Kinetics of the Thermal Oxidation of Heavy Oils during Catalytic in-situ Combustion Process

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Abstract. In order to investigate the kinetic parameters for in situ combustion of heavy crude oil and the catalytic effect of metal oxides, α·Fe_2O_3 particles were synthesized by applying microwave-assisted calcination method. Thermal analysis was conducted and kinetic parameters were evaluated via thermogravimetric analysis and tube tests. The results show that addition of α·Fe_2O_3 results in a substantial reduction in the activation energy of the heavy oil and increase in the frequency factor at the same conversion rate, making the reaction more intense. The kinetic tube tests reveal that high temperature oxidation reactions produce a large amount of CO and CO_2. The addition of α·Fe_2O_3 caused the formation of multiple active sites on rock and enhanced the entire ISC process.

Keywords: Heavy Oil; in situ Combustion; Metal Oxides; Thermal Oxidation; Catalyst.

1. Introduction

In situ production of heavy oil or bitumen requires massive heat. The approaches of steam-based thermal recovery, including steam flooding, cyclic steam stimulation and steam assisted gravity drainage, are the most common ones[1-3]. In situ combustion (ISC) is cost-effective compared with steam stimulation due to the heat being generated via downhole exothermic oxidation reactions. This process involves injecting air or oxygen enriched gases into the formation, igniting a portion of the crude oil to create a combustion front to propagate through the reservoir. The crude oil in front of the combustion is heated and viscosity is reduced significantly[4-5]. The distilled light components and steam move forward, leaving the undistilled heavy components to crack and pyrolyze at high temperature. The remaining cracking product, coke, is used as fuel to maintain combustion. The hot gases generated in the combustion also enhance crude oil production. The produced crude oil is the light components volatilized and cracked during the combustion process, therefore, the quality is greatly improved.

ISC technique is more practical than steam-based methods due to its high efficiency. The laboratory results show that the residual oil saturation in the burned area is nearly zero, and the final recovery rate is as high as 80-90%. The previous ISC projects have reported the oil recovery of 45-80%.

Although ISC is efficient and cost effective, it also has drawbacks. The ISC process is influenced by various factors such as formation pressure, crude oil properties, operating parameters, etc. Due to the external heat loss, reservoir temperatures may decrease significantly, resulting in poor combustion performance and even operation failures[6-8].

Generally speaking, reaction kinetics can be defined as the rate and the extent of chemical conversion from reactants to products. Kinetics are important for ISC process, so as to characterize crude reactivity, identify conditions necessary for ignition and sustaining combustion, and obtain inputs to kinetic models for numerical simulation of ISC[9-12]. This paper intends to investigate the thermal behaviours and kinetic parameters during the ISC of heavy crude oil.

2. Experimental

2.1 Materials

The crude oil sample is obtained from Liaohe oilfield, and the viscosity of the crude oil degassed on the ground is 21435 mPa·s at 50℃. Its properties are shown in Table 1, including the pseudo components: saturates, aromatics, resins and asphaltenes.

Table 1. The properties of the heavy crude sample

sample	element analysis(wt%)				atom ratio	SARA(wt%)			
	C	H	S	N	H/C	saturates	aromatics	resins	asphaltenes
heady crude	85.90	11.80	0.21	0.71	1.61	17.24	38.60	32.66	11.50

The gas chromatography of the oil sample is shown in Figure 1, the distribution of crude oil hydrocarbon is mainly concentrated in C_{20} to C_{33}. The n-alkanes of crude oil basically disappeared, only steranes, terpene alkanes and other cycloalkanes with slightly stronger resistance to degradation were preserved. The chromatographic separation could not be separated due to the presence of a large number of heteroatomic compounds, which made the baseline seriously high and formed a large envelope. This indicates that the degree of biodegradation is high and the crude oil is heavy.

