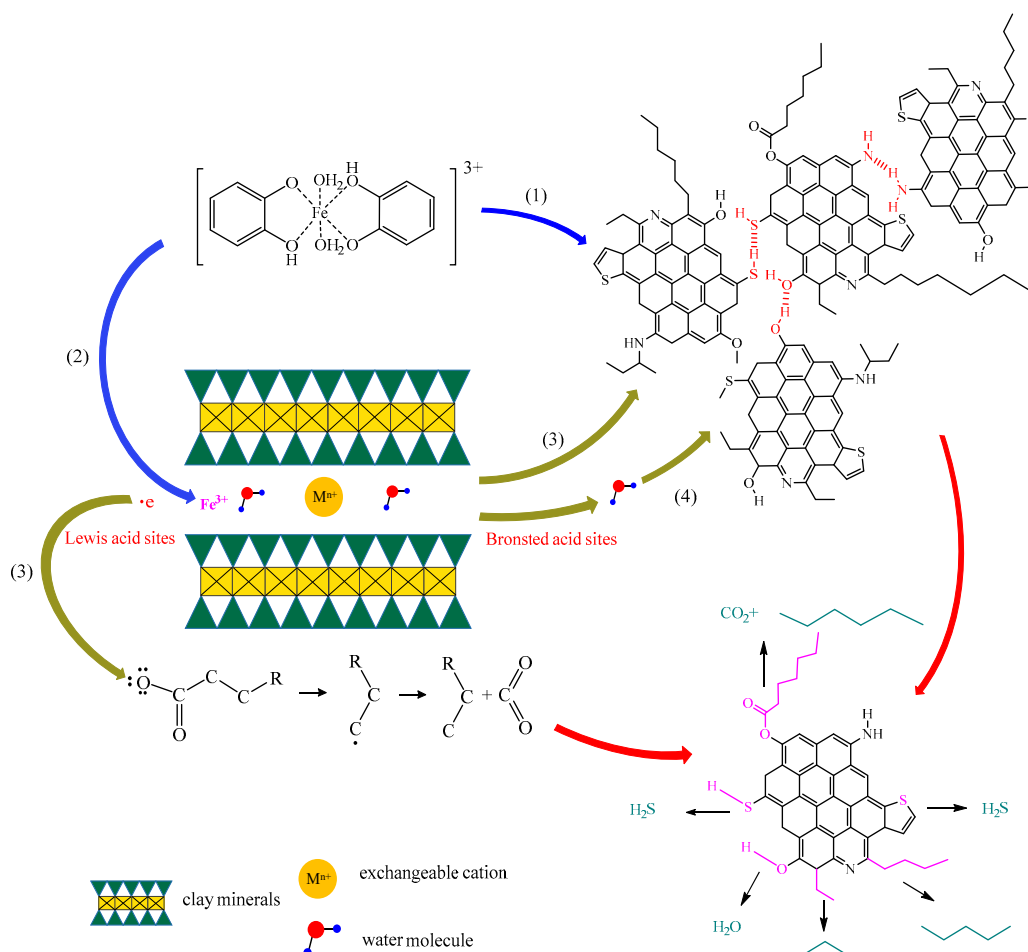

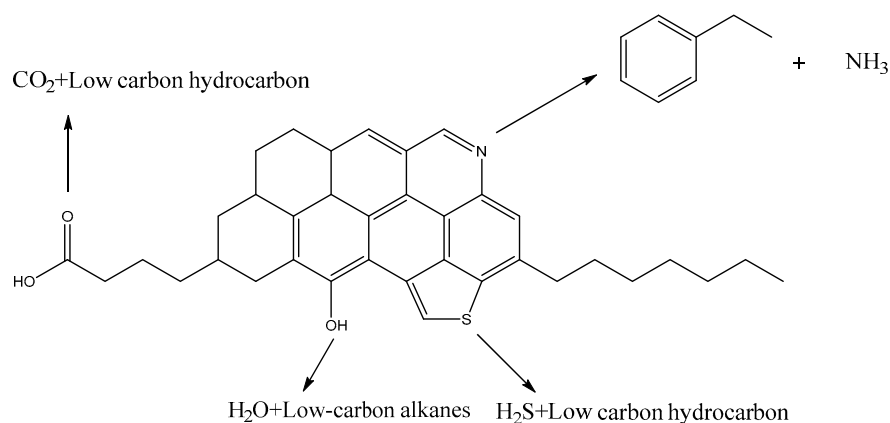**Figure 14.** Synergistic catalysis mechanism of exogenous catalysts and clay minerals.

