Fast Pyrolysis of Qinhuangdao Vacuum Residue at High Temperature by Py-GC/MS

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Abstract. The liquid-phase cracking is inevitable in the pyrolysis of heavy oil because of the high boiling point of residues. To enhance the gas-phase cracking of residues, the reaction temperature and heating rate processing scheme was performed in a Py-GC/MS apparatus. The results showed that the yields of gasoline and diesel fractions reached the maximum at 750°C and 2000°C/s. Thus, to reduce coking amount and raise liquid yield in industrial thermal processing of vacuum residue, the reaction temperature and heating rate should be enhanced.

1. Introduction

Petroleum residues refer usually to the heavy fractions generated in petroleum refining, including atmosphere residue (AR), vacuum residue (VR). The newly exploited heavy crudes, such as shale oil, oil sands bitumen, and coal tar, also have properties similar to such petroleum residues. The typical residues are high in metals and Conradson carbon residue (CCR) [1]. Thus, it will create huge challenges and opportunities in conversion of these heavy petroleum residues into light distillates. Generally, the main processes are based on carbon rejection and hydrogen addition technologies [2]. The former is associated with thermal or catalytic thermal treatment, which includes mainly the tiebreaking [3], residue fluid catalytic cracking (RFCC) [4], and the delayed coking and fluid/flexi coking [5, 6].

The reaction temperature and heating rate are significant factors because of the variations of the heat and mass transfer during VR thermal cracking, which will affect the products distribution in pyrolysis. However, many researchers who considered higher temperatures in their thermal cracking studies focused on reporting the product distribution without considering the effect of transport phenomena and the phase in which cracking occurred on their results. In addition, it is noted that less publication exists about the influences of the heating rate in VR cracking. In this study, the effect of reaction temperature and heating rate on the pyrolysis products of residue were investigated using an analytical Py-GC/TOF-MS.

2. Experimental section

Feedstock. A vacuum residue (VR) provided by Qinhuangdao oil field (Heibei Province, China) was used as the heavy feedstock and its properties are shown in Table 1. The VR has high density and viscosity.
Py-GC/TOF-MS Analysis. The Py-GC/TOF-MS experiments were conducted using a Pyro probe 5200 Series pyrolyser (CDS Analytical Inc.) with direct connection to a DANI gas chromatograph coupled to a time of flight mass spectrometer. Each experiment was conducted with 0.400±0.005 mg of oil sample in a quartz boat. An analytical balance with the readability of 0.001 mg was used for weight, to ensure the accurate quantity of samples and residues.

The pyrolysis was carried out at the set temperature from 650°C to 850°C and selected heating rate of 500°C/s to 20000°C/s, respectively. The GC separation of pyrolysis vapors were done by a DB-5MS column (60m × 0.25mm, 0.25μm film thickness) with Helium (99.999%) carrier gas (1mL/min). The GC inlet was 280°C and a split ratio of 50:1 was used. The oven was programmed to start at 30°C (hold for 15 min) and then ramp to 60°C with 1°C/min (hold for 1min), and then raise to 200°C with the heating rate of 3 °C/min followed by 10°C/min up to a final temperature of 280°C. The mass spectrometer was operated in EI mode at 70eV, and the mass spectra were obtained from m/z 35 to 500. The chromatographic peaks were identified according to the NIST mass spectral library.

One drawback of the Py-GC/MS apparatus is that it did not allow the product collection. However, the chromatographic peak area of a compound is considered linear with its quantity. Thus, the peak area value of products can be compared to reveal the Qinhuangdao of its yields under different reaction conditions.

Table 1. Properties of Qinhuangdao Vacuum Residue

|                      | Density(20°C), kg/m³ | Viscosity (100°C), mm²·s⁻¹ | CCR⁰, C, H, S, N, O, H/C |
|----------------------|----------------------|-----------------------------|-------------------------|
|                      | 993                  | 1866                        | 17.16, 86.32, 11.34, 0.64, 0.75, 0.95, 1.57 |

CCR is the Conrad son carbon residue.

