

## Pyrolysis Products Formation Characteristics and Kinetics of Heavy Oil Base Cracked Oil

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**Summary:** In this study, the pyrolysis products formation and kinetics of base cracked oil were studied by a TG-FTIR device, which can provide a reference basis for heavy oil and gas reaction and industrial application. The results exhibited that the saturated fraction was mainly composed of chain alkanes and cycloalkanes. The aromatic fraction mainly contains polycyclic aromatic hydrocarbons and alkyl substituted aromatic hydrocarbons. The resin fraction is mainly multi-cyclic aromatic hydrocarbons. As the fraction becomes heavier, the initial and termination cracking temperature of saturate, aromatic, the amount of carbon residue gradually increases and coking intensifies. The pyrolysis products of chemical group were mainly methane, ethylene,  $C_2^+$  hydrocarbons, and light aromatics, and the main contributing components for the generation of low carbon olefins are the saturated and aromatic fractions. The correlation coefficients  $R^2$  of the linear equations and fitting results were close to 1, and thus proving that the selected model was reasonable. The saturate fraction had the lowest activation energy of 78.82  $\text{kJ}\cdot\text{mol}^{-1}$ , while the aromatic, resin, and asphaltene have activation energies of 103.46  $\text{kJ}\cdot\text{mol}^{-1}$ , 108.87  $\text{kJ}\cdot\text{mol}^{-1}$ , and 110.56  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively.

**Keyword:** Heavy oil, Base cracked oil, Low carbon olefins, Kinetics.

### Introduction

Low-carbon olefins (such as ethylene, propylene, butene and butadiene) are regarded as very important basic organic chemical raw materials. Especially ethylene is often regarded as an indication of the level of development of petrochemicals in a country. With the increasing demand of low-carbon olefins, and the crude oil supply shows the development trend of heavy and poor quality [1,2], resulting in the relative scarcity of light cracking feedstocks, and the contradiction between supply and demand will also become increasingly prominent [3, 4]. As a result, how to use heavy oil to produce low-carbon olefins has become the focus and hotspot of research and attention of domestic and foreign petroleum refining industries.

At present, the world's ethylene (about 95%) and propylene (66%) are produced using light feedstocks such as natural gas, naphtha, or light diesel fuel reacted in tube furnaces by a steam cracking process [5]. It was well known that low-temperature reactions produce more cracked oil, while high-temperature reactions could produce more the products of  $C_1$ - $C_4$  hydrocarbons and coke. From the thermodynamic point of view, heavy oil cracking

conversion is a heat-absorbing reaction, thus increasing the reaction temperature is better for the conversion of heavy oil into small molecule hydrocarbons, but at the same time, the cracking coke rate will also be increased. Controlling the appropriate reaction temperature was the key to maximize the production of low-carbon olefins from heavy oil. Zhang [6] investigated the effects of reaction conditions on the compositional distribution of vacuum residue cracking products. The results showed that the reaction temperature has a significant effect on the composition of cracked gas, and the cracked gas yield gradually increases with increasing the reaction temperature. Of which the contribution rate of dry gas was the largest. Basu [7] investigated the reaction effect of naphtha catalyzed by calcium aluminate catalysts, and found that the low carbon olefin yield was reach about 40.0 wt% at 800 °C. Similarly, the cracking properties of naphtha using modified calcium aluminate and found that the low carbon olefin yield was reached about 40.0 wt%, but at this time the liquid yield of the product was low [8] at 800 °C,. Tang [9] found that the  $C_2^+$ + $C_3^+$  olefinicity of higher than 58.0% were achieved by cracking over calcium aluminate at 650 °C with a catalyst-to-oil ratio 7.0. Previous studies

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show that the influence of reaction temperature on the composition of cracking products has been widely studied. Most researchers have focused on the study of the composition of the primary cracking products of heavy oil or light oil. However, there was little research on the secondary conversion of base cracked oil for producing low carbon olefins.

In this study, the chemical group composition and structural characteristics of base cracked oil were investigated by column chromatographic separation. Elemental composition, infrared functional group structure and molecular structure of chemical group of base cracked oil will be analyzed by the elemental analyzer, FTIR, and GC/MS, respectively. On the basis of this, the TG-FTIR was utilized for study on the pyrolysis products formation of base cracked oil chemical group. The weight loss reaction characteristics and the products composition were elucidated, and the corresponding kinetic reaction model was established.

