Formation and Combustion Heat Release of Naphthenic-Based Crude Oil Cokes at Different Reaction Temperatures

Rigu Su, Xusheng Wang, Jianghe Sun, Junshi Tang, Sen Chen, Jingjun Pan,* and Yong Guo*

ABSTRACT: Petroleum cokes prepared from naphthenic crude oil differ significantly in terms of the oxygen content and hydrogen/carbon (H/C) ratio, which mainly depend on the different coking temperatures. Thermogravimetric-differential scanning calorimetry was applied to study the heat release and combustion weight loss of petroleum cokes prepared at 350 and 500 °C, respectively. The effect of different coke formation temperatures on the combustion properties of the coke formed during air injection in situ combustion (ISC) was also investigated. The results showed that the petroleum coke formed under oxygen exhibited an H/C ratio of 0.895 and an O/C ratio of 0.109 at 350 °C and an H/C ratio of 0.395 and an O/C ratio of 0.054 at 500 °C. As the temperature rises, the hydrogen atoms on the petroleum coke molecules intensify to separate and form water molecules and thus giving off heat. It can be further inferred that under the combustion temperature of air injection ISC, the coke at 350 °C can release more heat in the lower combustion temperature range, and the combustion weight loss is faster; however, the formation temperature continues to rise due to combustion at 500 °C, coke begins to release massive heat, and the combustion weight loss is as high as 97.95%. The combustion residuals of both temperature cokes and the residual solid content of the formation after combustion in porous media are both little, which can be used as fire flooding fuels at different formation temperatures to provide heat energy for oil displacement.

1. INTRODUCTION

Heavy oil has the characteristics of high content of heavy components, high viscosity, and poor fluidity, which cannot be exploited by conventional methods; however, its high viscosity—temperature sensitivity properties are obvious, and it can be extracted by various thermal-assisted viscosity reduction methods. Air injection in situ combustion (ISC) is a low-cost thermal heavy oil development method, which has received widespread attention and is regarded as a technique with broad application prospects. In the process of fire flooding, oxygen-containing gas (including air) is continuously injected into the oil layer and ignited; then, the petroleum coke was formed with the heavy components in crude oil and used as fuel, which can maintain the continuous combustion of the combustion front. ISC relies mainly on the combined effects of heat, flue gas, and steam generated to achieve the purpose of oil displacement and enhanced oil recovery.

Petroleum coke, an important fuel formed by the ISC process, undergoes two stages in the heating process, low-temperature oxidation (~250–400 °C) and high-temperature oxidation (above 400 °C) during the heating process. The high-temperature oxidation reaction of coke is the source of most of the formation energy and oxygen consumption, and the quality and content of coke formation as a fuel in the ISC process is the most important parameter. The amount and oxygen content of coke formed by oxidation of heavy oil at different temperatures and the ratio of H/C are the main factors for the difference of combustion heat and combustion rate of coke in the presence of oxygen. The oxygen element in the oxidation coke produced at lower temperatures is mainly present in the form of carboxyl, hydroxyl, carbonyl, active ether bonds and inactive ether bonds. With the increase in coke-forming temperature, the oxygen-containing functional groups in the coke molecules undergo conversion and bond-breaking reactions, which directly leads to a lower oxygen content but a higher hydrocarbon ratio in the petroleum coke produced at high temperatures.

In this paper, thermogravimetric-differential scanning calorimetry (TG-DSC), elemental analysis, and 13C nuclear
magnetic resonance ($^{13}$C NMR) spectrometry were used to investigate the elemental oxygen content, H/C ratio, oxygen-containing functional groups, and the heat release amount and combustion rate of cokes formed at different temperatures. The results of the study show that under the same heating rate and air flow conditions, the two types of petroleum coke, 350 and 500 °C, exert essentially the same amount of heat, while 350 °C coke is able to burn completely at a lower temperature, and 500 °C coke burns completely at a higher temperature than 350 °C coke, which is more suitable as a fuel for air injection fire flooding.