3. Results and discussion

3.1. Effect of Reaction Temperature on the Pyrolysis of Vacuum Residue

The reaction temperature is the main operating conditions that control the thermal conversion of heavy oil. Therefore, we investigated the effect of the reaction temperature on the product distribution and product quality by Py-GC/TOF-MS.

Figure 1 shows the ion chromatograms from fast pyrolysis of Qinhuangdao VR at 700°C. There are more than 150 peaks can be identified by GC/TOF-MS analysis. Heavy oil fast pyrolysis vapors consisted of permanent gases (CO, CO2, CH4, H2, etc.), volatile compounds (hydrocarbon compositions) and carbon residue (coke). However, GC/MS was only able to determine the organic
volatile compounds, and the hydrocarbon compositions were divided into three groups: composition of $C_2$-$C_4$ (low-carbon hydrocarbons); composition of $C_5$-$C_{12}$ (gasoline fractions) and composition of $C_{12+}$ (diesel fractions).

Figure 2. Effect of reaction temperature on the pyrolysis product distribution.

Figure 2 (a) presents the distribution of hydrocarbon compositions. The peak area of low-carbon hydrocarbons showed a significant rising when the pyrolysis temperature increased from 650°C to 850°C, indicating that more heavy oil was cracked into light fractions under higher temperature. However, the peak areas of gasoline and diesel fractions were all increased first, and then with the further increase of the pyrolysis temperature, the peak areas were all decreased. Heavy oil cracking is a complex parallel-sequential reaction process, and gasoline and diesel fractions as intermediate products could further cracking at higher temperature lead to their yields decreased after reaching maximum at 750°C. Moreover, when the reaction temperature is lower than 750°C, the components with higher boiling point cannot be effectively gasified, and the proportion of liquid phase reaction is larger, wherefore the yield of gasoline and diesel fraction is also lower. Figure 2 (b) shows the variation of residue yield with the reaction temperature from 650°C to 800°C. As the increase of reaction temperature, the residue yields decreased sharply, and then became stable. When the reaction temperature increased from 650 to 750°C, the final residue yield decreased from 8.85 to 7.64 wt.%, which indicates that the high-temperature operation is beneficial to reduce the coke yield. Thus, it can be inferred the optimal reaction temperature is approximately 750°C in this study.

Due to the high boiling of vacuum residue, hydrocarbons mainly occurred liquid-phase reactions in the thermal cracking process. The liquid phase reaction of VR is not conducive to mass and heat transfer, which is beneficial to the formation of coke. Therefore, increasing the reaction temperature to enhance the gas-phase cracking became the key matter for raising the liquid yield and reducing the coke yield.

3.2. Effect of Heating Rate on the Pyrolysis of Vacuum Residue

Heating rate is one of the most key parameters that has direct influence on the yield and composition of the products evolved during VR cracking. Figure 3 shows the distribution of hydrocarbon compositions under different heating rate. It could be observed that the yield of pyrolysis production reached the maximum at 2000°C/s. In the heavy oil pyrolysis process, cracking and condensation are two key reactions. The cracking reaction is endothermic and has lower activation energy, while the condensation reaction is exothermic and has higher activation energy. The higher heating rate can provide a large amount of energy at an instant and the structure of the VR is strongly attacked, which will be induced the bridge breaking and cross-linking reaction with different activation energies. Therefore, the cracking reaction increased while the condensation reaction is reduced by enhancing the heating rate, consequently, the yield of the pyrolysis products was improved. However, the heating rate is too high (5000°C/s, 20000°C/s) will affect the heat transfer and gas diffusion, so that heavy oil cannot be
effective gasification and liquid reaction ratio increased. Thus, the yields of gasoline and diesel fractions were decreased for the increasing of the condensation reaction.

![Graph showing peak areas of pyrolysis products under different heating rates](image)

**Figure 3.** Peak areas of pyrolysis products under different heating rate.

4. **Conclusion**
The high temperature processing scheme could enhance the gas-phase cracking of residue for raising the liquid yield and reducing the coke yield, but too high a temperature would also lead to the over-cracking of gasoline and diesel fractions. The optimal reaction temperature is approximately 750°C in this study. Heating rate has significant effect on the yield of gaseous products and the yield of the products increased with increasing the heating rate. The optimal heating rate is about 2000°C/s.

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