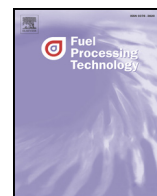




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Characterization of asphaltene isolated from low-temperature coal tar

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ABSTRACT

The asphaltene from low-temperature coal tar (LTCT) derived from Shanbei has been characterized through combination of conventional techniques, such as elemental analysis, molecular weight analyses, proton nuclear magnetic resonance, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The chemical structural analysis results confirm the view that asphaltenes are composed of confused aromatic rings bearing heteroatoms and alkyl and cycloalkyl constituents. Compared to asphaltenes from crude oils, the asphaltene from LTCT has lower molecular weight, higher aromaticity, higher contents of heteroatoms (especially oxygen) and shorter aliphatic side chains.

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1. Introduction

With the reduction of crude oil in the world, there is an urgent need for pursuing new kinds of energy [1]. As a substitute for crude oil, coal tar is expected to be used as liquid fuel feedstock. However, compared to conventional crude oil, coal tar is denser and poorer in quality [2]. Recently, hydrogenation process plays an important role in coal tar refining industry, which is one of the most important processes to make coal tar light [3–5].

Asphaltene is defined as a fraction of carbonaceous sources (such as petroleum, oil shale or coal) which is insoluble in low-boiling paraffin (such as *n*-heptane, *n*-pentane), but soluble in aromatic solvents (such as benzene, toluene) [6]. In general, asphaltene is the most complex and heaviest fraction of coal tar [7]. During the hydrotreating process of coal tar, the precipitation of asphaltene brought serious problems such as blocking pipe or even deactivating catalyst. In addition to this, asphaltenes also adversely affect the overall velocity and conversion of the hydrogenation [8]. Since these problems above have close correlation with their composition and structure, isolation and structural characterization of asphaltene from coal tar becomes more noticeable.

According to literatures [6,8–12], the chemical compositions and the structures of asphaltenes from crude oils and petroleum feedstock were analyzed and characterized by using various analytical techniques, such as elemental analysis, NMR, molecular weight analysis, FTIR and XRD.

Average structural parameters (ASP) (such as aromaticity, naphthenic rings, aromatic rings, length of alkyl side chains) are estimated

using ¹H NMR data, elemental analysis results and number-average molecular weight (M_n). The structural characterization of petroleum-derived products has been reported in several reports [9–13] using these analysis methods. The concept of an “average structural” has been proposed by Kershaw and Black [13] to represent asphaltenes because of its complexity and broader molecular weight distribution.

FTIR, as a versatile analysis technique [14,15], has been used to determine the aliphatic, aromatic CH content or to identify other functional groups in asphaltenes by some authors [16,17].

Using a variety of analysis techniques, the molecular weights of asphaltenes have been determined. In general, it includes lots of methods such as gel permeation chromatography (GPC) [8,18], vapor pressure osmometry (VPO) [7,19,20] and mass spectrometry (MS) [17]. However, each of these techniques has its own limitations [11]. Moreover, different values of molecular weight of asphaltenes were obtained since different methods and experimental conditions have been used. Besides, the values of molecular weight are also closely related to asphaltene origins and properties.

Recently, the X-ray photoelectron spectroscopy (XPS) technique was used to characterize the functional groups of asphaltene surface. Wilhems et al. [21] presented an XPS study of nitrogen speciation on the surface of asphaltenes isolated from seven crude oils. The results showed that the nitrogen containing compounds were mainly of pyridinic and pyrrolic types. The carbon and atom (S, O, and N) forms of the asphaltenes from two kinds of Chinese residue oil were obtained by using the XPS technique [22]. The results indicated that C–C and C–H species were the main types in the samples. In addition, some authors used the same method to analyze the differences of functional groups between two Cold Lake asphaltenes [23].

However, few researchers have studied the compositions and structure characteristics of the asphaltene from low-temperature coal tar

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(LTCT). Furthermore, asphaltenes are grouped into different classes based on solubility, so they don't have any well-defined molecular structure characterization [6,18]. They differ significantly in chemical compositions and structures depending on their origins.

In the present work the chemical structure characteristics of the asphaltene from LTCT from Shanbei were investigated by employing conventional techniques such as elemental analysis, GPC, ^1H NMR, IR and XPS. Better understanding of its composition and molecular structure is helpful to further understand its transformation mechanism during the hydrotreating process.

2. Materials and methods

2.1. Feedstock sample

LTCT used as the feedstock in this study was derived from Shanbei (northern Shaanxi province) low rank coal using Low Temperature Pyrolysis Process ($T < 800\text{ }^\circ\text{C}$). The density of the feed material was measured to be $\rho = 1.092\text{ g/cm}^3$ at $20\text{ }^\circ\text{C}$. Its elemental composition was C: 83.40%, H: 8.31%, N: 1.16%, S: 0.38% and O: 6.75% (by difference). Compared with conventional crude oil, the feedstock showed inferior performances such as greater density and higher oxygen content.

2.2. Asphaltene sample preparation

Briefly, LTCT was ultrasonically extracted with toluene (volume ratio 1:30) for 2 h at $40\text{ }^\circ\text{C}$. After allowing the resulting solution to stand for 24 h at room temperature, it was filtered through a $3\text{ }\mu\text{m}$ quantitative filter in order to remove the insoluble fraction. Subsequently, the solution was concentrated at reduced pressure. Then *n*-heptane was quickly added to the concentrated solution in a volume ratio of 20:1. Some brown asphaltene floccules appeared and the mixture was stirred for about 1 h. After that, the mixture was filtered through a $3\text{ }\mu\text{m}$ quantitative filter. Then the residue collected was washed with *n*-heptane for several times so as to make the absence of maltene. Finally, the residue was dried in vacuum at $80\text{ }^\circ\text{C}$ and the asphaltene was obtained.