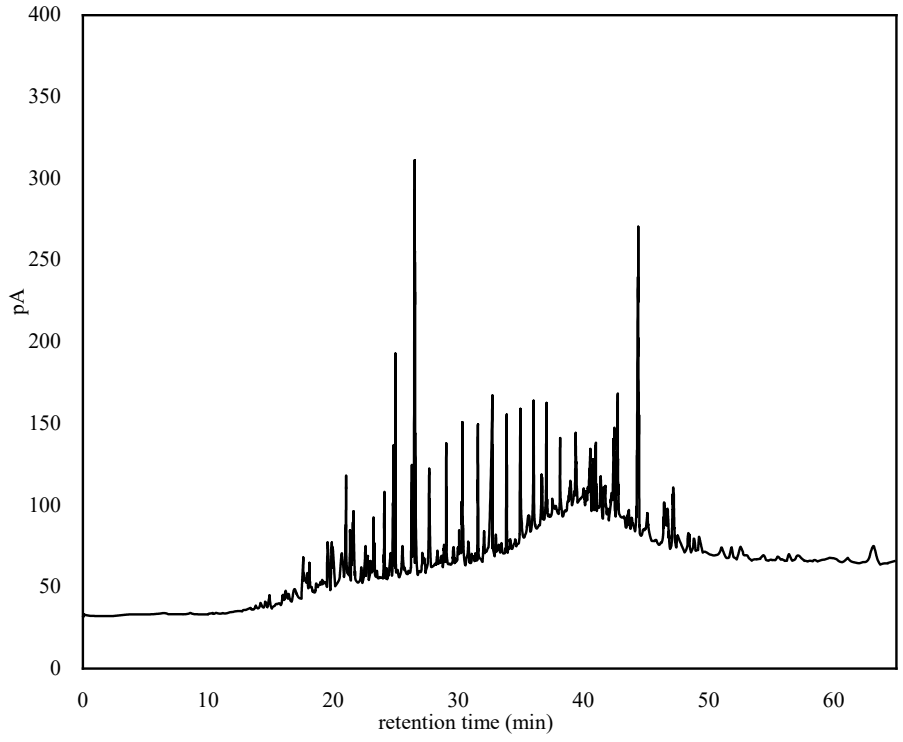


Figure 1. Gas chromatography of the initial oil sample

The $\alpha \cdot Fe_2O_3$ catalyst was selected for the combustion experimental study. The metal oxide particles were synthesized by applying microwave-assisted calcination method. The resonance and relaxation properties of electromagnetic radiation was used to maintain uniform heat distribution throughout the reaction. The precursor used was $FeCl_3 \cdot 6H_2O$, and NaOH was used as a precipitant, followed by titration of the mixture into $FeCl_3$ solution. Figure 2 shows the X-ray Powder Diffraction

(XRD) pattern of α·Fe_2O_3. It can be seen that the α·Fe_2O_3 particles are polyhedral morphology and are basically consistent with the standard diffraction peak (NO.33-0664) corresponding to the standard α·Fe_2O_3 powder diffraction card, and there are no other impurity diffraction peaks. This demonstrates that the particles are high purity α·Fe_2O_3. The average particle size of α·Fe_2O_3 is 152 nm and the BET surface area was 58.7 m^2/g.

