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Interaction between saturates, aromatics and resins during pyrolysis and oxidation of heavy oil

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ABSTRACT

Pyrolysis and oxidation of heavy oil is the fundamental of in situ combustion process. Heavy oil from Xinjiang, China and its main components, saturates, aromatics and resins (SAR), were used as samples to study their pyrolysis and oxidation characteristics with a thermogravimetric analyzer (TGA) and a fixed-bed reactor. The DTG curves and the detected gas products differed between pyrolysis and oxidation of the heavy oil. Elemental analysis of pyrolysis and oxidation cokes indicates that low temperature oxidation (LTO) primarily accounted for the differences. Compared with independent pyrolysis and oxidation of saturates, aromatics and resins, they showed little interactions during co-pyrolysis, but significant interactions during co-oxidation. When saturates co-oxidized with aromatics or resins, both the beginning temperatures of LTO were increased, the DTG curve at high temperature oxidation (HTO) remained unchanged during co-oxidation with aromatics, while the DTG peaks at HTO changed from two into one during co-oxidation with resins. Co-oxidation of aromatics and resins showed similar effect at HTO. Oxygen-adding reactions of saturates, aromatics, and resins at low temperature promoted the polycondensation between intermediate products and altered the subsequent cracking reactions, which caused special characteristics during their co-oxidation.

1. Introduction

Petroleum is an important fossil fuel. Given the exploitation of petroleum resource, the amount of easily exploited light oil decreases, whereas the proportion of heavy oil in the oil reserves increases. Thermal recovery technologies are widely used today, such as steam stimulation and steam drive. However, their recovery efficiencies decrease with the oil saturation decreasing (Liu, 2011). In situ combustion (ISC) is an enhanced recovery method, which has an outstanding performance especially on heavy oil exploitation. ISC projects in operation in India, Romania, etc. exhibit good economics (Kok, 2012; Mahinpey et al., 2007). New technologies such as horizontal well are being developed. The basic process of ISC is as follows. Air is injected into the field, and heavy oil is ignited; with increasing temperature, the viscosity and chemical composition of the heavy oil change makes for the easy oil recovery (Prats, 1982). The oxidation and pyrolysis characteristics of heavy oil are among the keys to ISC performance.

The composition of heavy oil is complicate. There are at least 5 kinds of chemical components of which the molecular weight is around

362 g/mol according FT-MS experiments, for example $C_{25}H_{31}O_2$, $C_{22}H_{35}O_2S$, $C_{24}H_{43}O_2$, etc. (Qian et al., 2001). Each chemical compound has different pyrolysis or oxidation reactivity at various pressures and temperatures. Therefore, the reaction mechanism of heavy oil during ISC is highly complex. However, the overall reaction process presents a number of characteristics. According to a large amount of experimental results of heavy oil oxidation, Fassihi (1981) divided heavy oil oxidation process into three sections: low-temperature oxidation (LTO), coke formation, and high-temperature oxidation (HTO). Low-temperature oxidation is a process wherein heavy oil contacts with oxygen in a low-temperature section, during which the oxygen-adding reaction and the coke precursor's forming process occur. Alexander et al. (1962) found that the amount of coke formation increased from 1.1 g/100–2.4 g/100 g oil sand because of LTO, which means that LTO significantly influenced the coke forming process. According to the GC-MS analysis of the LTO products, Khansari et al. (2014) found chemicals with oxygen-containing functional groups, such as aldehyde, carbonyl, ether, and carboxyl; thus, LTO included many complex reactions. Furthermore, LTO is mixed with an evaporation process. The heavy oil used by Kok (2011) lost more than 50%

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weight by evaporation. Therefore, evaporation and complex multi-component reactions make studying the mechanism of the LTO process difficult. Coke formation is a process in which LTO products further polymerize and crack to form coke. No exact boundary between LTO and coke formation process exists. Some scholars compared the amount and characteristics of coke in the processes of pyrolysis and oxidation (Cinar et al., 2011). The effects of temperature and holding time on the amount of coke produced were also studied (Xu et al., 2016). However, limited research discussed the coking mechanism and the effect of heavy oil components and experimental conditions on the characteristics of the coke produced. Some researchers believed that coke combustion is the main process of HTO, but others indicated that coke combustion and transformation take place in HTO (Cinar et al., 2011). Ren et al. (2007) indicated that the coke combustion process should use a two-step model rather than a one-step model for description.