## Experimental

### Materials and Reagents

Chromatographic aluminium oxide was purchased from Qingdao Jingke chemical reagent Co., Ltd, China, and calcined in air at 500 °C for 6 h without further purification. N-heptane, toluene and ethanol were all purchased from Sinopharm group Co., Ltd, China. The column chromatography test was guided

by NB/SH/T 0509-2010 standard [10] to separate base cracked oil into four chemical groups (saturate, aromatic, resin, and asphaltene). Atmosphere residue base cracked oil properties are listed in Table-1.

Table-1: Chemical group composition of cracked oil.

Components	Contents /wt%
Saturate	53.93
Aromatic	27.20
Resin	16.72
Asphaltene	0.65

### Pyrolysis test of base cracked oil

The experiment was used a TG-FTIR device. Of which the thermogravimetric instrument was applied a TGA400 device (Perkin Elmer co., USA), and the Fourier Transform Infrared spectrometer was a Spectrum Two device (Perkin Elmer Co., USA). Schematic diagram of TG-FTIR was shown in Fig. 1.

Firstly, 5 mg of the base cracked oil was added into a platinum crucible, and the pyrolysis was carried out under atmospheric pressure with high-purity Helium as the carrier gas (100 mL/min), and the reaction temperature was increased from room temperature to the final temperature of 700 °C at a heating rate of 20 °C/min. Finally, the pyrolysis oil and gas generated was purged by He to an infrared cell for on-line detection. The resolution of FTIR spectrometer was 4 cm<sup>-1</sup> and the wave number range was 500~4000cm<sup>-1</sup>.



Fig. 1: Schematic diagram of TG-FTIR.

### Characterization

The FT-IR spectrum of the samples were determined by a Nicolet 501P Fourier Transform Infrared Spectrometer (Nicolet co., USA) with KBr press, and the range of the tested wave number was 500~4000  $\text{cm}^{-1}$ ; the wave number accuracy was  $\leq 0.1 \text{ cm}^{-1}$ . The content of elements in the chemical group of cracked oil was determined by an Ario Macrocube elemental analyzer (Elementar Co., Germany).

### Results and Discussion

#### Elemental composition of the base cracked oil chemical group

Elemental analysis is an important parameter for measuring organic matter, which reflects the chemical structure of organic matter and it contains lightness components. The results of the analyses carried out on the chemical groups of cracked oil are shown in Table-2.

Table-2: Chemical group element composition of cracked oil.

Group	C (%)	H (%)	N (%)	S (%)	O (%)	H/C
Saturate	85.58	13.90	0.03	0.21	0.28	1.95
Aromatic	86.31	12.11	0.61	0.46	0.50	1.68
Resin	86.92	10.71	1.24	0.50	0.63	1.48
Asphaltene	87.78	9.83	1.06	0.45	0.88	1.34

From Table-2, it could be seen that the sum of C and H elements of all chemical groups was more than 97%. The saturate has the highest hydrogen /carbon atomic ratio (H/C ratio) and low heteroatom content. The H/C ratio of aromatic product is lower, and the content of N, S, and O heteroatoms is obviously higher compared with those of the saturate, which indicates that there are contained aromatic hydrocarbons and other non-hydrocarbons substances. For resin and asphaltene, the content of the heteroatoms and H/C ratio are higher in comparison with those of saturate and aromatic, which results in the difficulty of its conversion and easy to be coked.

### Functional groups of the cracked oil chemical group

In this section, the qualitative determination of functional groups of cracked oil by the IR spectrum [11] was carried out. Four chemical groups have corresponding characteristic peaks at different positions were shown in Fig. 2.