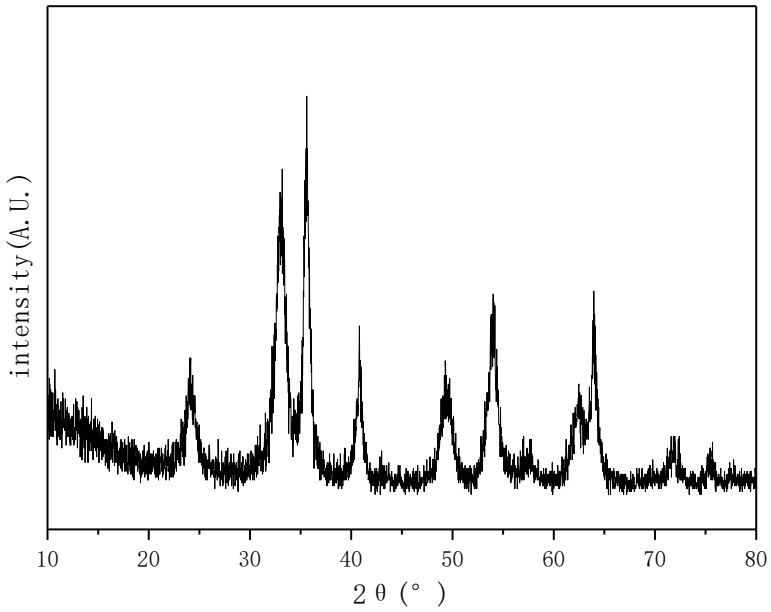


Figure 2. XRD pattern of α·Fe_2O_3

2.2 Thermogravimetric Analysis (TG) Analysis

The sample was prepared by oil-sand mixing, where the super-thick oil was dehydrated and mixed uniformly with the simulated sand in a certain mass ratio. A 50 mg sample of oil sand was taken out of the mixed sample and put into a crucible and placed in a thermal analyzer. The experiments were carried out under air circulation environment at atmospheric pressure, and nitrogen gas was selected as the protective gas. The constant mass flow rate of nitrogen gas was set to 20 mL/min for each experiment, so that the gas filled the whole reaction chamber and then covered the crucible surface. The programmed temperature range was set from 25°C to 700°C, and the heating rates were set to 5°C/min, 10°C/min, and 15°C/min. The test was started when the temperature and flow rate were stable, and completed when the temperature reached 700°C.



Figure 3. Photo of the kinetic experimental tube

The kinetic experiments were performed on a kinetic tube, and the experimental setup is shown in Figure 3. The kinetic tube consists of a thick-walled stainless steel cylinder (12.3 cm in length and 4.8 cm in outer diameter) sealed at both ends by steel plugs and copper gaskets. The sealing cap is screwed onto the steel plug and tightened by four bolts. The bottom steel plug is connected to a long bent tube for preheating of the air. Two thin-walled steel cups are placed in the experimental tube. The upper cup is 7.1 cm long with an inner diameter of 2.7 cm and is used to hold the sample. The bottom steel cup is used to hold the sand. Both cups were perforated at the bottom to allow air circulation, and a 200 mesh sieve was placed at the bottom of both cups.

In the experiments, 50g of oil sand (or with catalyst added) mixed into the experimental tube, and the tube is placed vertically to reduce the effect of gravity. A back pressure valve is connected to the outlet end of the experimental tube to keep the system at a constant pressure of 0.5 MPa. The experimental tube is placed in the oven and air is injected. The oven is heated to 700°C at a heating rate of 180°C/h. The air is supplied by a high-pressure cylinder and preheated by a heating coil into the experimental tube. During the ISC experiments, the pressure at the inlet end was kept at 0.8 MPa and the pressure at the outlet end was kept at 0.6 MPa. The gas flow rate into and out of the kinetic experimental tube was monitored by independent electronic flow meters, and the concentrations of O_2, CO, CO_2 and CH_4 in the produced gases were analyzed by a gas analyzer. The temperature was measured every 2 minutes during the experiments. When the temperature of the crude oil sample in the experimental tube reaches 650°C, the oven is turned off and the temperature of the system is gradually cooled to room temperature.

3. Results and Discussion

3.1 Thermal Analysis

The experimental results of thermogravimetric analysis and derivative thermogravimetry of oil sands and catalyst + oil sands are shown in Figures 4 and 5.