Figure 15. Chemical changes occurring in the hydrothermal cracking of heavy oil.

4. Summary and Conclusions

In conclusion, reaction time, oil-to-water ratio, and mineral type all affect the viscosity reduction effect of heavy oil–water thermal cracking. In addition, the addition of external catalysts and hydrogen donors can enhance the catalytic effect in reducing viscosity. Under optimized conditions, the viscosity reduction rates of oil–water, oil–water+ sodium montmorillonite, oil–water+ sodium montmorillonite +C-Fe, and oil–water+ sodium montmorillonite + C-Fe + ethanol oil samples reached 31.56%, 41.53%, 60.47%, and 75.25%, indicating that exogenous catalysts and in situ clay have a synergistic catalytic effect on the aquathermolysis of heavy oil. After the catalytic aquathermolysis of heavy oil, the thermogravimetric analysis showed that the light components increased, and the oil–water + sodium montmorillonite + C-Fe oil samples changed significantly. DSC showed that with the wax precipitation point of crude oil, the wax peaks all shifted to the right, and the wax content increased. Under the synergistic catalytic aquathermolysis of heavy oil with exogenous catalyst and minerals, it is helpful to break the C-C, C-N, and C-S bonds. The addition of a hydrogen donor further improves the viscosity reduction effect. This work will benefit related research on oilfield exploration.

References

1. Shaban, S.; Dessouky, S.; Badawi, A.E.F.; El Sabagh, A.; Zahran, A.; Mousa, M. Upgrading and viscosity reduction of Heavy oil by catalyst ionic liquid. *Energy Fuel* **2014**, *28*, 6545–6553. [CrossRef]
2. Li, Y.; Li, Q.; Wang, X.; Yu, L.; Yang, J. Aquathermolysis of heavy crude oil with ferric oleate catalyst. *Pet. Sci.* **2018**, *15*, 613–624. [CrossRef]
3. Pang, Z.; Wang, Q.; Tian, C.; Chen, J. Study on Hydrothermal Cracking of Heavy Oil under the Coexisting Conditions of Supercritical Water and Non-condensate Gas. *ACS Omega* **2023**, *8*, 18029–18040. [CrossRef]
4. Guo, K.; Li, H.; Yu, Z. In-situ heavy and extra-heavy oil recovery: A review. *Fuel* **2016**, *185*, 886–902. [CrossRef]
5. Muraza, O.; Galadima, A. Aquathermolysis of heavy oil: A review and perspective on catalyst development. *Fuel* **2015**, *157*, 219–231. [CrossRef]
6. Vakhin, A.V.; Khelkhal, M.A.; Mukhamatdinov, I.I.; Mukhamatdinova, R.E.; Tajik, A.; Slavkina, O.V.; Malaniy, S.Y.; Gafurov, M.R.; Nasybullin, A.R.; Morozov, O.G. Changes in Heavy Oil Saturates and Aromatics in the Presence of Microwave Radiation and Iron-Based Nanoparticles. *Catalysts* **2022**, *12*, 514. [CrossRef]
7. Huang, S.; Cao, M.; Huang, Q.; Liu, B.; Jiang, J. Study on reaction equations of heavy oil aquathermolysis with superheated steam. *Int. J. Environ. Sci. Technol.* **2019**, *16*, 5023–5032. [CrossRef]
8. Ushakova, A.; Zatsepin, V.; Khelkhal, M.; Sitnov, S.; Vakhin, A. In Situ Combustion of Heavy, Medium, and Light Crude Oils: Low-Temperature Oxidation in Terms of a Chain Reaction Approach. *Energy Fuels* **2022**, *36*, 7710–7721. [CrossRef]
9. Demirbas, A.; Bafail, A.; Nizami, A.S. Heavy oil upgrading: Unlocking the future fuel supply. *Pet. Sci. Technol.* **2016**, *34*, 303–308. [CrossRef]
10. Hou, J.; Li, C.; Gao, H.; Chen, M.; Huang, W.; Chen, Y.; Zhou, C. Recyclable oleic acid modified magnetic NiFe$_2$O$_4$ nanoparticles for catalytic aquathermolysis of Liaohe heavy oil. *Fuel* **2017**, *200*, 193–198. [CrossRef]
11. Chang, J.; Fujimoto, K.; Tsubaki, N. Effect of Initiative Additives on Hydro-Thermal Cracking of Heavy Oils and Model Compound. *Energy Fuels* **2003**, *17*, 457–461. [CrossRef]
12. Chen, G.; Yuan, W.; Yan, J.; Meng, M.; Guo, Z.; Gu, X.; Zhang, J.; Qu, C.; Song, H.; Jeje, A. Zn(II) Complex Catalyzed Coupling Aquathermolysis of Water-Heavy Oil-Methanol at Low Temperature. *Pet. Chem.* **2018**, *58*, 197–202. [CrossRef]