As could be seen Fig.2 the IR spectrum of saturate was contained the deformation vibration peaks of methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2$ ) of alkanes, and the telescopic vibration peaks of hydrocarbon single bonds, and the wave numbers of their corresponding IR absorption peaks are 1374  $\text{cm}^{-1}$  ( $-\text{CH}_3$ ), 1458  $\text{cm}^{-1}$  ( $-\text{CH}_2$ ), 2919  $\text{cm}^{-1}$ , and 2854  $\text{cm}^{-1}$  (the telescopic vibration peaks of C-H). Among Fig.2 (a), the IR absorption peak with a wave number of 724  $\text{cm}^{-1}$  was a distorted vibrational peak of methylene ( $-\text{CH}_2$ ) with more than four carbons in alkanes, indicating that the saturate contains long-chain alkanes. Among Fig. 2 (b), the C=C skeleton stretching vibration peaks of aromatics was observed at 1600  $\text{cm}^{-1}$ , the C-H deformation vibration peaks of aromatics are observed at 870  $\text{cm}^{-1}$  and 810  $\text{cm}^{-1}$ . In addition, Fig. 2 (c) and Fig.2 (d) were also found the structure of aryl, methyl, methylene, and hydroxyl. Of which 3793 and 3700  $\text{cm}^{-1}$  are belonged to hydroxyl peaks, 2344 and 2199  $\text{cm}^{-1}$  are belonged to the  $\text{RC}\equiv\text{CR}$  vibration peaks of alkynes, 2046 and 1960  $\text{cm}^{-1}$  are belonged to asymmetric vibration peaks of propadiene. 1028  $\text{cm}^{-1}$ , 1095  $\text{cm}^{-1}$  and 1260 are belonged to the C-O telescopic vibrational of alcohols or C-O-C vibrational peak of ethers. 531  $\text{cm}^{-1}$  and 463  $\text{cm}^{-1}$  was belonged to the C-H and C-C bending vibration peaks. Based on the above analysis, it can be find that the aromatic is mainly contained the substances of aromatic, olefins and saturated hydrocarbons. The resin and asphaltene are dominated by polycyclic aromatic hydrocarbons, and the fused ring is surrounded by alkyl side chains with heteroatoms, which can be used to link other aromatic compounds via the alkyl side chains.

