Article

Influence of Carbonate Minerals on Heavy Oil Oxidation Behavior and Kinetics by TG-FTIR

Kristina A. Ariskina ¹, Zhenfeng Ding ², Mustafa Abaas ¹, Chengdong Yuan ^{1,3,*}, Dmitrii A. Emelianov ¹, Qing Chen ⁴ and Mikhail A. Varfolomeev ^{3,*}

¹ Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia; ariskina.kristina@gmail.com (K.A.A.); mustafa988@yahoo.com (M.A.); dima_emelyan@mail.ru (D.A.E.)

² Research Institute of Petroleum Exploration and Development, PetroChina, Beijing 100083, China; dingzhenfeng@petrochina.com.cn

³ Department of Petroleum Engineering, Kazan Federal University, 420008 Kazan, Russia

⁴ Research Institute of Petroleum Engineering, Tarim Oilfield Company, PetroChina, Korla 841000, China; chq-tlm@petrochina.com.cn

* Correspondence: jchengdong@kpfu.ru (C.Y.); mikhail.varfolomeev@kpfu.ru (M.A.V.)

Abstract: The impact of rock minerals on the performance of in situ combustion (ISC) techniques for enhanced oil recovery (EOR) is very important. This work is aimed at investigating the influence of carbonate rocks (dolomite and calcite) on heavy oil oxidation by Thermogravimetry–Fourier-Transform-Infrared (TG-FT-IR) coupled analysis. Two heavy oils with 19.70° and 14.10° API were investigated. Kinetic analysis was performed using TG data by differential and integral isoconversional methods. From TG-DTG curves, three reaction stages, i.e., low-temperature oxidation (LTO), fuel deposition (FD), and high-temperature oxidation (HTO), were defined for both two heavy oil samples, and their reaction mechanism was explained combining the FT-IR data. After the addition of calcite or dolomite, three reaction stages became two with the disappearance of FD, and a significant shift of reaction stages into lower temperatures was also observed. These significant changes in oxidation behavior are because calcite and dolomite promoted the coke formation and combustion by reducing the activation energy barrier and changing reaction pathways, which results in a smooth transition from LTO to HTO. Dolomite exhibited a slightly better promotion effect on LTO-FD than calcite, while calcite exhibited a better acceleration effect on FD-HTO than dolomite in terms of shifting reaction stages. Generally, calcite exhibited a better catalytic effect than dolomite. In spite of the different catalytic performance of calcite and dolomite, they do both show positive effects on combustion process regardless of the difference in the properties and composition of heavy oils. The findings in this work indicate that calcite and dolomite rocks are favorable for the ISC process, and when it comes to the ISC kinetics, the interaction between crude oil and rock must be considered.

Keywords: heavy oil oxidation; kinetics; dolomite rock; calcite rock; TG-FT-IR; in situ combustion

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1. Introduction

The in situ combustion (ISC) technique for heavy oil recovery has several merits in comparison with other thermal enhanced oil recovery (EOR) methods, such as readily accessible injection fluid (air) with low cost without having to consider the location of reservoirs, high oil recovery yielded by a multiple displacement mechanism, in situ upgrading of heavy oil, high thermal efficiency with less heat loss on the ground and well bore, and a wide applicability for different types of reservoir conditions [1–5]. ISC is the oldest thermal recovery method with a history of about one century [4]. However, in spite of having so many merits and a long history, ISC is still not widely applied in oil fields due to its complexity and the lack of understanding, which originally comes of the complicated chemical reactions between crude oils and air occurring in the porous media of rock in ISC processes [1,6]. These reactions strongly depend upon the composition of crude oils

and rock as well as their interaction during the reactions at elevated temperatures [5,7–9]. Therefore, it is always necessary to perform the fundamental research to understand the oxidation reaction processes and kinetics of different types of crude oils as well as their mutual interaction with different rock minerals.

Rock, as the porous media where the oxidation reactions occur, has been reported to have a significant influence on the chemical reactions occurring in ISC processes. Since the 1980s, a lot of work has been performed to try to understand the influence of rock minerals. Some positive effects of different rocks or rock minerals on the different stages of oxidation reactions of crude oils, including low-temperature oxidation (LTO), fuel deposition (FD), and high-temperature oxidation (HTO), have been found, for instance:

- Acceleration of crude oil oxidation by kaolinite's catalytic and surface area effect [10];
- Shifting of oxidation reactions into lower temperature and reduction in activity energy by increased the specific surface area effect of clays [11];
- Enhancement in the deposition and combustion of fuel (coke) by clays [1,12,13];
- Promotion in the LTO of linear alkanes by illite [14];
- Decrease in the apparent activation energy of oxidation reaction of crude oils by clays [15–18];
- Promotion of fuel formation by carbonate rock [19];
- Reduced activation energy but not affected reaction model by limestone (major calcite + minor dolomite) [20];
- Promotion of LTO with higher oxygen consumption and carbon oxides release by montmorillonite > illite > chlorite > kaolinite [21];
- Increased heat release in LTO by montmorillonite [22];
- Promoting the formation of cribriform structures on asphaltenes surface that aids the combustion of asphaltenes by increasing its surface area by clays (90 wt % kaolinite and 10 wt % illite) [23];
- Merging FD into HTO, shifting reaction intervals (LTO and HTO) into lower temperatures, and significantly reducing activation energy by 54% quartz and 46% mica [24];
- Shift of the reaction intervals into lower temperature and lower activation energy by surface area and catalytic effect of kaolinite, bentonite, and illite [25];
- Clay minerals may be favorable for the combustion of asphaltenes by forming cribriform structures that increase the surface area of asphaltenes [23].

Some of these positive effects were also observed in the presence of different types of reservoir rocks [26–28]. However, some negative effect was also observed for carbonate minerals. For instance, it was found that the presence of carbonate minerals has a negative effect on the combustion and cracking reactions of asphaltenes [5].

The concise review indicates that different rocks and rock minerals have been studied. However, it can be seen that sometimes, there are some different opinions in terms of the effect of rock minerals. For instance, someone concluded that montmorillonite has the best catalytic effect among other clay minerals such as kaolinite and illite [21,29], but in another research, kaolinite or illite might show a better catalytic effect [10,25]. This on the one side can be caused by the different composition of these clay minerals, because the “montmorillonite” in one work can be different from the “montmorillonite” in another work in terms of composition. Therefore, a detailed characterization is always necessary to determine the composition of the used minerals, and unfortunately, this information sometimes is not provided. On the other side, this also depends on the composition of crude oils, since the oxidation behavior of different oils is different, and ISC has different requirements to maintain successful and stable combustion for light, medium, and heavy oil [6,30]. Minerals can show a different effect for different oils, which is similar to other catalysts [30]. Therefore, for a specific reservoir, the effect of rock or rock minerals should be always studied before ISC is applied. This is why this work has never been stopped since the 1980s, because the composition of rock minerals and crude oils usually has a big difference from one reservoir to another.

From the summarized concise literature review, we can also see that more attention was paid to the clay minerals and less studies were focused on carbonate minerals [31]. In fact, sandstone rocks contain more clay minerals, while carbonate rocks usually contain no or little clay minerals. However, carbonate rock hosts more than 60% of the world's known oil reserves [24]. Therefore, more attention should be paid to carbonate minerals, too. The target of this work is to study the possible catalytic effect of two typical carbonate rocks in the Tatarstan republic (Russia) on the oxidation of heavy oils with different properties and composition. This work can enrich the database about the effect of different rock minerals on different types of oils, which can provide a guide for the field application of ISC and improve the theory related to ISC.

2. Materials and Methods

2.1. Samples Characterization

Two heavy crude oil samples, designated as crude oil-1 and crude oil-2, were provided by different oil fields located in Republic of Tatarstan, Russia. In these two oil fields, the ISC method has been considered to have potential for EOR. The dynamic viscosity of the heavy oils was determined using the Brookfield DV-II + Pro rotary viscometer at the temperature of 25 °C. The Saturate, Aromatic, Resin, and Asphaltene (SARA) fractions of the heavy oil samples were analyzed by the ASTM D 4124 method (ASTM D 4124–09, 2018). The properties and composition of the two heavy oils are presented in Table 1. The heavier crude oil-2 has around 1.5 times higher viscosity than crude oil-1 but less content of asphaltenes.

Table 1. Properties of the heavy oils.

Property	Oil-1	Oil-2
API gravity (°)	19.70	14.10
Viscosity (MPa·s)	1438.50	2073.00
Saturates (%)	30.74	28.79
Aromatics (%)	40.22	44.32
Resins (%)	20.47	20.98
Asphaltenes (%)	8.57	5.91

The composition of two carbonate rocks was quantitatively analyzed by X-ray diffractometer. XRD spectra and the composition of two carbonated rocks are shown in Figure 1 and Table 2, respectively. One carbonate rock is identified as calcite rock containing 75% calcite and 25% dolomite. Another is characterized as dolomite rock containing 91.5% dolomite, 6.0% calcite, and a small amount of albite (2.2%) and quartz (0.3%). Calcite and dolomite rocks were crushed to particles (63–100 mesh).

Table 2. Mineral composition of calcite and dolomite rocks.

Rock Type	Mineral Content, %			
	Calcite	Dolomite	Albite	Quartz
Calcite rock	75.0	25.0	–	–
Dolomite rock	6.0	91.5	2.2	0.3

Figure 1. XRD patterns of calcite and dolomite rocks.