13. Chen, G.; Yan, J.; Bai, Y.; Gu, X.; Zhang, J.; Li, Y.; Jeje, A. Clean aquathermolysis of heavy oil catalyzed by Fe(III) complex at relatively low temperature. *Pet. Sci. Technol.* **2017**, *35*, 113–119. [CrossRef]
14. Mukhamed'yarova, A.N.; Gareev, B.I.; Nurgaliev, D.K.; Aliev, F.A.; Vakhin, A.V. A Review on the Role of Amorphous Aluminum Compounds in Catalysis: Avenues of Investigation and Potential Application in Petrochemistry and Oil Refining. *Processes* **2021**, *9*, 1811. [CrossRef]
15. Clark, P.; Dowling, N.; Hyne, J.; Lesage, K. The chemistry of organosulphur compound types occurring in heavy oils: 4. the high-temperature reaction of thiophene and tetrahydrothiophene with aqueous solutions of aluminium and first-row transition-metal cations. *Fuel* **1987**, *66*, 1353–1357. [CrossRef]
16. Ma, L.; Zhang, S.; Zhang, X.; Dong, S.; Yu, T.; Slaný, M.; Chen, G. Enhanced aquathermolysis of Heavy oil catalysed by bentonite supported Fe (III) complex in the present of ethanol. *J. Chem. Technol. Biotechnol.* **2022**, *97*, 1128–1137. [CrossRef]
17. Maity, S.K.; Ancheyta, J.; Marroquín, G. Catalytic Aquathermolysis Used for Viscosity Reduction of Heavy Crude Oils: A Review. *Energy Fuels* **2010**, *24*, 2809–2816. [CrossRef]
18. Zhong, L.; Liu, Y.; Fan, H.; Jiang, S.J. Liaohe Extra-Heavy Crude Oil Underground Aquathermolytic Treatments Using Catalyst and Hydrogen Donors under Steam Injection Conditions. In Proceedings of the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 8–9 October 2003. [CrossRef]
19. Clark, P.; Hyne, J. Chemistry of organosulphur compound types occurring in heavy oil sands: 3. Reaction of thiophene and tetrahydrothiophene with vanadyl and nickel salts. *Fuel* **1984**, *63*, 1649–1654. [CrossRef]
20. Chen, G.; Yuan, W.; Wu, Y.; Zhang, J.; Song, H.; Jeje, A.; Song, S.; Qu, C. Catalytic aquathermolysis of heavy oil by coordination complex at relatively low temperature. *Pet. Chem.* **2017**, *57*, 881–884. [CrossRef]
21. Zhao, F.; Liu, Y.; Lu, N.; Xu, T.; Zhu, G.; Wang, K. A review on upgrading and viscosity reduction of heavy oil and bitumen by underground catalytic cracking. *Energy Rep.* **2021**, *7*, 4249–4272. [CrossRef]
22. Al-Muntaser, A.A.; Varfolomeev, M.A.; Suwaid, M.A.; Saleh, M.M.; Djimasbe, R.; Yuan, C.; Zairov, R.R.; Ancheyta, J. Effect of decalin as hydrogen-donor for in-situ upgrading of Heavy crude oil in presence of nickel-based catalyst. *Fuel* **2022**, *313*, 122652. [CrossRef]
23. Zhao, F.; Liu, Y.; Fu, Z.; Zhao, X. Using hydrogen donor with oil-soluble catalysts for upgrading Heavy oil. *Russ. J. Appl. Chem.* **2014**, *87*, 1498–1506. [CrossRef]
24. Muneer, A.S.; Varfolomeev, M.A.; Al-muntaser, A.A.; Yuan, C.; Valentina, L.S.; Almaz, Z.; Farit, G.V.; Ilfat, Z.R.; Dmitrii, A.; Artem, E.C. In-situ catalytic upgrading of heavy oil using oil-soluble transition metal-based catalysts. *Fuel* **2020**, *282*, 118753. [CrossRef]