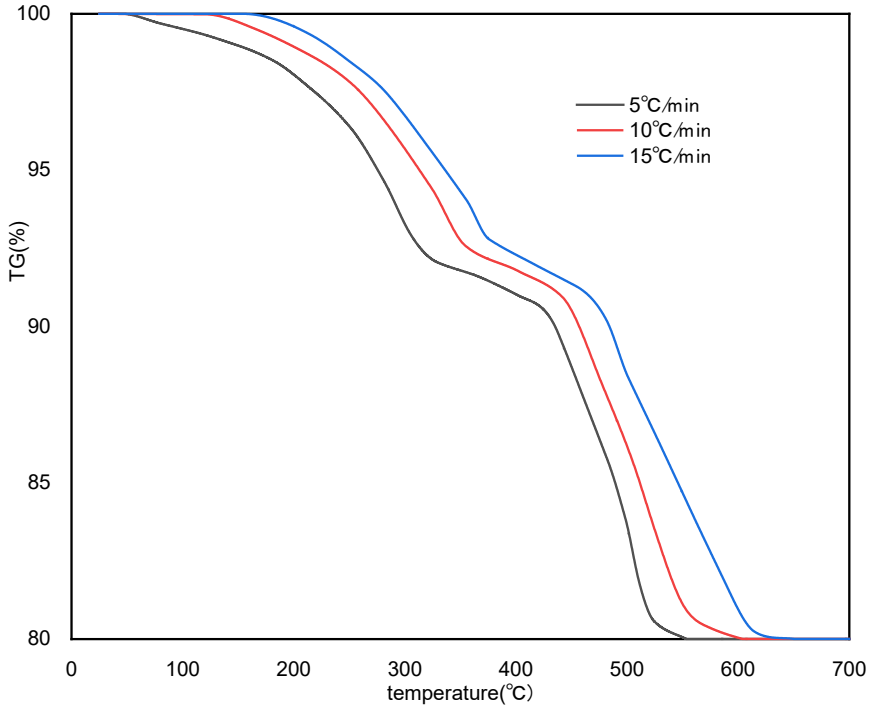


Figure 4. TG curves at different heating rates

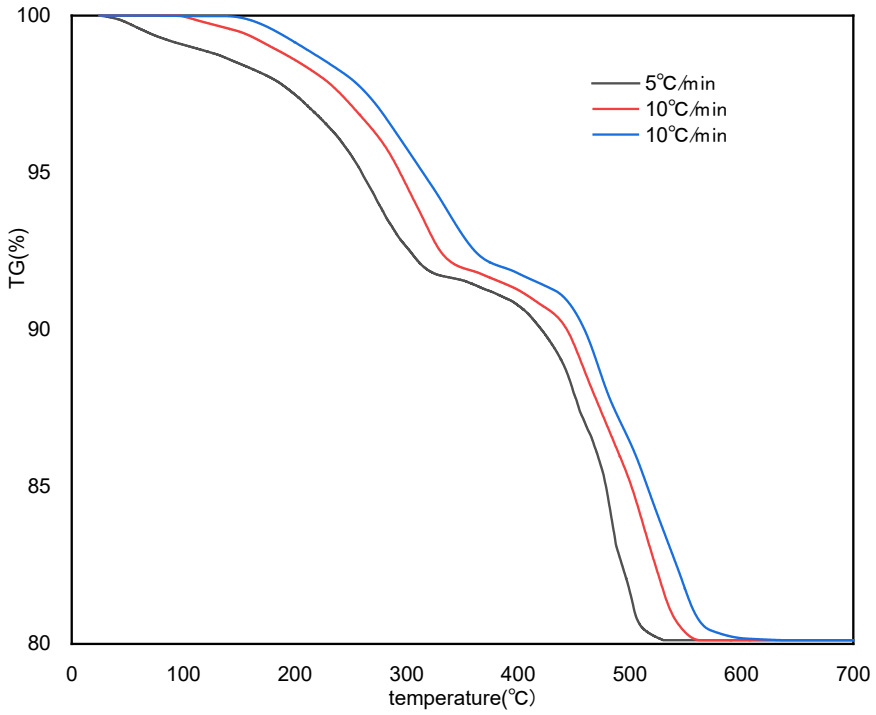


Figure 5. TG curves at different heating rates under catalytic condition

From the experimental results, the combustion process of oil sands samples with added catalyst can be divided into four stages.

1. Distillation stage. The low temperature oxidation interval of the oil sands was 48-153°C with a temperature variation range of 105°C. After the addition of catalyst, the temperature interval was 30-141°C with a temperature variation of 111°C.