2.2. Thermogravimetry–Fourier-Transform-Infrared (TG-FT-IR) Coupled Analysis

The coupling of TG 209 F1 Libra Thermogravimetry (Netzsch, Germany) and an ALPHA II FT-IR spectrometer (Bruker, Germany) was used to study the oxidation reactions of the two heavy oils and the influence of calcite and dolomite rock at elevated temperature. For a more accurate estimation of kinetics by isoconversional methods, the experiments were performed at four heating rates of 4, 6, 8, and 10 °C/min [32]. The other conditions for TG-FT-IR experiments are as follows: the temperature range of 30–700 °C; 45 mL·min^{−1}, and 30 mL·min^{−1}—protective gas flow rate and airflow rate, respectively; total sample masses of about 10 mg and 50 mg were loaded in the crucible in experiments for pure heavy oil and for the mixture, respectively. For the sample of oil + carbonate rocks, the heavy oil was thoroughly mixed with carbonate rock at the percent ratio of 20% to 80%. The TG equipment was calibrated for each heating rate before experiments as described by Yuan et al. [6].

3. Results and Discussion

3.1. Thermal Behavior of Heavy Oil Characterized by TG-FT-IR

The thermal behavior of the two heavy crude oils with different physical–chemical properties characterized by TG is presented in Figure 2. Three main stages were iden-

tified as LTO, FD, and HTO from low to high temperature, respectively [6,27,33,34]. In addition, oil-1 also exhibits a distinct mass loss peak in DTG curves at approximately 100 °C. This is the evaporation of water contained in the heavy oil, which can be supported by the water peak appearing in the FT-IR spectra of effluent gases (Figure 3). LTO (approximately <420 °C) is characterized by the largest mass loss ($\approx 60\%$) due to the evaporation of light-medium hydrocarbon fractions, which is supported by the peak of saturated C-H bonds in gaseous products in FT-IR spectra. Note that the evaporation of hydrocarbons (distillation process) plays a vital role in the oil displacement mechanism in the ISC process. The main reaction that occurs in LTO is the formation of hydroperoxides by oxygen addition reactions (Reaction (R1)) and their subsequent isomerization/decomposition reactions (also described as bond scission reactions) [30,33].

where RH represents hydrocarbons and ROOH represents hydroperoxides.

Figure 2. TG/DTG curves of oil-1 (left) and oil-2 (right) at different heating rates.

Figure 3. FT-IR spectra of the main gaseous products absorbance as a function of the temperature for crude oil-1 (left) and crude oil-2 (right).

According to the FT-IR spectra (Figure 3), it can be concluded that the oxygen addition reactions were dominant before 200 °C almost without releasing any other gaseous products except for saturated C-H bonds (for oil-1, the release of water was mainly from the initial water in oil). From about 200 °C, the isomerization/decomposition reactions started to prevail, and those reactions that produce water started first (such as from Reactions (R2)–(R4)), which was followed by those reactions producing CO and volatile compounds with C=O groups indicated by the peaks of CO and C=O groups from about 300 to 400 °C.

where RO[·], R[·], ·OH, and ROH represent alkoxy free radicals, alkyl free radicals, hydroxyl radicals, and alcohols, respectively. Yuan et al. [6] also showed that the reactions producing water occurred earlier at lower temperature than those releasing C=O groups and CO. Generally, the main products in LTO include carboxylic acids, ketones, alcohols, aldehydes, cyclic ethers, carbonyl derivatives, water, CO, and CO₂ [35–39]. More details about the reaction pathways of LTO were described by Yuan et al. [40].

After LTO, there is an FD stage (420–510 °C) where cracking/pyrolysis reactions occurred to generate coke, which is followed by coke combustion in HTO. In HTO, the main products are CO₂ and CO, which is indicated by their intensive peaks in the FT-IR spectra. In general, there is no big difference in the thermal oxidation behavior of two oils in terms of the temperature ranges and peak temperature of reaction stages (Table 3).

Table 3. Temperature range, peak temperature, and mass loss for each reaction region obtained from the TG/DTG curves of pure oils oxidation.

Heating Rate (°C/min)	LTO			FD			HTO		
	Temp. Range (°C)	Peak Temp. (°C)	Mass Loss (%)	Temp. Range (°C)	Peak Temp. (°C)	Mass Loss (%)	Temp. Range (°C)	Peak Temp. (°C)	Mass Loss (%)
Crude oil-1									
4	<367.5	318.7	55.4	367.5–469.1	418.1	18.3	482.6–597.1	522.7	24.8
6	<393.8	333.1	57.7	393.8–486.6	453.4	18.6	490.3–627.4	527.7	21.7
8	<405.5	346.8	59.2	405.5–492.5	455.8	17.7	503.6–644.0	536.5	21.3
10	<426.1	351.0	64.0	426.1–508.2	460.1	14.9	515.6–652.8	556.9	18.1
Crude oil-2									
4	<366.4	314.1	56.2	366.4–472.6	429.5	17.8	472.6–593.5	534.4	25.5
6	<381.8	330.4	57.7	381.8–486.2	448.5	19.0	486.2–624.4	545.0	23.0
8	<392.4	339.7	59.2	392.4–500.7	452.4	18.9	500.7–642.9	562.2	21.6
10	<428.2	347.6	65.4	428.2–510.4	457.7	13.0	510.4–666.9	574.4	21.2

Temp. represents temperature.