2. EXPERIMENTAL SECTION

2.1. Preparation, Separation, and Purification of Petroleum Cokes. Petroleum coke was prepared using a low-pressure oxidation reaction method in a kettle furnace at 350 and 500 °C, respectively. 30 g of crude oil in Xinjiang not affected by ISC (date of sampling: April 2021, viscosity at 50 °C: 1650 mPa•s) was placed at the bottom of the reaction kettle, and air (composed of 18.5% O$_2$ and 81.5% N$_2$) was supplied to the surface of oil at a flow rate of 50 mL/min. A thermocouple was inserted from the top of the kettle to measure the surface temperature of the crude oil directly, and the pressure inside the kettle was 0.1 MPa. The coking procedure was carried out at a temperature increase of 3 °C/min and was stopped at the target temperature for 60 min, and then, heating was stopped to allow the temperature to naturally drop to room temperature. After that, the kettle was opened to collect the solid sample generated. In this way, 350 and 500 °C coke products of heavy oil were obtained.

The coke products were ground and crushed, then transferred to a 250 mL single-necked round-bottom flask with 100 mL of hexane and heated to reflux for 5 h. The solution was cooled to room temperature for solid–liquid separation, and the separated solids were repeatedly extracted thermally three times using hexane. The petroleum coke solids were repeatedly extracted three times with 100 mL of chloroform at 25 °C for 5 h each time. The separated solids were then extracted with 100 mL of trichloroethylene for 5 h, repeated three times. The solids were collected by centrifugation and dried under vacuum to obtain a sample of petroleum coke to be tested. The chloroform and trichloroethylene solutions were collected, and the solvent evaporated to obtain the asphaltene (large organic non-hydrocarbons) prepared by the above reaction. The coke purification process is shown in Figure 1.

2.2. Characterization of Crude Oil and Petroleum Cokes. Composition features of the target crude oil were characterized by the tandem gas chromatography mass spectrometer (7890B-5977A, Agilent, USA) and electrospray mass spectrometer (6545 LC/Q-TOF, Agilent, USA). Composition features of the petroleum coke samples were characterized by elemental analysis (Vario EL Cube, made by Elementar in Germany) and $^{13}$C NMR (Advance III HD 400 MHz, Bruker, Switzerland).

2.3. TG-DSC Analysis. TG-DSC analysis was conducted on a TG-DSC analyzer (STA449F3, made by Netzsch in Germany). In the test, two groups of 85 μL open aluminum oxide crucibles with a mass difference less than 1% were used as sample crucible and reference crucible, respectively. Then, they were placed into the furnace, and the set temperature program was run to obtain blank data. 4.2824 mg of the petroleum coke sample was weighed and placed in the sample crucible and then put into the furnace. After being purged with carrier gas (air with a flow rate of 50 mL/min) for 10 min, the furnace was heated from 22 to 800 °C at a temperature rise rate of 10 °C/min. The set temperature program was run to measure and obtain blank correction heat flow and weight loss data (including time, temperature, total heat flow, and sample mass).

3. RESULTS AND DISCUSSION

3.1. Basic Properties of Heavy Oil Exploited by ISC and Characterization of Coke Elements. Naphthenic crude oil contains a large number of naphthenic and aromatic hydrocarbons, and the composition of crude oil is closely related to the coke yield. The molecular-weight distribution and four-component analysis of heavy oil and prepared petroleum coke were carried out by linked gas chromatography-mass spectrometry. The changes in the composition of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) elements in different temperature petroleum cokes were analyzed and studied. The results of linked gas chromatography-mass spectrometry analysis and linked ESI-MS characterization show that the alkane components of Xinjiang crude oil mainly include various substances with naphthenic hydrocarbon structure (Figure 2). The average molecular weight of heavy oil is 600, and molecular weights of the main substances range from 250 to 1050. The contents of saturated alkane, aromatic hydrocarbon, non-hydrocarbon resin, and asphalt in crude oil account for 31.89, 9.02, 47.57, and 11.52%, respectively. The substances with higher-molecular weight account for 59.09% of the total heavy oil, and the percentages

![Figure 1. Purification process of the petroleum cokes.](https://doi.org/10.1021/acsomega.2c00976)
of C, H, O, and N in heavy crude oil are 85.50, 12.29, 1.58, and 0.49%, respectively.