2.3. Asphaltene characterization

Elemental composition of carbon, hydrogen, sulfur and nitrogen contents was obtained by using a VarioEL III analyzer. Fourier transform infrared spectrum (FTIR) was obtained in a Bruker Equinox-55 spectrophotometer using a KBr pellet with the scanning range from 400 cm^{-1} to 4000 cm^{-1} . The ^1H NMR was collected with a Varian-FT-80A spectrometer operating at 400 MHz. The main technical parameters were as follows: a flip angle of 45° and a repetition rate of 3 s. Tetramethylsilane (TMS) was selected to be as an internal standard and deuterated DMSO (DMSO- d_6) was used as solvent. For GPC analysis, the asphaltene sample was dissolved in HPLC-grade tetrahydrofuran (THF) to prepare solution with a concentration of 0.5 mg/mL. HPLC-grade THF was used as a mobile phase and the solvent flow rate was 1 mL/min. The separation was performed on a Waters 150C instrument. The relationships between retention time and molecular weight were calibrated with a set of standard polystyrene samples. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5400 Instrument equipped with an Al $K\alpha$ source ($h\nu = 1486.6\text{ eV}$) at a pressure below 8×10^{-9} Torr. The spectra were recorded at 20 eV pass energies. The spectra were calibrated with the main C 1s peak at 284.8 eV.

3. Results and discussion

3.1. Composition analysis

The LTCT feedstock showed the following composition: 84.0% maltene, 13.2% asphaltene and 1.3% toluene insoluble with a total

recovery of 98.5%. The small loss is probably due to volatile in the feedstock, part of which is easily lost in the process of removing heptane or toluene. There are some differences with respect to asphaltene content of 13.2% in LTCT and less than 2% in crude oil [17]. These data suggests that LTCT is heavier with higher asphaltene content.

The elemental analysis of asphaltene from LTCT is as follows: C: 76.0%, H: 5.1%, N: 2.7%, S: 1.5%, O: 14.7% (by difference) and H/C ratio of 0.805. From the elemental analysis, it can be concluded that the asphaltene from LTCT contains higher heteroatoms, particularly oxygen, but slightly lower sulfur than other asphaltenes from crude oil and petroleum [8,9,11,19,22]. The analysis confirms that contents of heteroatoms (S, N and O) in asphaltenes significantly differ depending on their origins [8–12,18–20,22]. Furthermore the asphaltene from LTCT contains lower H/C ratio, which implies a higher aromatic degree even if it may be due also to its higher heteroatom contents.

The molecular weights (MWs) from the GPC method of the asphaltene from LTCT were M_w 782 and M_n 652. Yasar et al. [18] used the same method reports for asphaltenes from petroleum feedstocks derived from different fields in southeast of Turkey, the M_n from 579 to 1010 and M_w from 812 to 1342. However, according to Calemma et al. [8], the M_n of the asphaltenes from three different feedstocks (crude oil, vacuum residue and atmospheric residue) were in the range of 1181–2050, that is much higher than those of the asphaltene from LTCT.

With other techniques, the average molecular weights of asphaltenes of crude oils from West Africa and North Sea, as determined by laser desorption ionization mass spectrometry (LDI-MS), are 500, 700 and 445, respectively [17]. The molecular weight of asphaltene derived from Tahe (China) atmospheric residue determined by using VPO method was 7122 [19]. The average molecular weight of asphaltene from a heavy oil derived from the Lloydminster area, Canada, as determined by vapor-pressure osmometry (VPO), is 2450 [7].

The results of the molecular weights of asphaltenes from different origins further confirm the view that molecular weight values significantly differ depending on the measure methods and their origins. Anyway, the asphaltene from LTCT contains lower molecular weight than asphaltenes derived from petroleum. It is well-known that petroleum asphaltenes are bigger than coal asphaltenes [24], the result is consistent with this expectation.

3.2. FTIR structural characterization

Specific functional groups in complex materials can be distinguished by using IR. The IR spectrum of the asphaltene from LTCT is shown in Fig. 1. The spectrum differed greatly from those of asphaltenes from crude oils [12,17] in the following aspects. On the one hand, a strong absorption peak at 3318 cm^{-1} (between $3600\text{--}3100\text{ cm}^{-1}$) is observed in

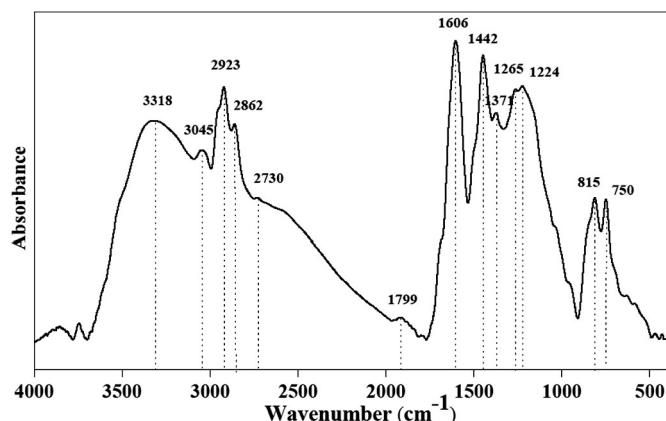


Fig. 1. Bands of FTIR spectrum of the asphaltene from LTCT.

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