3.2. Influence of Calcite and Dolomite Rocks on the Thermal Behavior of Heavy Oil

Figure 4 shows the comparison of TG/DTG curves of the heavy oils + calcite and heavy oils + dolomite. In the presence of dolomite and calcite, the reaction stages were changed from three to two. It seems as though the FD stage between LTO and HTO disappeared, and both LTO and HTO were shifted into lower temperatures. In fact, a fuel deposition (coke formation) reaction still occurred, but it was accelerated by the calcite and dolomite minerals. This can be proved by the FT-IR spectra of the released gases (Figure 5). It can be observed that the peak of saturated C-H bonds in the FD stage for pure heavy oil oxidation disappeared and merged together with the second peak in the later stage of LTO (Figure 3), which, consequently, leads to an intensive, wider peak in Figure 5. In addition, the peak of CO was also changed from two separate peaks to one main peak with a shoulder. A much wider CO₂ peak appeared from about 300 °C to the end of HTO. All the signs indicate that the formation of coke happened earlier even at the final of LTO, and its subsequent combustion also occurred more easily at lower temperatures, which makes

the reactions smoothly transition from LTO to HTO without an obvious transition stage of FD in TG/DTG curves. Nevertheless, considering the fact that fuel deposition reactions occurred in both LTO and HTO, therefore, it is more accurate to name the observed two reaction stages in Figure 5 as low-temperature oxidation-fuel deposition (LTO-FD) and fuel deposition-high-temperature oxidation (FD-HTO) instead of only LTO and HTO. The temperature data are shown in Table 4 for each reaction stage. If comparing the peak temperature of LTO-FD and FD-HTO with calcite rock or dolomite rock in Table 4 with that of LTO and HTO of pure heavy oil without minerals (Table 3), it can be found that the reaction stages were significantly shifted into lower temperatures. A similar promotion effect of calcite was also observed by Abaas et al. [31]. Take the data at 10 °C/min as examples, for oil-1, the peak temperature of LTO was shifted from 351.0 to 332.0 °C and 320.7 °C and the peak temperature of HTO was shifted from 556.9 to 463.0 °C and 476.0 °C in the presence of calcite and dolomite, respectively. For oil-2, the peak temperature of LTO and HTO was shifted from 347.6 °C and 574.4 °C to 320.7 °C and 440.1 °C for calcite and to 316.0 °C and 505.3 °C for dolomite, respectively. It should be noted that both two minerals showed little effects on the initial stage of LTO, and they showed a more positive influence on FD-HTO than LTO-FD, which indicates that these rocks more significantly affect the coke formation and combustion. If comparing calcite and dolomite, calcite showed a much higher promotion effect on FD-HTO than dolomite from the point of view of shifting reaction stages into lower temperature, while dolomite showed a slightly better effect on LTO-FD (mainly isomerization/decomposition reactions took place at the final stage of LTO) than calcite. Note that calcite promoted the FD-HTO of oil-2 more than oil-1, which means that the catalytic effect of minerals also depends on the nature of crude oils.

Table 4. Temperature range, peak temperature, and mass loss for each reaction region obtained from the TG/DTG curves of oils in the presence of calcite/dolomite rock.

Heating Rate (°C/min)	LTO-FD			FD-HTO		
	Temp. Range (°C)	Peak Temp. (°C)	Mass Loss (%)	Temp. Range (°C)	Peak Temp. (°C)	Mass Loss (%)
Crude oil-1 with calcite rock						
4	<372.3	308.0	12.6	372.3–524.1	428.3	6.1
6	<381.3	319.1	12.7	381.3–534.8	440.6	6.1
8	<383.0	323.2	12.3	383.0–540.6	447.9	6.4
10	<391.2	332.0	12.3	391.2–572.3	463.0	6.5
Crude oil-1 with dolomite rock						
4	<367.3	295.0	11.7	367.3–526.6	445.2	7.2
6	<378.8	307.4	11.8	378.8–538.9	460.7	7.2
8	<384.6	312.9	11.9	384.6–552.1	468.4	7.3
10	<397.0	320.7	11.9	397.0–567.8	476.0	7.3
Crude oil-2 with calcite rock						
4	<360.7	289.9	13.0	360.7–526.3	404.3	6.9
6	<369.0	309.4	12.9	369.0–532.9	425.0	6.9
8	<376.4	316.2	13.1	376.4–545.3	430.4	6.8
10	<383.0	320.7	13.0	383.0–572.8	440.1	6.9
Crude oil-2 with dolomite rock						
4	<361.1	293.9	12.0	361.1–522.5	470.7	7.3
6	<375.1	303.7	12.2	375.1–548.9	487.0	7.2
8	<385.9	311.1	12.4	385.9–554.7	496.0	7.1
10	<394.9	316.0	12.4	394.9–582.6	505.3	7.0

Figure 4. TG/DTG curves of crude oil-1 (left) and crude oil-2 (right) with calcite/dolomite rock at a heating rate of 10 °C/min.