Petroleum coke was prepared from crude oil at 350 and 500 °C, and the variation of C, H, O, and N content in the coke was obtained by elemental analysis. The C, H, O, and N contents of the petroleum coke at 350 °C were 79.21, 5.91, 11.49, and 0.81%, respectively, whereas the C, H, O, and N contents of the petroleum coke at 500 °C were 83.90, 2.76, 6.05, and 1.61%, respectively. It can be obviously seen that the O element in the petroleum cokes prepared at 350 and 500 °C is significantly higher than that of target crude oil, and the H content decreased with the increase in temperature. The H/C ratios of crude oil and 350 and 500 °C petroleum cokes are 1.725, 0.895, and 0.395, respectively, and the oxygen-carbon (O/C) ratios were 0.014, 0.109, and 0.054. The H/C of the coke decreases as the temperature of the coking reaction increases, and the loss of H is greater than C. The main reasons for this are probably the increased cracking and dehydroaromatization reactions on the one hand and the high-temperature chain breakage of the alkyl groups as side chains on the other hand. As the coking temperature increases, the O/C ratio of crude oil first increases and then decreases. The reason for this phenomenon is that during the heating coking reaction, the crude oil is first oxidized with O2 in the air to generate a large amount of petroleum cokes containing oxygen functional groups, and as the temperature increases further, the more reactive oxygen-containing functional groups are cleaved to produce carbon dioxide gas, which leads to a decrease in O/C of the high-temperature petroleum coke.

3.2. NMR Characters of Non-petroleum Coke Solids Prepared at 350 and 500 °C.

The petroleum coke carbon spectra were first studied at 350 and 500 °C using 13C solid NMR, and the petroleum coke carbon spectra were resolved by peak splitting using peakfit software.19,20 Studies have shown that when comparing cokes at different temperatures, the coke produced at 350 °C has a more abundant aliphatic carbon type in the case of same sp3 hybridization.19 With the increase in coke-forming temperature, the cracking and removal of the retained saturated alkane side chains on the low-temperature coke occurs, resulting in a significant increase in the area of the aromatic peaks that make up the coke skeleton.6,21 The oxygen functional groups of the fatty ethers, aliphatic aromatic ether oxygen functional groups, and carboxyl oxygen functional groups of the cokes are significantly reduced, whereas the carbonyl ketone-type carbon content is significantly increased.

Non-petroleum coke solid substances prepared at 350 and 500 °C are asphaltenes with large molecular weight, which are deposited in the formation together with coke as the fuel for ISC. The 13C NMR spectrum of asphaltene is shown in Figure 3, which shows that the asphalt products prepared at 350 °C had significant peaks in the NMR carbon spectra δ (ppm): 116.59, 37.41, 37.07, 34.40, 32.78, 31.92, 29.69, 26.67, 24.46, 22.67, 19.69, and 14.10. δ values of 14.10, 19.69, 22.67, and 24.46 indicate that this type of products contains lots of terminal methyl groups, including alkane terminal methyl groups of straight and branch chains and terminal methyl groups of alkyl chains connected to lone electron pairs, compared to the baseline; this indicates a high number of methyl groups.