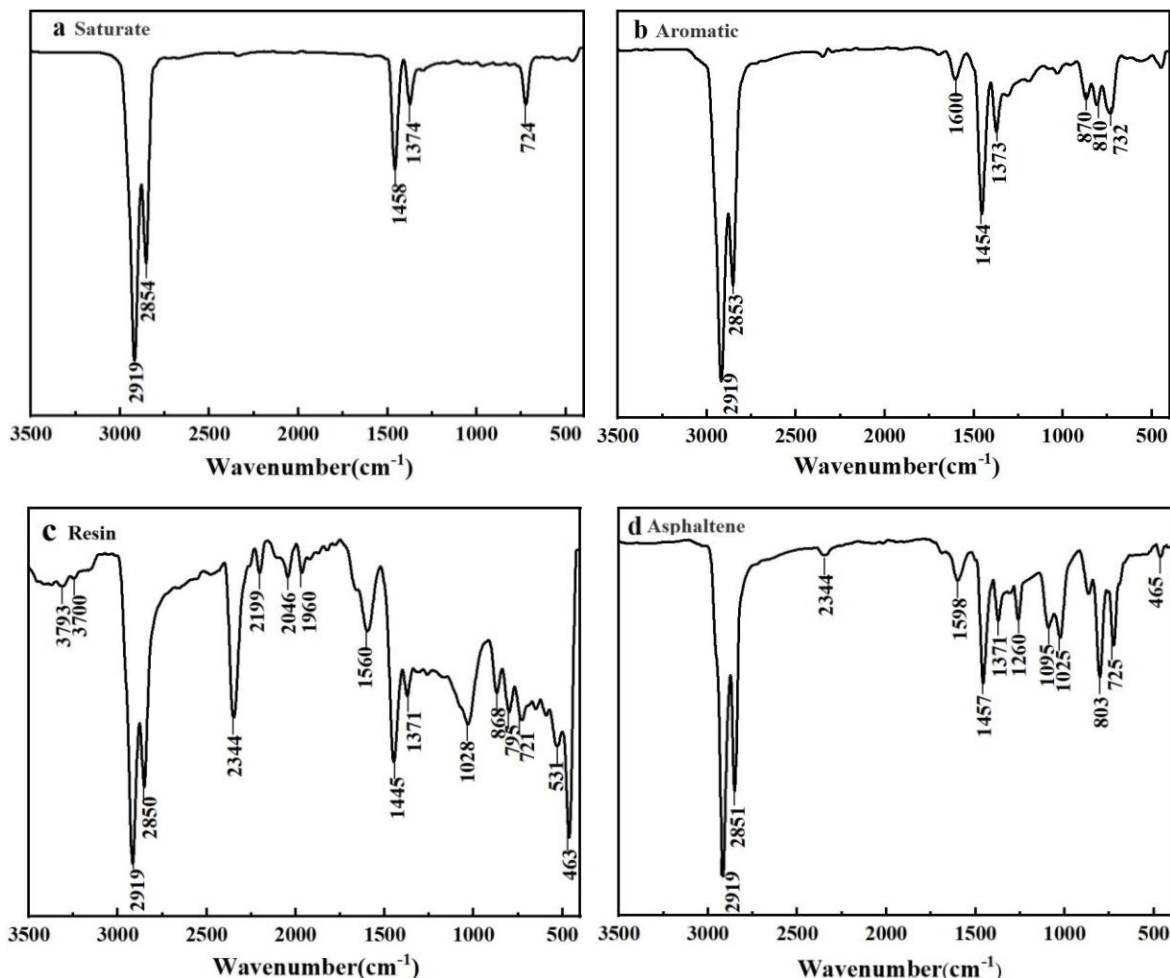


Fig. 2: Infrared Spectrograms of Four Chemical Groups.

#### *Pyrolysis weight loss behavior of base cracked oil chemical groups*

In this section, the heat loss behavior of base cracked oil chemical group was performed with the heating rate of 20°C/min, and the results were shown in Fig. 3.

TG/DTG curves of base cracking oil four chemical groups were shown in Fig.3. It shows that the fraction of saturate and aromatic possess the lowest initial reaction temperature of than that of resin and asphaltene. The initial and termination pyrolysis temperature was 315 °C and 493°C for saturate, respectively. This reflects that saturate has the highest

pyrolysis activity but the worst thermal stability. At this stage saturate fraction undergoes alkyl chain breaking and ring opening of cycloalkanes, dehydrogenation and condensation. For aromatic group, the initial and termination pyrolysis temperature was 408 °C and 525°C, respectively. The main reactions were the reaction of breaking of alkyl chain and alkyl side chain, the naphthene ring opening reaction, and the dehydrocondensation reaction of cycloalkanes and aromatic hydrocarbons. The residue of aromatic was 8.46%, which was higher than that of saturate. For resin and asphaltene, it exhibited that the lower conversion (about 70%) due to its complex molecular structure.

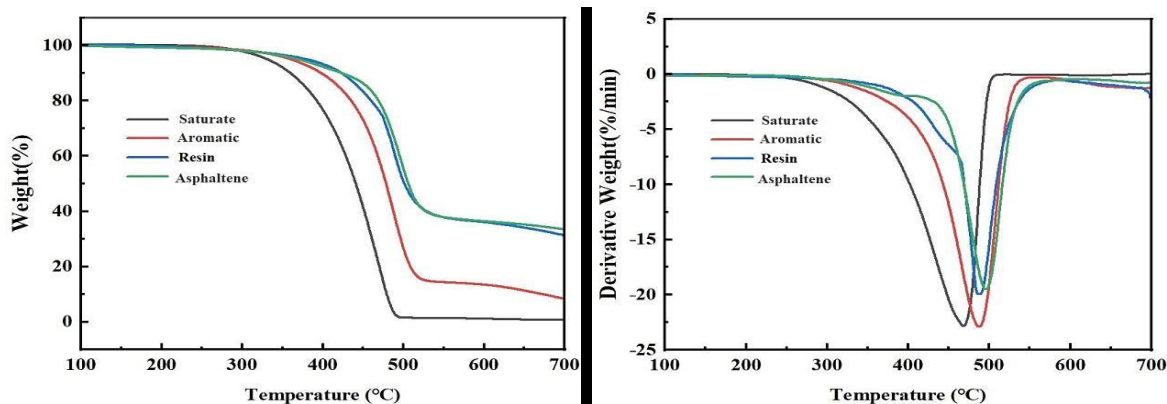


Fig. 3: TG/DTG curves of four chemical groups.