2. Low temperature oxidation. The low temperature oxidation zone of the oil sands was 153-322°C with a temperature variation of 169°C; after the addition of catalyst, the temperature range was 141-318°C with a temperature variation of 177°C. The low temperature oxidation stage moved to a lower temperature region after the addition of catalyst, and the catalyst made the reaction proceed more vigorously and the rate of weight loss accelerated.

3. Fuel deposition. The fuel deposition range of crude oil was 322-431°C with a temperature variation of 109°C; after the addition of catalyst, the temperature range was 318-407°C with a temperature variation of 89°C. The decrease in the temperature range indicates that the addition of catalyst has a significant effect on the starting and ending temperature points of the fuel deposition of the crude oil combustion process, moving the reaction temperature toward the lower range and shortening the reaction time. At the same time, the increase in the temperature range indicates that the addition of catalyst makes the crude oil deposit more fuel, which makes the reaction in the subsequent high temperature oxidation more adequate.

4. High temperature oxidation. The high temperature oxidation zone of the crude oil was 431-556°C with a temperature variation of 125°C; after the addition of catalyst, the temperature range was 407-527°C with a temperature variation of 120°C. The low temperature oxidation moved toward the lower region after the addition of catalyst, while the temperature range was reduced indicating that the catalyst made the reaction proceed more vigorously, while the weight loss rate of the sample was accelerated. This is consistent with the trend shown by the kinetic calculations.

3.2 Kinetics Analysis

Figure 6 shows the activation energy E_α values related to the conversion rate by applying the integral isoconversion method. It can be seen that the activation energies calculated by the Kissinger-Akahira-Sunose (KAS) and Starink methods do not differ much, and the activation energy calculated

by the Flynn-Wall-Ozawa (FWO) method is on the high side. The results of the activation energy values calculated using the Starink method are shown in Table 3.

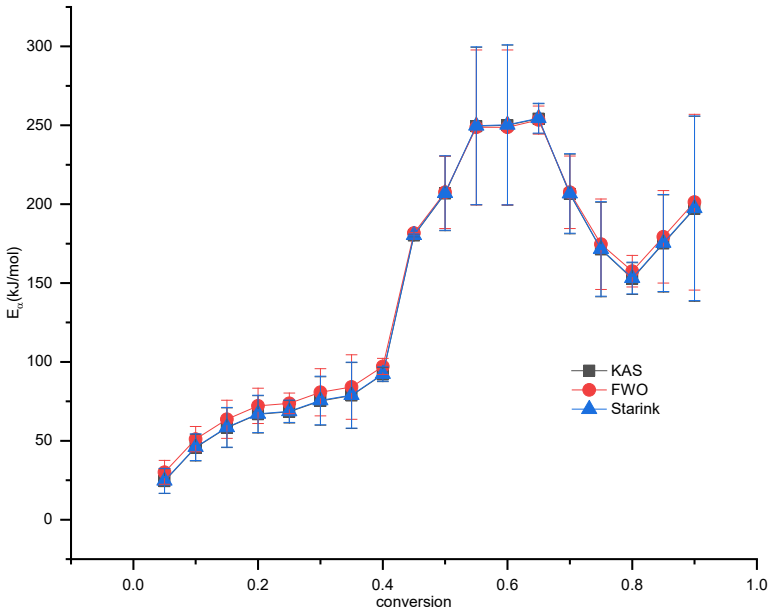


Figure 6. The change of activation energy with conversion rate (oil sands+α·Fe_2O_3)

The kinetic results show that the activation energy changes significantly with the conversion rate, indicating that ISC is a complex multi-step reaction process. As long as the temperature is constantly changing during the experiment, then an isoconversion method will produce an experimental E_α correlation with α. Furthermore, the experimental E_α versus α correlation can always be related and converted to an Eα versus temperature T correlation. When a catalyst is added, the activation energy decreases and the frequency factor increases for the same conversion, indicating a more vigorous reaction. Kinetic calculation results are shown in Table 2.