Figure 5. The absorbance of gaseous products as a function of the temperature for oil-1 with calcite rock (1), oil-1 with dolomite rock (2), oil-2 with calcite rock (3), and oil-2 with dolomite rock (4).

3.3. Influence of Calcite and Dolomite on the Kinetic Analysis of Heavy Oil Oxidation

Unlike the kinetics calculation for one- and two-component systems where kinetic parameters could be determined quite accurately, the kinetic analysis of crude oil is more complicated due to its multi-component composition. Considering this, isoconversional (model-free) kinetic methods were used for the calculation of apparent activation energy. In this work, three isoconversional methods, i.e., Kissinger–Akahira–Sunose (KAS), Friedman, and Ozawa–Flynn–Wall (OFW) methods, were employed. All these kinetic methods are generally based on the Arrhenius' reaction rate equation (Equation (1)) [41].

$$\frac{d\alpha}{dt} = A \cdot e^{-\frac{E_\alpha}{R \cdot T}} \cdot f(\alpha) \quad (1)$$

where α is the conversion degree, t is the time, A is the preexponential factor, E_α is the activation energy, R is the gas constant, T is the temperature, and $f(\alpha)$ is the function reflecting the reaction model. By taking the natural logarithm of the Arrhenius Equation (1), the Friedman method is obtained as shown in Equation (2) [32]:

$$\ln \left[\beta_i \left(\frac{d\alpha}{dt} \right)_{\alpha, i} \right] = \ln[f(\alpha) \cdot A] - \frac{E_\alpha}{R \cdot T_{\alpha, i}} \quad (2)$$

where β represents heating rate, and i represents different temperature programs (different heating rates in this work). The OFW and KAS methods use Equations (3) and (4), respectively [32]:

$$\ln(\beta_i) = \text{Const} - 1.052 \left(\frac{E_\alpha}{R \cdot T_\alpha} \right) \quad (3)$$

$$\ln \left(\frac{\beta_i}{T_{\alpha, i}^2} \right) = \text{Const} - C \left(\frac{E_\alpha}{R \cdot T_\alpha} \right). \quad (4)$$

The plot of $\ln \left[\beta_i \left(\frac{d\alpha}{dt} \right)_{\alpha, i} \right]$ vs. $\frac{1}{R \cdot T_{\alpha, i}}$, $\ln(\beta_i)$ vs. $\frac{1}{R \cdot T_\alpha}$, and $\ln \left(\frac{\beta_i}{T_{\alpha, i}^2} \right)$ vs. $\frac{1}{R \cdot T_\alpha}$ obtained from Friedman, OFW, and KAS methods can help to determine the values of E_α at different α , as shown in Figures 6–8. For the two heavy oils, the dependence of E on α shows a similar trend for all three methods. In LTO, E_α increases slightly with α in the initial stage (about 50–130 kJ/mol for oil-1 and 75–140 kJ/mol for oil-2). In this stage, calcite and dolomite almost did not change E_α . This is in agreement with those observations from TG/DTG curves that calcite and dolomite rocks had little effect on the initial stage. At the final stage of LTO, E_α increases faster with the reactions transitioning from LTO to FD, and a jump and fluctuation of E_α values (maximum about 540 kJ/mol) are observed in the FD stage. This indicates the complexity and difficulty of coke formation oxidative cracking/pyrolysis and isomerization/decomposition reactions. However, after the addition of calcite or dolomite, the jump-fluctuation behavior of E_α values do not appear, and they are kept almost stable or slightly decrease after the increase at the final stage of LTO. The significant decrease of E_α values and the elimination of jump-fluctuation behavior indicate that the coke formation and combustion reactions were effectively catalyzed by calcite and dolomite and became easier due to the reduction in the activation energy barrier, which results in a smooth transition from LTO to HTO. The significant reduction of E_α also implies that the reaction pathways of coke formation and combustion were changed [24]. In addition to the ease of coke formation, this also implies that once the coke is formed, it is ready for combustion and can be immediately consumed. This is very important for sustaining a stable combustion front in the field application of the ISC process. In addition, we can see that calcite gives a better catalytic effect than dolomite in terms of E_α reduction. This phenomenon was also observed by Abass.