#### *Pyrolysis products formation of base cracked oil chemical groups*

In the section, gaseous products escaping during pyrolysis could be detected online by the infrared spectroscopy, while the weight loss behavior of the chemical groups of the cracked oil could be correlated with the pyrolysis gaseous products. The IR spectrum of pyrolysis products of the chemical groups at different temperatures was shown in Fig.4. It shows that the main products of the pyrolysis products of the chemical groups are CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons, and light aromatic hydrocarbons. But the presence of H<sub>2</sub> could not be detected by TG-FTIR because of its special structure with dipole symmetry [10].

For saturate, the pyrolysis process could be divided into 5 stages. Of which the pyrolysis temperature was reached to 337 °C, only the characteristic peak of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons appeared. The characteristic peaks of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and ethylene became stronger, and inconspicuous light aromatic hydrocarbons and methane peak were observed with the pyrolysis temperature increasing to 470, 499, 510 °C. It should be attributed to the secondary reaction of aliphatic hydrocarbons intensified and ring opening of cycloalkanes. As a result, the content of ethylene and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons was obviously increased. Finally, the less characteristic peak of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and ethylene was found when the temperature was increased to 622 °C.

For Aromatic, the characteristic peak of C<sub>2</sub><sup>+</sup>

aliphatic hydrocarbons were appeared, and the characteristic peak of CO<sub>2</sub> was observed at 413 °C. The characteristic peaks of ethylene and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons as well as the characteristic peaks of C-H deformation vibration could be clearly seen, and the characteristic peaks of light aromatic hydrocarbons and methane are not so obvious when the temperature was increased to 491 °C. The characteristic peaks of ethylene and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons were stronger, and those of methane and light aromatic hydrocarbons were gradually conspicuous at 514 °C and 525 °C, This should be attributed to the breaking reaction of the straight-chain alkanes and aromatic cycloalkyl side chains were occurred, and thus indicating that the content of these products was obviously increased. Finally, the less C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and inconspicuous ethylene peak were observed. But the characteristic peak of CO was found with increasing the temperature to 635 °C.

For resin, the characteristic peaks of the C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and inconspicuous ethylene could be observed at 455 °C. The characteristic peaks of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and ethylene could be clearly observed, and inconspicuous characteristic peaks of the light aromatic hydrocarbons and methane were also found at 499 °C. This was mainly due to the breakage of side chains of the aromatic ring alkyls via the β-site breakage. The characteristic peaks of the ethylene and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons were stronger, while the peaks of methane and light aromatic hydrocarbons were conspicuous at 516 °C and 525 °C. The characteristic peaks of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and ethylene were decreased, while the characteristic peaks of CO and CO<sub>2</sub> were found at 685 °C.