The broad peaks in the range 26.67−37.41 are representative of the presence of lots of methylene and hypomethylenes, which constitute the branched and long alkyl-chain structure of the compounds. In addition, peaks in the low field region in this region also indicate the presence of ether or hydroxy oxygen-containing groups. δ equals to 116.59, indicating the possibility of cyano in this class of compounds, whereas δ in the 120−140 range for broad peaks indicates that this type of

![Figure 2. GC–MS and ESI-MS of target crude oil.](https://doi.org/10.1021/acsomega.2c00976

![Figure 3. 13C NMR spectrum of asphaltene after coke-forming.](https://doi.org/10.1021/acsomega.2c00976

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15108
compounds contains a lot of aromatic carbons. The asphalt product prepared at 500 °C has peaks obviously identified at the following δ (ppm): 205.61, 128.94, 128.58, 128.15, 127.43, 126.57, 123.80, 116.67, 31.66, 29.78, 22.72, 19.95, and 14.19 in the spectrum. δ values of 14.19, 19.95, and 22.67 indicate that this type of products contains a large number of terminal methyl groups, including alkane terminal methyl groups of straight and branch chains. Compared with the peak broadening in the corresponding region of 350 °C coke, the smaller values indicate high singleness of terminal methyl groups. δ values at the peaks of 29.78 and 31.66 represent that this type of compounds contains methyl groups and/or methylenes connected to carbonyl groups. A δ value of 116.67 indicates the possibility for cyano groups existing in this type of compounds. A δ value at the wide broadening in the range of 120–135 indicates that this type of compounds contains units of carbonyl structures.

The 13C NMR spectrum further shows that the asphalt prepared at 350 °C has long alkyl-side chains, and more reactive oxygen functional groups are contained in the structure of asphalt. The asphalt product prepared at 500 °C has conjugated aromatic rings as its main structure, and aliphatic hydrocarbons of side chains have a relatively single structure, mainly methyl groups. In addition, oxygen elements connected to aromatic rings mainly exist in the carbonyl structure, which is consistent with the reported findings of solid 13C NMR spectrum.10

3.3. Combustion Characteristics of Cokes Prepared at Different Temperatures. The asphaltene and petroleum cokes prepared at 350 and 500 °C were subjected to TG-DSC analysis, and it can measure the proportion of combustibles, the starting temperature of combustion, and the heat release, with the results shown in Table 1. TG-DSC studies have shown that asphaltene and petroleum cokes produced by reactions at different temperatures can be burned adequately in an air atmosphere with ash contents in the range of 1.12–3.00%. The heat release of 350 °C asphalt products is 11,889 J/g when it burns, and the maximum exothermic temperature is 538.3 °C, whereas the heat release of 500 °C asphalt products is 15,015 J/g with the maximum exothermic temperature of 536.3 °C. For asphalt produced in coke prepared at different temperatures, there is no significant difference in the maximum exothermic temperature, and the heat release of 500 °C asphalts is higher than that of 350 °C asphalts. The heat release of petroleum coke prepared at 350 °C is 21,590 J/g, and the maximum heat release temperature is 494.5 °C, whereas the heat release of petroleum coke prepared at 500 °C is 23,004 J/g with the maximum heat release temperature of 582.5 °C. The heat release, combustion starting temperature, and maximum heat release temperature of petroleum coke prepared at 500 °C are all higher than those of petroleum coke prepared at 350 °C. Petroleum coke exerts much more heat than asphalts, indicating that it is the main provider of heat for ISC.

3.4. TGA-DSC Spectrum of Cokes Prepared under Different Conditions. The adsorption of small molecules by solid is a spontaneous process, that is, ΔG < 0. After being adsorbed, the adsorbed material changes from a three-dimensional state of motion to a state where it can only move in two dimensions (the surface of the solid), a process in which the entropy of the adsorbed material decreases, so ΔS < 0. ΔH = ΔG + TΔS, so ΔH < 0, that is to say, the process in which a solid adsorbs another substance is exothermic.

The thermal variation pattern for the reaction of 350 °C petroleum coke is shown in Figure 4, the process in which solid adsorbs gas is exothermic, whereas the process of gas desorption is endothermic. The pyrolysis process at a final temperature of 55–175 °C is an endothermic reaction process, but the endothermic effect is weak. It is an endothermic desorption process absorbing residual gas. With the increase in temperature, when the final temperature reaches 282–392 °C, the pyrolysis process is weakly exothermic, which is the first stage of the exothermic reaction process. In this stage, the cracked hydrogen burns with the presence of oxygen and gives off heat. When the final temperature rises to 495 °C, the pyrolysis process becomes strongly exothermic, which is the second stage of the exothermic reaction process. In this stage, the side-chain aliphatic hydrocarbon carbon of petroleum coke burns and gives off heat. The pyrolysis process at a final temperature of 540 °C is also strongly exothermic, which is the third stage of the exothermic reaction process. In this stage, the aromatic carbon of petroleum coke burns and gives off heat.

