

## Effect of characteristics of inferior residues on thermal coke induction periods

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**Abstract:** Using 4 inferior residual oils as raw materials, the effect of feedstock properties on the characteristics of coke formation during initial thermal conversion process was studied. The results show that the influence for coke induction period of different oils affected by temperature can be measured with the sensitivity parameters. The shorter the coke induction period of the residue, the bigger the sensitivity parameter. The coke induction period has a higher decrease rate with the reaction temperature rising. The coke formation property generally depends on feedstock's basic properties, and the influence of various properties of inferior residual oils on coke formation is different under the same reaction conditions. Carbon residue, ash, relative molecular mass, asphaltene precipitation onset point and stability parameter have strong correlations with the coke induction period, especially for the colloidal stability of oil reflected by asphaltene precipitation onset point and stability parameter. The colloidal stability of the inferior residual oils is related to the coke formation characteristics. The worse the stability of the residue, the more likely the coke is to form. The coke forming process is a gradual destruction of the colloid system during thermal reaction.

**Key words:** inferior residue; delayed coking; characteristic; coke induction period; colloidal stability

The recovery ratio of light crude oil is getting lower and lower, heavy crude oil and even overweight heavy oil are taken more and more seriously by the oil refining industry<sup>[1]</sup>. China's crude oil is overweight, residual oil content is generally more than 50%<sup>[2]</sup> and higher in thickened oil. In order to obtain a higher yield of light oil, the residual oil is generally required to heat to a higher reaction temperature for hydrogenation or decarbonization<sup>[3]</sup>.

In recent years, coking of inferior residue oil of high-metal, high-residue carbon has become the preferred residue lightening process, of which more than 85% of the process is delayed coking<sup>[4,5]</sup>. During residue heating, especially when the residue of low quality is heated in the delayed coking heating furnace tube, residue molecules occur the thermal cracking to result in light oil distillate, and the feed fluidity gets better, but the colloid stability will be worse. When the reaction reaches to a certain extent, the coking rate is significantly accelerated to reach the coke induction period. The coke produced will deposit in the wall of heating furnace tube to enhance heat transfer resistance and flow resistance,

which will shorten the device cycle of coking unit.

The mechanism of coke formation of oil has been a more general understanding. The Yan model of residue colloidal structure<sup>[6]</sup> suggested that asphaltene is the micelle phase or dispersed phase, the resin is peptizer, the oil fraction (the saturated fraction and the aromatic fraction) is dispersion medium in the residue of colloidal systems; asphaltene forms a lyophilic sol through the interaction between resins and oils. Wiehe<sup>[7]</sup> first proposed the concept of coke induction period and analyzed phase separation kinetics model during formation of petroleum coke. The coke formation of residues consists of physical and chemical coke. As a precursor of chemical coke, physical coke is mainly formed by deposition of the original asphaltene in residues; the chemical coke depends the amount of coke formation, including alkane dehydrogenation, aromatic dealkylation and condensation to generate large amounts of coke.

In order to better guide industrial production, researchers pay more attention to the factors of coke formation of residue. Wang et al<sup>[8]</sup> studied the relationship between hydrogen

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supply capacity and coke formation trend on Liaohe and Gudao residues, and found that residual coking trend is closely related with its internal hydrogen transfer capacity. The higher the hydrogen transfer capacity of asphaltenes, the stronger the inhibition ability of free radical condensation to form coke. Guo et al<sup>[9]</sup> obtained coking rate of Jinzhou Petrochemical sub-component by thermogravimetry method in the order of asphaltenes > resins > aromatics > saturates. Wang et al<sup>[10]</sup> found that the original asphaltene in benzene solution associated with each other with 2 or 3 molecules, but the asphaltene of residual oil after heat treatment is associated with 3–6 molecules. They analyzed that the relationship between size of the association index and thermal coke formation trend of residue is a positive correlation. Guo et al<sup>[11]</sup> found that the higher the content of heavy metals in heavy oil, the shorter thermal conversion process of coke induction period. With the increase of heavy metal content in the feedstock oil, the more the coke formed in thermal reaction with the larger coke particles.

Effect of inferior heavy oil property on its coke induction period is little reported. According to the mechanism of coke formation, it is of great significance to investigate relationship between the properties of inferior heavy oil, especially the stability of colloid system and the coke induction period. The result will guide the long period, high efficiency and safe operation of the coking unit.

## 1 Experimental

### 1.1 The materials

In this study, 4 inferior residues (A, B, C, D) were selected as the test materials. The basic properties and compositions of the samples are shown respectively in Tables 1 and 2.

### 1.2 Micro-reactor experiment

The reaction is carried out in a micro thermal reaction kettle. 6–8 g (weighted to the nearest 0.01 g) oil sample was poured into a precisely weighed quartz tube with marks, and then put the oil sample tube into a reaction kettle and tighten it. Pass nitrogen to a certain pressure, make a leak test and replace the air of kettle to a certain pressure. The reaction vessel was heated in a tin bath, start the reaction and timing. When the reaction time was up, the kettle was put into water to quench the reaction. After 1 h, when the reactor was cooled to room temperature, vent the kettle gas, and then remove the reactor to take out the oil sample for further analysis.

### 1.3 Analysis and testing

#### 1.3.1 Determination of coke formation rate

The oil sample with toluene in the quartz tube after reaction was completely transferred to the conical flask 1, placed in an oil bath at 130°C and heated to reflux for 1.0 h. The conical flask was sealed and placed in dark room at room temperature for 1.5–2.5 h. The solution in the Erlenmeyer flask 1 was filtered through a marked filter paper soaked with toluene for 24 h and weighed, making the insoluble in the Erlenmeyer flask 1 transferred to the filter paper as much as possible.

Table 1 Properties of four heavy oils

Item	A	B	C	D
Density $\rho_{20}/(\text{g}\cdot\text{cm}^{-3})$	1.0163	0.9978	1.0047	0.9997
Viscosity $\mu_{100}/(\text{Pa}\cdot\text{s})$	250.0	65.10	192.3	68.50
Carbon residue w/%	18.22	15.43	17.89	16.49
Ash w/%	0.24	0.16	0.21	0.18
Relative molecular mass	1470	966	1218	1178
H/C atomic ratio	1.57	1.59	1.56	1.59
Ni/ $(\mu\text{g}\cdot\text{g}^{-1})$	29	19	26	20
V/ $(\mu\text{g}\cdot\text{g}^{-1})$	0.25	0.12	0.19	0.15

Table 2 SARA compositions of four heavy oils

Item	A	B	C	D
Saturates w/%	6.16	9.78	6.37	9.01
Aromatics w/%	29.39	30.59	30.56	30.12
Resins w/%	55.30	56.85	55.95	56.48
Asphaltenes w/%	9.15	2.78	7.12	4.39

Remove the filter paper into the extractor using the Erlenmeyer flask 2 solution in 130°C oil bath extraction, until the extractor solution becomes clear, and with a glass rod dipped in a drop of solution on a clean filter paper and there is no trace after drying naturally. The filter paper is removed, dried in a vacuum, placed in a desiccator to cool to room temperature and weighed, and the mass of the filter paper is subtracted to obtain the toluene insoluble content of the oil sample.

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