Figure 6. Dependence of apparent activation energy upon the conversion degree calculated using the Friedman method. (Left): crude oil–1; (Right): crude oil–2.

Figure 7. Dependence of apparent activation energy upon the conversion degree calculated using the OFW method. (Left): crude oil–1; (Right): crude oil–2.

Figure 8. Dependence of apparent activation energy upon the conversion degree calculated using the KAS method. (Left): crude oil–1; (Right): crude oil–2.

4. Conclusions

The thermo-kinetic analysis was carried out to reveal the effect of carbonate rocks (calcite and dolomite rocks) on the heavy oil oxidation. Three stages, i.e., LTO, FD, and HTO, were defined from TG/DTG curves for both heavy oil-1 and heavy oil-2. Despite there being some differences in the viscosity and the content of asphaltenes, the two oils showed very similar temperature intervals and peak temperatures for each reaction stage. With the addition of calcite or dolomite rocks, three reaction stages became two with the disappear of the FD interval in the TG-DTG curves. Simultaneously, a significant shift of reaction intervals to lower temperatures was observed. The FT-IR data showed that after the addition of calcite or dolomite rock, fuel formation reactions started from the final stage of LTO and crossed to the HTO, which was the main reason that FD disappeared in TG-DTG curves. Both calcite and dolomite accelerated coke formation and combustion by reducing the activation energy barrier and changing reaction pathways, which thus resulted in a smooth transition from LTO to HTO. That is also the reason the two minerals exhibited a more positive influence on FD-HTO and showed little effects in the beginning of LTO. When comparing the two minerals, calcite showed a much higher promotion effect on FD-HTO than dolomite, while dolomite showed a slightly better effect on LTO-FD (mainly isomerization/decomposition reactions at the final stage of LTO) than calcite in terms of shifting reaction stages. When it comes to activation energy reduction, calcite exhibited a better catalytic effect, and the influence of calcite rock on the coke formation and combustion for heavy oil-2 is more significant than that for heavy oil-1.

In general, both calcite and dolomite do positively affect the coke formation and combustion regardless of the difference in the properties and composition of heavy oils. The ease of coke formation and combustion is favorable for sustaining a stable combustion front. This is very important for the field application of ISC process. In addition, this implies that the ISC process is promising for heavy oil recovery in carbonate reservoirs because of the catalytic effect of calcite and dolomite. Considering the fact that the combustion behavior characterized by different methods is diverse, it is recommended to study the catalytic effect of these carbonate minerals by other methods as well in the future, such as differential scanning calorimetry, accelerating rate calorimeter, and combustion tube, etc., to get an overall understanding of the catalytic performance of these minerals.

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References

1. Hascakir, B.; Ross, C.M.; Castanier, L.M.; Kovscek, A.R. Fuel formation and conversion during in-situ combustion of crude oil. *SPE J.* **2013**, *18*, 1217–1228. [CrossRef]
2. Yuan, C.; Varfolomeev, M.A.; Emelianov, D.A.; Suwaid, M.A.; Khachatryan, A.A.; Starshinova, V.L.; Vakhitov, I.R.; Al-Muntaser, A.A. Copper stearate as a catalyst for improving the oxidation performance of heavy oil in in-situ combustion process. *Appl. Catal. A Gen.* **2018**, *564*, 79–89. [CrossRef]
3. Mehrabi-Kalajahi, S.; Varfolomeev, M.A.; Yuan, C.; Zinnatullin, A.L.; Rodionov, N.O.; Vagizov, F.G.; Osin, Y.N.; Yakimova, L.S. Improving heavy oil oxidation performance by oil-dispersed CoFe_2O_4 nanoparticles in In-situ combustion process for enhanced oil recovery. *Fuel* **2021**, *285*, 119216. [CrossRef]
4. Sarathi, P.S. *In-Situ Combustion Handbook—Principles and Practices*; United States Department of Energy, National Petroleum Technology Office: Tulsa, OK, USA, 1999.