Table 2. Kinetic calculation results

conversion	oil sand			oil sand +α·Fe_2O_3		
	E_α(kJ/mol)	lnA	R^2	E_α(kJ/mol)	lnA	R^2
0.1	54.44	8.06	0.99888	45.97	8.65	0.98537
0.2	78.91	9.86		67.08	11.18	
0.3	90.95	11.18		75.58	12.20	
0.4	96.91	12.74		92.36	14.22	
0.5	230.69	26.55		207.07	27.98	
0.6	301.04	34.29		250.33	35.17	
0.7	231.99	26.59		206.78	28.25	
0.8	163.30	19.18		153.21	21.52	
0.9	256.01	29.34		197.45	30.83	

By comparison, it was found that the combustion process of the samples with the addition of catalyst changed more significantly, and the temperature interval, temperature range and weight loss rate corresponding to each stage were changed. After adding the catalyst, the low and high

temperature oxidation intervals of the samples decreased, and the beginning and ending points of the temperature interval of fuel deposition were reduced and the range of the interval decreased, changing from 322-431°C to 318-407°C.

3.3 The Combustion Kinetic Tube Tests

The viscosity of heavy crude oil after ISC was 1766.75 mPa·s, and reduced further to 1312.02 mPa·s by addition of the catalyst. Figure 7 shows the gas chromatography of the oil produced by catalytic ISC. It can be seen that there are abundant low carbon number series of n-alkanes and isomeric hydrocarbons in the whole hydrocarbon chromatogram. The distribution trend is basically consistent with the normal crude oil, which indicates the oil is upgraded dramatically by application of ISC technique.

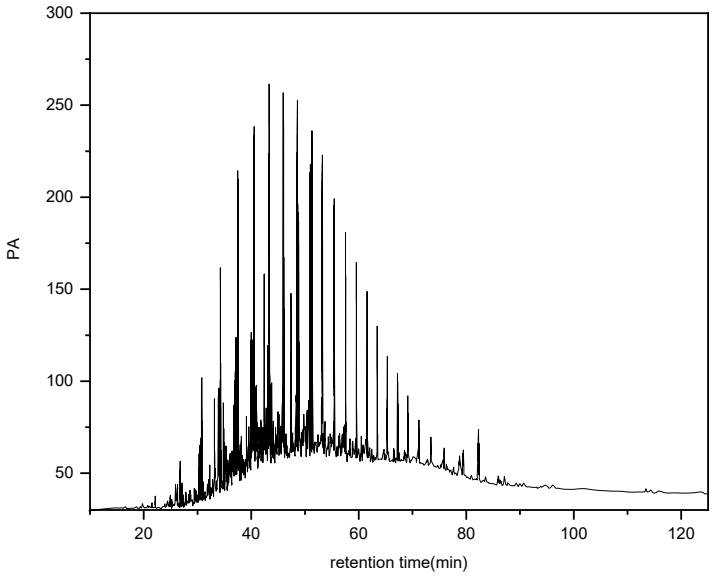


Figure 7. Gas chromatography of the oil produced by catalytic ISC

Figure 8 gives a comparison of the temperature profile in the kinetic tube tests with and without catalyst. The addition of α·Fe_2O_3 caused the formation of multiple active sites on rock, which enhanced the fuel deposition. As can be seen from the figure, the exothermic peak is more pronounced and the combustion is more intense with the addition of catalyst. The temperature rise for the experiment without catalyst was 55°C, and the rise increased to 224°C with the addition of catalyst.