The thermal variation pattern for the reaction of 500 °C petroleum coke is shown in Figure 5, and the petroleum coke also has a desorption process, in which solid adsorbs gas. At the final temperature of 98–270 °C, the pyrolysis process is an endothermic reaction process, but the endothermic effect is weak. It is an endothermic desorption process absorbing residual gas. With the increase in temperature, when the final temperature reaches 510 °C, the pyrolysis process is weakly exothermic, which is the first stage of the exothermic reaction process. In this stage, the cracked hydrogen burns with oxygen and gives off heat. From the elemental analysis data, it can also be concluded that the H/C ratio of 500 °C coke is smaller than that of 350 °C coke, and the content of hydrogen elements in high-temperature coke is lower. Therefore, the combustion and exothermic reaction of cracked hydrogen is weak in the case of high-temperature coke. When the final temperature rises to 610 °C, the pyrolysis process is also weakly exothermic, which is the second stage of the exothermic reaction process. In this stage, the side-chain aliphatic hydrocarbon carbon of petroleum coke burns and gives off heat. According to the solid 13C NMR spectrum of coke,11 the content of saturated aliphatic hydrocarbon carbon in the petroleum coke formed at 500 °C in the case of sp² hybridization decreases significantly with the increase in coking temperature. When the final temperature rises to 678 °C, the pyrolysis process becomes strongly exothermic, which is the third stage of the exothermic reaction process. In this stage, the oxidation of aromatic carbon elements of coke into carbon dioxide begins, and the

| test samples | 350 °C asphalt | 350 °C coke | 500 °C asphalt | 500 °C coke |
|--------------|---------------|-------------|---------------|-------------|
| mass loss, % | 98.17         | 97.00       | 98.28         | 97.95       |
| combustion starting point, °C | 473.7 | 431.8 | 486.3 | 470.0 |
| max. heat release temperature, °C | 538.3 | 494.5 | 536.3 | 582.5 |
| heat release ending point, °C | 581.1 | 614.5 | 623.1 | 699.6 |
| heat release, J/g | 11,889 | 21,590 | 15,115 | 23,004 |
Graphitization degree of coke prepared at high temperature is significantly improved.\textsuperscript{18}

By comparing Figures 3 and 4, it can be seen that the exothermic process of 350 °C petroleum coke is mainly in the range of 270−610 °C, and that of 500 °C petroleum coke is mainly in the range of 440−770 °C. The low coke generation temperature is 350 °C, when the atmospheric cracking temperature of crude oil is just reached, and there are fewer cracking reactions in crude oil. With the presence of oxygen, the components of crude oil are oxidized first and then polymerized into macromolecular coke. On the other hand, colloidal molecules with a large number of side-chain groups form cokes without participating in the cracking reaction, and these cokes formed at low temperature contain a large number of side-chain groups. In the combustion process, there is no decomposition and exothermic stage of oxygen-containing functional groups on the 250−400 °C surface, and obvious combustion and exothermic reaction begin from 440 °C. Thus, the combustion and exothermic peak of 500 °C coke moves to the high-temperature region.

3.5. Exothermic Properties and Weight Loss Rates of Petroleum Cokes. The oxidation and heat release of coke mainly comes from the reactions, in which carbon elements are completely oxidized into carbon dioxide and hydrogen elements are oxidized into water. The oxygen content of low-temperature coke prepared in this test is 1.9 times of that of high-temperature coke, and the H/C ratio of low-temperature coke is higher than that of the high-temperature coke prepared at high temperature is significantly improved.\textsuperscript{18}

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coke. In the case of the same gas flow rate and oxygen content, the oxygen elements of low-temperature coke participate in the combustion of carbon elements, making the combustion more efficient. The combustion residues of cokes prepared at two temperatures were both less, and little residual solids were left in the formation after combustion in porous media, which are more suitable for being used as fuel to provide heat energy for ISC.