5. Pope, C.; Ismail, N.B.; Hascakir, B. Impact of carbonates on reaction kinetics of a bitumen combustion. In Proceedings of the Society of Petroleum Engineers—SPE Canada Heavy Oil Conference 2020, Virtual, 29 September–2 October 2020.
6. Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A. Oxidation Behavior and Kinetics of Light, Medium, and Heavy Crude Oils Characterized by Thermogravimetry Coupled with Fourier Transform Infrared Spectroscopy. *Energy Fuels* **2018**, *32*, 5571–5580. [\[CrossRef\]](#)
7. Yuan, C.; Varfolomeev, M.A.; Emelianov, D.A.; Eskin, A.A.; Nagrimanov, R.N.; Kok, M.V.; Afanasiev, I.S.; Fedorchenko, G.D.; Kopylova, E.V. Oxidation Behavior of Light Crude Oil and Its SARA Fractions Characterized by TG and DSC Techniques: Differences and Connections. *Energy Fuels* **2018**, *32*, 801–808. [\[CrossRef\]](#)
8. Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A.; Pu, W.; Ushakova, A.S. Oxidation Behavior and Kinetics of Eight C₂₀–C₅₄ n-Alkanes by High Pressure Differential Scanning Calorimetry (HP-DSC). *Energy Fuels* **2018**, *32*, 7933–7942. [\[CrossRef\]](#)
9. Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A.; Abaas, M. Combustion behavior of aromatics and their interaction with n-alkane in in-situ combustion enhanced oil recovery process: Thermochemistry. *J. Ind. Eng. Chem.* **2019**, *76*, 467–475. [\[CrossRef\]](#)
10. Vossoughi, S.; Willhite, G.; El Shoubary, Y.; Bartlett, G. Study of the clay effect on crude oil combustion by thermogravimetry and differential scanning calorimetry. *J. Therm. Anal.* **1983**, *27*, 17–36. [\[CrossRef\]](#)
11. Drici, O.; Vossoughi, S. Study of the Surface Area Effect on Crude Oil Combustion By Thermal Analysis Techniques. *JPT J. Pet. Technol.* **1985**, *37*, 731–735. [\[CrossRef\]](#)
12. Kök, M.V. Influence of reservoir rock composition on the combustion kinetics of crude oil. *J. Therm. Anal. Calorim.* **2009**, *97*, 397–401. [\[CrossRef\]](#)
13. Zheng, R.; Pan, J.; Chen, L.; Tang, J.; Liu, D.; Song, Q.; Chen, L.; Yao, Q. Catalytic Effects of Montmorillonite on Coke Formation during Thermal Conversion of Heavy Oil. *Energy Fuels* **2018**, *32*, 6737–6745. [\[CrossRef\]](#)
14. Faure, P.; Landais, P. Evidence for clay minerals catalytic effects during low-temperature air oxidation of n-alkanes. *Fuel* **2000**, *79*, 1751–1756. [\[CrossRef\]](#)
15. Kök, M.V. Effect of clay on crude oil combustion by thermal analysis techniques. *J. Therm. Anal. Calorim.* **2006**, *84*, 361–366. [\[CrossRef\]](#)
16. Kok, M.V.; Gundogar, A.S. Effect of different clay concentrations on crude oil combustion kinetics by thermogravimetry. *J. Therm. Anal. Calorim.* **2010**, *99*, 779–783. [\[CrossRef\]](#)
17. Kok, M.V. Clay concentration and heating rate effect on crude oil combustion by thermogravimetry. *Fuel Process. Technol.* **2012**, *96*, 134–139. [\[CrossRef\]](#)
18. Varfolomeev, M.A.; Nurgaliev, D.K.; Kok, M.V. Calorimetric study approach for crude oil combustion in the presence of clay as catalyst. *Pet. Sci. Technol.* **2016**, *34*, 1624–1630. [\[CrossRef\]](#)
19. Yuan, C.D.; Pu, W.F.; Jin, F.Y.; Zhang, J.J.; Zhao, Q.N.; Li, D.; Li, Y.B.; Chen, Y.F. Characterizing the Fuel Deposition Process of Crude Oil Oxidation in Air Injection. *Energy Fuels* **2015**, *29*, 7622–7629. [\[CrossRef\]](#)
20. Karimian, M.; Schaffie, M.; Fazaelpoor, M.H. Estimation of the kinetic triplet for in-situ combustion of crude oil in the presence of limestone matrix. *Fuel* **2017**, *209*, 203–210. [\[CrossRef\]](#)
21. Zheng, R.; Pan, J.; Cai, G.; Liang, J.; Liu, D.; Song, Q.; Yao, Q. Effects of clay minerals on the low-temperature oxidation of heavy oil. *Fuel* **2019**, *254*, 115597. [\[CrossRef\]](#)
22. Yu, X.; Qu, Z.; Kan, C.; Zhao, X. Effect of Different Clay Minerals on Heavy Oil Oxidation during Ignition Process. *Energy Fuels* **2017**, *31*, 12839–12847. [\[CrossRef\]](#)
23. Ismail, N.B.; Hascakir, B. Impact of asphaltenes and clay interaction on in-situ combustion performance. *Fuel* **2020**, *268*, 117358. [\[CrossRef\]](#)
24. Ariskina, K.A.; Yuan, C.; Abaas, M.; Emelianov, D.A.; Rodionov, N.; Varfolomeev, M.A. Catalytic effect of clay rocks as natural catalysts on the combustion of heavy oil. *Appl. Clay Sci.* **2020**, *193*, 105662. [\[CrossRef\]](#)
25. Kök, M.V.; Varfolomeev, M.A.; Nurgaliev, D.K. TGA and DSC investigation of different clay mineral effects on the combustion behavior and kinetics of crude oil from Kazan region, Russia. *J. Pet. Sci. Eng.* **2021**, *200*, 108364. [\[CrossRef\]](#)
26. Pu, W.; Zhao, S.; Pan, J.; Wang, R.; Chen, L.; Kan, N.; Wang, L. Comparative analysis of quartz sand and detritus effects on thermal behavior and kinetics of heavy crude oil. *Thermochim. Acta* **2018**, *667*, 153–159. [\[CrossRef\]](#)
27. Verşan Kök, M.; Varfolomeev, M.A.; Nurgaliev, D.K. Thermal characterization of crude oils in the presence of limestone matrix by TGA-DTG-FTIR. *J. Pet. Sci. Eng.* **2017**, *154*, 495–501. [\[CrossRef\]](#)
28. Varfolomeev, M.A.; Nurgaliev, D.K.; Kok, M.V. Thermal, kinetics, and oxidation mechanism studies of light crude oils in limestone and sandstone matrix using TG-DTG-DTA: Effect of heating rate and mesh size. *Pet. Sci. Technol.* **2016**, *34*, 1647–1653. [\[CrossRef\]](#)
29. Guowei, Q.; Yaling, W.; Xu, D.; Wenlong, Q.; Mei, W.; Yanzhao, Z. Influence of clay minerals on oxidation reaction of light crude oil. *Pet. Sci. Technol.* **2019**, *37*, 566–572. [\[CrossRef\]](#)
30. Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A.; Rodionov, N.O.; Suwaid, M.A.; Vakhitov, I.R. Mechanistic and kinetic insight into catalytic oxidation process of heavy oil in in-situ combustion process using copper (II) stearate as oil soluble catalyst. *Fuel* **2021**, *284*. [\[CrossRef\]](#)
31. Abaas, M.; Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A.; Ariskina, K.A. Effect of calcite on crude oil combustion characterized by high-pressure differential scanning calorimetry (HP-DSC). *Pet. Sci. Technol.* **2019**, *37*, 1216–1221. [\[CrossRef\]](#)