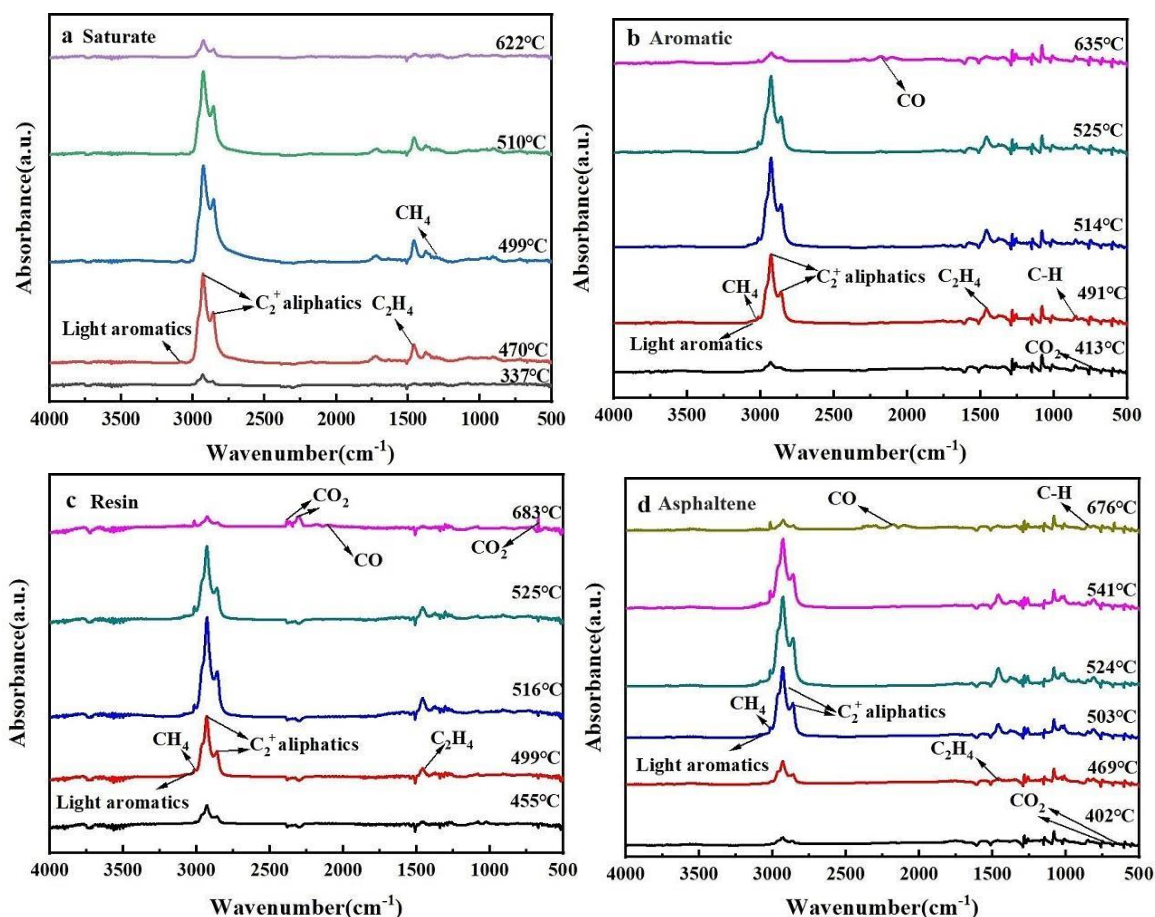


Fig. 4: IR spectrum of pyrolysis products of chemical groups at different temperature.

For asphaltene, the inconspicuous characteristic peaks of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and CO<sub>2</sub> were found at 402 °C. The conspicuous characteristic peaks of ethylene and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons were found at 469 °C. The characteristic peaks of C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons ethylene, light aromatic hydrocarbons and methane were gradually increased with increasing the pyrolysis temperature increased to 503-541 °C. Light aromatic hydrocarbons are produced by the breakage of oxygen-containing functional groups in aryl ether compounds and cycloalkanes dehydrocondensation. Finally, less C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and light aromatic hydrocarbons were observed, while CO and C-H deformation vibration characteristic peak (para-substituted) of the aromatic hydrocarbons was appeared with increasing the temperature to 676 °C.

#### Kinetic of the cracked oil chemical groups

The study of heavy oil pyrolysis kinetics could provide a deeper understanding of the reaction

process and mechanism. So far, there are two main types of methods to calculate the kinetics: model-free method and model method [12-14]. In this section, the Coats-Redfern method was chosen for the study of the pyrolysis kinetic law of cracked oil chemical groups.

The reaction time tends to be infinitesimal, and the non-isothermal pyrolysis reaction process of the chemical family could be viewed as an isothermal reaction process, so there was a kinetic equation for the pyrolysis reaction:

$$\frac{d\alpha}{dt} = A e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (1)$$

Eq: t- Reaction time.  $\alpha$  - Rate of weight loss of sample at a certain time,  $A$ - Preexponential, min<sup>-1</sup>,  $E_a$ - Activation energy, kJ·mol<sup>-1</sup>,  $f(\alpha)$  - Kinetic differential function.

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\infty} \times 100\% \quad (2)$$

Eq:  $w_0$ -Starting mass of the sample, mg.  $w_t$ -Mass of specimen at time t, mg.  $w_\infty$  is the final mass of the sample at the end of the reaction, mg.

At a constant rate of temperature increase ( $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ ), combine equations (1) and (2):

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (3)$$

The Coats-Redfern integral method is of the form  $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ , and substituting (3) yields equation (4).

$$g(\alpha) = -\frac{ART^2}{\beta E_a} \times \left[1 - \frac{2RT}{E_a}\right] \times E_a^{\left(\frac{-E_a}{RT}\right)} \quad (4)$$

Since  $2RT/E_a \ll 1$ , taking logarithms on both sides of equation (4) leads to equation (5):

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT} \quad (5)$$

The first-order reaction function model  $f(\alpha) = (1-\alpha)$  was chosen. The linear fitting equation

was plotted in terms of  $\ln\left[\frac{g(\alpha)}{T^2}\right]$  against  $\frac{1}{T}$  as in equation (6):

$$F(x) = ax + b \quad (6)$$

Eq:  $F(x) = \ln\left[\frac{g(\alpha)}{T^2}\right]$ . The slope is  $a = -\frac{E_a}{R}$ .

