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Thermogravimetric analysis of petroleum asphaltenes along with estimation of average chemical structure by nuclear magnetic resonance spectroscopy

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Abstract

Combining with the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) determinations, elemental analysis and molecular weight measurement, average molecular formula of the chemical unit for the asphaltenes from Chinese Daqing crude oil were calculated. Thermal pyrolysis kinetics of the asphaltenes had been studied using thermogravimetric analysis (TGA). The distributed activation energy model (DAEM) was used to analyze these complex systems. The results show that the peak activation energy for pyrolysis of the asphaltenes is 245 kJ mol^{-1} and the pre-exponential factor is 5.88×10^{14} s^{-1}. The DAEM method presented reasonably good results of the prediction of the weight loss curves. A linear relationship can be found from the plots of logarithm of the pre-exponential factor against the activation energy at selected conversion values. This phenomenon known as the compensation effect was explained and it was in agreement with the estimated chemical structure determined by NMR.

Keywords: Asphaltene; Pyrolysis; Thermogravimetric analysis (TGA); Nuclear magnetic resonance (NMR); Distributed activation energy model (DAEM)

1. Introduction

Asphaltenes are the essential components with the largest average molecular weight in crude oils or petroleum vacuum residues [1]. Some experimental evidence [2–6] suggested that these oils be at continuous colloidal aggregated states, in which asphaltene aggregates with resins adsorbed on their surface. The stability for this special structure strongly depends on the solubility and the interfacial properties of asphaltenes. The precipitation of asphaltenes in crude oil well production tubing is a practical as well as theoretical problem, owing to its negative impact on the petroleum industry. The thermal decomposition of asphaltenes is of interest because of the tendency of them to form high yields of coke and to cause catalyst deactivation during processing. Many studies [7–12] have been reported on the chemical structure, interfacial property and pyrolysis kinetics of asphaltenes. Pyrolysis of asphaltenes is viewed chemically as depolymerization in parallel with thermal decomposition of functional groups, which can supply clues to the structure of the parent hydrocarbon. When asphaltenes are heated prior to gasification, their large volatile content is released, leaving a char. Pyrolysis is the rapid first step in combustion and gasification processes in which the resulting char subsequently reacts with oxygen, steam, hydrogen or carbon dioxide. Hence, knowledge of thermal conversion kinetics of asphaltenes is of considerable importance. Recently, Geng and Liao [13] gave a reasonable review of asphaltene pyrolysis and reported the kinetic studies and the geochemical applications. Dieckmann et al [14] used asphaltene pyrolysis kinetics to infer information about oil expulsion temperatures.

In this work, asphaltenes for Daqing crude oil, one typical Chinese crude oil, were separated and the thermal pyrolysis

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kinetics was studied using thermogravimetric analysis. Combining with the NMR determination, elemental analysis and molecular weight measurement, the average molecular formula of the asphaltene unit was calculated. The aim is to give internal relations between the NMR and the TGA results.

2. Experimental

2.1. Separation of asphaltenes

Asphaltenes used in the experiments were extracted from Daqing crude oil coming from Daqing Oil Field Co. Ltd. in China. The separation of asphaltene fractions from the crude oil was carried out by *n*-pentane precipitation. Thirty volumes of *n*-pentane was added to the crude oil. The mixture was in a state of reflux for 1 h, and then was cooled and left to stand for 24 h. The precipitated asphaltene fraction was filtered and Soxhlet-extracted with *n*-pentane and dried in a vacuum drying oven. The asphaltene sample is a laminate brittle solid with metal luster.

2.2. Characteristic parameters

Elementary composition of the asphaltenes was determined by an elemental analyser of Carlo Erba EA1110. The molecular weight was measured by the VPO method using a Knauer type molecular weight meter with benzene as solvent. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DMX500 NMR spectrometer with $CDCl_3$ as solvent. The chemical shift is referred to the TMS standard.

2.3. Thermogravimetric analysis

The experiments used a NETZSCH STA 409 PG/PC TGA. The heating rates employed were 10, 15 and 20 °C min^{-1} up to the final temperatures of 800 °C. Ultra-high-purity nitrogen at room temperature was used at a flow rate controlled to 50 ml min^{-1} for 20 min before starting each run. The initial temperature of the furnace was controlled at 30 °C and lasted for 5 min. The samples were then heated to the final temperature at each heating rate and were held at that final temperature for 10 min. The sample weight was over the range from 9 to 11 mg. During the TGA experiments, the sample temperature increased linearly with time and the weight loss of volatiles was recorded directly.

Table 1
Results of elemental analysis of asphaltenes

C (%)	84.17
H (%)	9.06
N (%)	1.94
S (%)	2.67
O[a] (%)	2.2

[a] Calculated by difference.

3. Results and discussion

3.1. Structrual parameters and model molecule

Elemental analysis results for the asphaltenes are listed in Table 1. The ^{1}H and ^{13}C NMR measurement results are given in Table 2.

It appears that carbon and hydrogen are two major elements with total mass fractions of 93% in Daqing asphaltenes. Heteroatoms, nitrogen, sulphur and oxygen, with the range from about 2 to 3% are observed, which may give rise to strong intermolecular forces for asphaltene aggregations. Recently, nuclear magnetic resonance spectroscopy has become a powerful tool for the analysis of petroleum products [15–18]. The average structural group parameters as the usual definition [19,20] obtained from NMR measurements for the investigated asphaltenes are presented in Table 3.

It is known that the asphaltenes have been proposed to be repeating units of similar composition and that the unit sheets are conceived as being held together in the particle by intermolecular forces and by aliphatic chains [1,4,8,9]. The apparent molecular weight of the asphaltenes is dependent on the nature of solvent and also on the temperature because of the different association degree in different environment or under different condition. Published data for the molecular weights of petroleum asphaltenes generally range from 1000 to 5000 [7]. In this work, the molecular weights determined in benzene at 45 °C by the VPO method for the asphaltenes are 3950. The average molecular weight of a unit sheet in the asphaltene model molecule can be calculated from a combination of NMR measurements and elemental

Table 2
Relative contents of hydrogen and carbon atoms on different positions in asphaltenes from ^{1}H and ^{13}C NMR determinations

H/C type	Chemical shift (δ)	Definition	Relative content
H_{aro}	10.0 ~ 6.0	Hydrogens attached to aromatic ring carbons	0.1152
H_{ali}	4.0 ~ 0.4	Aliphatic hydrogen atoms	0.8848
H_α	4.0 ~ 2.0	Hydrogens attached to carbons in alkyl substitution α to aromatic ring carbons	0.1332
H_β	2.0 ~ 1.0	Hydrogens in alkyl substitution β or further from aromatic ring	0.5432
H_γ	1.0 ~ 0.4	Hydrogens in terminal or isolated CH_3 groups of saturates or hydrogens in alkyl groups substituted in position γ- and further from aromatic ring	0.2084
C_a	160 ~ 100	Aromatic carbon atoms	0.4427
C_{ali}	60 ~ 5.0	Aliphatic carbon atoms	0.5573