-
32. Vyazovkin, S.; Chrissafis, K.; Di Lorenzo, M.L.; Koga, N.; Pijolat, M.; Roduit, B.; Sbirrazzuoli, N.; Suñol, J.J. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim. Acta* **2014**, *590*, 1–23. [[CrossRef](#)]
 33. Freitag, N.P. Chemical-reaction mechanisms that govern oxidation rates during in-situ combustion and high-pressure air injection. *SPE Reserv. Eval. Eng.* **2016**, *19*, 645–654. [[CrossRef](#)]
 34. Zhao, S.; Pu, W.; Sun, B.; Gu, F.; Wang, L. Comparative evaluation on the thermal behaviors and kinetics of combustion of heavy crude oil and its SARA fractions. *Fuel* **2019**, *239*, 117–125. [[CrossRef](#)]
 35. Amanam, U.U.; Koh Yoo, K.H.; Castanier, L.; Kovscek, A.R. Investigation of the Effects of Select Metal Nanoparticles on Heavy Oil Combustion in Porous Media. *Energy Fuels* **2020**, *34*, 130–141. [[CrossRef](#)]
 36. Pu, W.F.; Yuan, C.D.; Jin, F.Y.; Wang, L.; Qian, Z.; Li, Y.B.; Li, D.; Chen, Y.F. Low-temperature oxidation and characterization of heavy oil via thermal analysis. *Energy Fuels* **2015**, *29*, 1151–1159. [[CrossRef](#)]
 37. Niu, B.; Ren, S.; Liu, Y.; Wang, D.; Tang, L.; Chen, B. Low-temperature oxidation of oil components in an air injection process for improved oil recovery. *Energy Fuels* **2011**, *25*, 4299–4304. [[CrossRef](#)]
 38. Zhao, S.; Pu, W.; Varfolomeev, M.A.; Yuan, C.; Pan, J.; Wang, R.; Chen, L.; Kan, N. Low-temperature oxidation of light and heavy oils via thermal analysis: Kinetic analysis and temperature zone division. *J. Pet. Sci. Eng.* **2018**, *168*, 246–255. [[CrossRef](#)]
 39. Murugan, P.; Mani, T.; Mahinpey, N.; Asghari, K. The low temperature oxidation of Fosterton asphaltene and its combustion kinetics. *Fuel Process. Technol.* **2011**, *92*, 1056–1061. [[CrossRef](#)]
 40. Yuan, C.; Emelianov, D.A.; Varfolomeev, M.A.; Abaas, M. Comparison of oxidation behavior of linear and branched alkanes. *Fuel Process. Technol.* **2019**, *188*, 203–211. [[CrossRef](#)]
 41. Vyazovkin, S. *Isoconversional Kinetics of Thermally Stimulated Processes*; Springer: Berlin/Heidelberg, Germany, 2015; ISBN 9783319141756.