25. Zhao, F.; Wang, X.; Wang, Y.; Shi, Y. Study of catalytic aquathermolysis of heavy oil in the presence of a hydrogen donor. *J. Chem. Pharm. Res.* **2012**, *48*, 273–282. [CrossRef]
26. Zhou, Z.; Slaný, M.; Kuzielová, E.; Zhang, W.; Ma, L.; Dong, S.; Zhang, J.; Chen, G. Influence of reservoir minerals and ethanol on catalytic aquathermolysis of Heavy oil. *Fuel* **2022**, *307*, 121871. [CrossRef]
27. Kuzmić, A.E.; Radošević, M.; Bogdanić, G.; Srića, V.; Vuković, R. Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives. *Fuel* **2008**, *87*, 2943–2950. [CrossRef]
28. Hu, J.; Gan, J.; Li, J.; Luo, Y.; Wang, G.; Wu, L.; Gong, Y. Extraction of crude oil from petrochemical sludge: Characterization of products using thermogravimetric analysis. *Fuel* **2017**, *188*, 166–172. [CrossRef]
29. Ovalles, C.; Filgueiras, E.; Morales, A.; Scott, C.E.; Gonzalez-Gimenez, F.; Embaid, B.P. Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen. *Fuel* **2003**, *82*, 887–892. [CrossRef]
30. Aliev, F.A.; Mukhamatdinov, I.I.; Sitnov, S.A.; Ziganshina, M.R.; Onishchenko, Y.V.; Sharifullin, A.V.; Vakhin, A.V. In-situ Heavy oil aquathermolysis in the presence of nanodispersed catalysts based on transition metals. *Processes* **2021**, *9*, 127. [CrossRef]
31. Cornejo, J.; Celis, R.; Pavlovic, I.; Ulibarri, M.A. Interactions of pesticides with clays and layered double hydroxides: A review. *Clay Miner.* **2008**, *43*, 155–175. [CrossRef]
32. Boulet, P.; Greenwell, H.C.; Stackhouse, S.; Coveney, P.V. Recent advances in understanding the structure and reactivity of clays using electronic structure calculations. *Theochem* **2005**, *762*, 33–48. [CrossRef]
33. Wu, L.M.; Zhou, C.H.; Keeling, J.; Tong, D.S.; Yu, W.H. Towards an understanding of the role of clay minerals in crude oil formation, migration and accumulation. *Earth. Sci. Rev.* **2012**, *115*, 373–386. [CrossRef]
34. Johns, W.D. Clay mineral catalysis and petroleum generation. *Annu. Rev. Earth. Planet. Sci.* **1979**, *7*, 183–198. [CrossRef]
35. Brown, D.R.; Rhodes, C.N. Bronsted and Lewis acid catalysis with ion-exchanged clays. *Catal. Lett.* **1997**, *45*, 35–40. [CrossRef]
36. Bruce, C.H. Smectite dehydration-its relation to structural development and hydrocarbon accumulation in Northern Gulf of Mexico Basin. *AAPG Bull.* **1984**, *68*, 673–683. [CrossRef]
37. Reddy, C.R.; Bhat, Y.S.; Nagendrappa, G.; Prakash, B.J. Bronsted and Lewis acidity of modified montmorillonite clay catalysts determined by FT-IR spectroscopy. *Catal. Today.* **2009**, *141*, 157–160. [CrossRef]
38. Yan, L.; Stucki, J.W. Effects of structural Fe oxidation state on the coupling of interlayer water and structural Si-O stretching vibrations in montmorillonite. *Langmuir* **1999**, *15*, 4648–4657. [CrossRef]