The combustion of coke mainly occurs on the particle surface, which is affected by particle surface area, oxygen, and carbon dioxide concentration on the surface, reaction rate constant, and other factors. The morphology of 350 °C petroleum coke is mainly a loose lamellar structure mixed with tiny particles, showing an amorphous loose distribution, and gas molecules can flow freely between lamellar layers. The TG curve of 350 °C petroleum coke is shown in Figure 6, and it can be known that the 97% of the components have been burned, and the maximum heat release temperature is in the range of 480 to 550 °C, so combustion at lower temperature can release stored heat. While the 500 °C petroleum coke is composed of dense lamellar tiny particles, and its TG curve is shown in Figure 7, the 97.95% of the components burn, and the heat energy released comes mainly from the oxidative combustion of elemental carbon. The maximum exothermic temperature of combustion is in the range of 670–700 °C, that is, combustion at high temperature releases the stored heat.

The differences in the properties of the petroleum coke prepared at different temperatures indicate that the oxidation activity of cokes is also different. By comparing the DTG curves of cokes prepared at two different temperatures, it can be concluded that when the temperature reaches 490 °C, the low-temperature coke has the maximum weight loss rate, most active pyrolysis reaction, maximum decomposition, and the maximum heat release; when the temperature reaches 546 °C, the pyrolysis reaction occurs again. For high-temperature coke, its weight loss rate and heat release reach the maximum when the temperature reaches 670 °C. The comparison of these results deeply indicated that the low-temperature coke can be decomposed and lose weight at a lower temperature, and it also has an even greater weight loss in the case of pyrolysis. When combustion makes the formation temperature elevated, the high-temperature coke begins to pyrolyze and lose weight, releasing more heat.

4. CONCLUSIONS

The paper reveals that the H/C ratio, O/C ratio, and aliphatic hydrocarbon side-chain content of low-temperature coke are higher than those prepared at 500 °C, while the latter has a higher graphitization degree. The oxidation and heat release of coke mainly are from the reactions, in which carbon elements are completely oxidized into carbon dioxide, and hydrogen elements are oxidized into water. According to the results of TG-DSC and TG-DTG, the oxygen elements of low-temperature coke participate in the combustion of carbon elements, making the combustion more efficient, releasing more heat at lower temperature, and resulting in even greater weight loss during pyrolysis. As combustion warms the formation, high-temperature coke begins to release more heat. The coke prepared at the two temperatures both have insignificant combustion residues and even less residual solids left in the formation after combustion in porous media, which are therefore suitable as fuels to provide heat to the ISC at different formation temperatures.

AUTHOR INFORMATION

Corresponding Authors
Jingjun Pan – Research Institute of Engineering Technology, PetroChina Xinjiang Oilfield Company, Karamay, Xinjiang 834000, China; Email: panjingjun@petrochina.com.cn
Yong Guo – CAS Lanzhou Institute of Chemical Physics, Lanzhou, Gansu 730000, China; orcid.org/0000-0002-8294-3867; Email: guoyong@licp.cas.cn

Authors
Rigu Su – Research Institute of Engineering Technology, PetroChina Xinjiang Oilfield Company, Karamay, Xinjiang 834000, China
Xusheng Wang – CAS Lanzhou Institute of Chemical Physics, Lanzhou, Gansu 730000, China
Jianghe Sun – Research Institute of Engineering Technology, PetroChina Xinjiang Oilfield Company, Karamay, Xinjiang 834000, China
Junshi Tang – PetroChina Research Institute of Petroleum Exploration and Development, Beijing 100120, China
Sen Chen — Research Institute of Engineering Technology, PetroChina Xinjiang Oilfield Company, Karamay, Xinjiang 834000, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00976

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