The intercept is  $b = \ln\frac{AR}{\beta E_a}$ .

By fitting the weightlessness data of cracked oil chemical group, if the linear correlation coefficient of the linear equation was close to 1, the selected model was reasonable.

Based on the fitting results, the activation energy  $E_a$  and the preexponential  $A$  could be calculated. Kinetic parameters for base cracked oil chemical group pyrolysis were shown in Table-3. As could be seen from Table-3, the correlation coefficients  $R^2$  of the linear equations and fitting results were close to 1, and thus proving that the selected model was reasonable. The saturate had the lowest activation energy ( $78.82\text{ kJ}\cdot\text{mol}^{-1}$ ), while the resin and asphaltene have the highest activation energies of  $108.87\text{ kJ}\cdot\text{mol}^{-1}$  and  $110.56\text{ kJ}\cdot\text{mol}^{-1}$ , respectively. It should be attributed to the breakage of C-C bond and C-H bond of straight-chain alkanes and isomerized alkanes would mainly occur in saturate fraction, and the bond energy was relatively lower, so the activation energy was lower. The aromatic was mainly occurred the breakage of alkyl side chain of aromatic hydrocarbon compounds or de-alkylation reaction with increasing the pyrolysis temperature. Thus, the activation energy was evidently higher than that of saturate. Resin and asphaltene was mainly composed of polycyclic compounds and highly condensed cyclic compounds. This reflected that the higher activation energy of resin and asphaltene.

Table-3: Kinetic parameters for base cracked oil chemical group pyrolysis.

Chemical group	$E_a\text{ kJ}\cdot\text{mol}^{-1}$	$A\text{ min}^{-1}$	$R^2$	Kinetic Model
Saturate	78.82	$2.28 \times 10^6$	0.991	$d_a/d_t = 2.28 \times 10^6 (1-\alpha) \exp(-9479/T)$
Aromatic	103.46	$7.14 \times 10^7$	0.990	$d_a/d_t = 7.14 \times 10^7 (1-\alpha) \exp(-12443/T)$
Resin	108.87	$1.13 \times 10^8$	0.979	$d_a/d_t = 1.13 \times 10^8 (1-\alpha) \exp(-13094/T)$
Asphaltene	110.56	$1.59 \times 10^8$	0.992	$d_a/d_t = 1.59 \times 10^8 (1-\alpha) \exp(-13297/T)$

## Conclusion

The pyrolysis reaction properties and kinetics of base cracked oil were investigated by the TG-FTIR, which could provide a referable basis for the gas-phase reaction of heavy oil. The results indicated that saturate was mainly composed of the chain alkanes and cycloalkanes. The aromatic mainly contains the polycyclic aromatic hydrocarbons and alkyl substituted polycyclic aromatic hydrocarbons. The resin and asphaltene fraction was mainly composed of thick cyclic aromatic hydrocarbon. As the fraction becomes heavier, the initial and termination pyrolysis temperature of four chemical groups were gradually increased, and the amount of carbon residue was gradually increased and coking intensifies. The pyrolysis products are mainly methane, ethylene, light aromatic hydrocarbons and C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons. Of which C<sub>2</sub><sup>+</sup> aliphatic hydrocarbons and ethylene produced by pyrolysis all show the trend of increasing firstly and decreasing later. The saturate and aromatic are the main sources of low carbon olefins. The correlation coefficients R<sup>2</sup> of the linear equations and fitting results were close to 1, and thus proving that the selected model was reasonable. The saturate had the lowest activation energy (78.82 kJ·mol<sup>-1</sup>), while the aromatic, resin, and asphaltene have activation energies of 103.46 kJ·mol<sup>-1</sup>, 108.87 kJ·mol<sup>-1</sup>, and 110.56 kJ·mol<sup>-1</sup>, respectively.

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