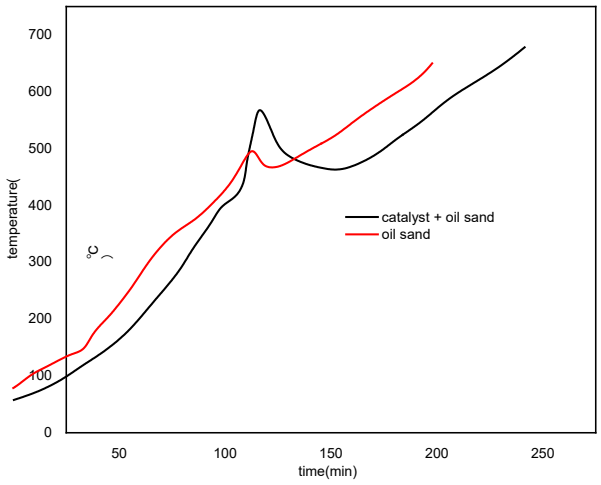


Figure 8. Temperature profile in kinetic tube tests

In high temperature oxidation reactions, the fuel burns, producing CO and CO_2. The fuels are generally formed from the heavy components in the asphaltene, and when the fuel burns, the temperature rises. The higher the content of the heavy fraction in the crude oil, the more fuel is produced and the more intense the combustion exothermic reaction. The amount of fuel generated is the most important factor affecting the magnitude of the temperature increase. The magnitude of the temperature increase in the high-temperature combustion reaction is related to the content of heavy components before combustion in the kinetic experiments. Figure 9 gives the variation of the concentration of combustion gases with time for the kinetic tube test.

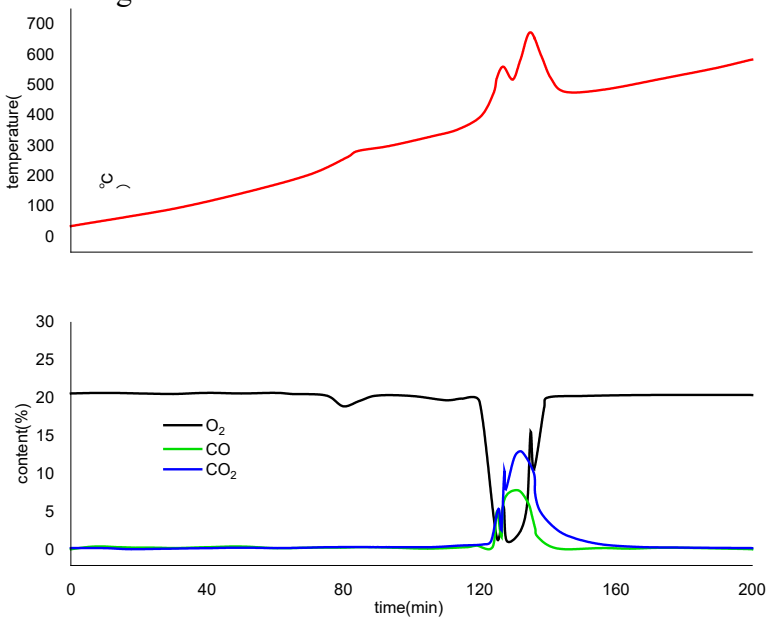


Figure 9. Concentration of combustion gases and exothermic behaviour in the tube test

It can be seen that as the reaction proceeds, a low temperature oxidation reaction occurs and a small amount of oxygen is consumed. After the high temperature oxidation reaction occurs, a large amount of oxygen is consumed and the concentrations of CO and CO_2 increase sharply, and the curve shows a low peak in O_2 concentration and a peak in CO and CO_2 concentration. When the fuel is gradually exhausted, the concentration of O_2 returns to the initial level, and the concentration of CO and CO_2 decreases to the initial level.

4. Conclusion

(1) Microwave-assisted calcination method was applied to synthesize $\alpha{\cdot}Fe_2O_3$ particles, and the characterization shows that it is suitable for enhancing ISC of heavy oils.

(2) The addition of metal oxide particles ($\alpha{\cdot}Fe_2O_3$) results in a substantial reduction in the activation energy of the heavy oil, thus making the oxidization reactions easier to proceed.

(3) The thermogravimetric analysis of the heavy oil showed that the activation energy changed significantly with the conversion rate, indicating that the ISC is a complex multi-step reaction process. When $\alpha{\cdot}Fe_2O_3$ was added, the activation energy decreased and the frequency factor increased at the same conversion rate, indicating that the reaction was more violent.

(4) The kinetic tube tests reveal that high temperature oxidation reactions produce a large amount of CO and CO_2. The addition of $\alpha{\cdot}Fe_2O_3$ caused the formation of multiple active sites on rock, and enhanced the entire process.

Acknowledgments

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