TGA/DTA/DSC analysis is widely used to study the heavy oil oxidation process. DTG/DSC curves have two peaks, which correspond to LTO and HTO (Ouarda and Vossoughi, 1985 and Bae, 1977). Therefore, two overall reactions are used to describe the heavy oil oxidation process. Heavy oil samples from Saskatchewan are analyzed using the ramp temperature program by Ren (2007). The study showed that the temperature range of LTO was 100–370 °C. Evaporation was the main process from 100 to 270 °C. LTO reactions occurred beyond 270 °C, which increased the weight loss rate. The temperature range of HTO was from 420 to 550 °C. The temperature ranges of LTO and HTO are nearly the same according to studies on heavy oil thermal analysis. However, the amount of weight loss in LTO and HTO differed in other studies. Kok and Gul's (2013) results showed a 50% evaporation weight loss, whereas the weight loss of HTO is 35%. However, Ren's results (2007) showed that only 30% weight was lost because of evaporation and 35% in HTO. Moreover, the activation energies of LTO and HTO in different studies are different. The activation energy of LTO is 30–60 kJ/mol (Chen et al., 2014 and Kok and Gul, 2013). Kok and Gul (2013) used the results of two light oil samples to calculate the activation energy of HTO. The API gravities of samples 1 and 2 were 32.8 and 31.5 at 60 °F respectively. The results showed that the activation energy of oil sample 1 is 127 kJ/mol, whereas oil sample 2 is only 90 kJ/mol. Cinar et al. (2008) indicated that the activation energy of HTO is 50 kJ/mol. Therefore, the large divergence in the HTO activation energy exists, and the conclusion is not unified. Different scholars came up with different results because the component and characteristic of the heavy oil used in different studies are not the same. Limited research focused on the influence of components on the HTO process. Sarma et al. (2002) studied the heat releases of three oil samples during LTO and HTO. The viscosities of the oil samples were 2.58, 7.68 and 12.8 mPa.s at 25 °C respectively. They found that lower viscosity oil with sands at 10 MPa had a higher heat release rate in the low-temperature section, whereas lower heat release rate in the high-temperature section. High viscosity oil usually contained an increased amount of resins and asphaltenes, for example oil 1 (51935 mPa.s at 25 °C) contained twice the amount of resins and asphaltenes than oil 2 (37 mPa.s at 25 °C) (Akin et al., 2000). Thus, viscosity can reflect the influence of components on the reaction performance of heavy oil.

Given the complexity of detailed components, heavy oil is commonly divided into saturates, aromatics, resins, and asphaltenes (SARA). SARA are separated by different degrees of solubility in different solvents. Each fraction contains numerous chemicals that have similar physical and chemical properties. Kok and Gul (2013) studied the oxidation process of SARA using TGA. The research summarized the weight loss rule of each component and calculated the pre-exponential factors and activation energies of SARA during LTO and HTO. The research found that the weight loss processes are different among SARA. Saturates lost 90% of the weight in LTO, whereas resins lost 60% of the weight in HTO. Wiehe (1993) studied

the heavy oil coking process during oxidation. The research found that saturates, aromatics, and resins transformed into asphaltenes after LTO, and asphaltenes precipitated from the oil phase and formed coke. Freitag and Verkoczy (2005) used pressure differential scanning calorimetry (PDSC) to study the heat release of SARA oxidation and found a significant difference in the heat release characteristics of four components. They also found that the saturates oxidation process can be influenced by aromatics, resins, and asphaltenes. Given the increasing amount of other components, the DSC peak of saturates shifted from 250 to 330 °C. Verkoczy (1993) found that the amount of coke formed by heavy oil is equal to the sum of coke production of SARA during pyrolysis. However, during oxidation, the sum of SARA coke production is about 5–10% higher than the amount of coke formed by heavy oil, which indicated the interactions among SARA during oxidation.

Understanding the pyrolysis and oxidation characteristics of heavy oil is important for ISC development. Most research used heavy oil as the experimental sample; however, obtaining detailed mechanism information is difficult because of the complexity of heavy oil. SARA analysis is a typical method to describe the components of heavy oil. This research studied the characteristics of the pyrolysis and oxidation of heavy oil and the main SARA fractions using TGA and fixed bed reactor. The research also studied the interactions among SARA, which helped further explore heavy oil pyrolysis and oxidation mechanisms.

2. Experimental

2.1. Samples

This study used oil sample from Xinjiang. The viscosity was 1878 mPa.s (50 °C), and the °API was 18. Water and impurity were removed from the oil sample according to the Chinese national standards SY/T 6316 and SY/T 6520. Water content was less than 0.5% after processing.

SARA fractions were separated from the oil sample according to the Chinese national standards NBSHT 0509–2010. This method used n-heptane, toluene, toluene-ethanol (1:1), and ethanol as solvents for separation. A Soxhlet extractor and a chromatography column were used as experimental devices. The separation processes are as follows. Neutral alumina for chromatography was placed in a muffle furnace at 500 °C for 6 h to activate. The oil sample was weighed. Approximately 50 mL n-heptane was added to the oil sample per gram and placed in the Soxhlet extractor and then heated and boiled for 2 h. The mixed solvent was cooled and filtered. The filter paper was placed in the Soxhlet extractor, and extracted with n-heptane-oil solvent until the liquid turned colorless, thus none-asphaltenes solution was obtained. Then the sediment in the filter paper was extracted with toluene until the solvent turned colorless. The asphaltenes-toluene solution was then obtained. N-heptane solvent was poured into neutral alumina column chromatography, and n-heptane was used to wash saturates, toluene for aromatics, toluene-ethanol (1:1), toluene, and ethanol for resins. Therefore, the saturates, aromatics, and resins were acquired after removing the solvent. The content of SARA in the oil sample is shown in Table 1.

A small amount of asphaltenes was found in the oil sample. The study used the oil sample and the main SARA fractions (saturates,

Table 1
SARA analysis of heavy oil sample.

Heavy oil	Weight percent (%)
Saturates	41.6
Aromatics	19.1
Resins	37.2
Asphaltenes	2.1

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