



## Full Length Article

## Bond cleavage and reactive radical intermediates in heavy tar thermal cracking

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## ABSTRACT

Thermal cracking is an important step of heavy tar processing, in which covalent bonds are initially cleaved to form free radical fragments. The free radical fragments, namely the reactive intermediates, react with each other to form lighter products and coke. Quantity and activity of these reactive radicals determine the products distribution and process operation. Since few studies can be found about the reactive radicals from thermal cracking of heavy tar, we quantify their generation and analyze their activity using two tars provided by ExxonMobil Chemical Company. The tars are heavy fractions of steam cracking of naphtha and heavier hydrocarbon streams. It is found that these heavy tars crack significantly at 350 °C. The reactive radicals generated in 10 min for Tar-1 at 350 and 400 °C are 2.62 and 4.73 mmol/g-tar, respectively, and 1.27 and 3.88 mmol/g-tar, respectively, for Tar-2. The bonds cleaved in 10 min at 400 °C are about 1.50% and 1.30% of total covalent bonds in Tar-1 and Tar-2, respectively, and the bond cleavage activation energies are 31.00 and 38.80 kJ/mol, respectively. The differences in bond cleavage were analyzed from the viewpoint of the composition and structural differences between the two heavy tars, in terms of asphaltene content, aromaticity, and substitutive degree of aromatic ring, for example. The reactive radicals were further categorized into low activity ones and high activity ones and were correlated with stable radicals which have survived the cracking.

## 1. Introduction

Upgrading of heavy tar is an important process in petroleum refining, such as catalytic cracking, hydro-refining and delayed coking [1,2]. In all cases, the heavy tar needs to be heated to a certain temperature before being entered into a reactor. Industrial practice shows that coke deposition in preheaters and pipelines is a major problem [3–5]. In addition, catalysts in hydro-refining process also suffer from coke deposition and deactivation. Numerous studies about coking of heavy tar can be found in the literature, such studies provide information about the amounts, kinetics and mechanisms of coking [6–8].

It is generally recognized that coke is formed mainly from thermal cracking of heavy tars [8]. In this process, the covalent bonds in heavy tar molecules are cracked into radical fragments containing one or more unpaired electrons. These radical fragments react through coupling and condensation to form lighter products and coke [9,10]. The radical fragments and the unpaired electrons within them are simply and collectively termed as radicals. It is obvious that the behavior of the reactive radicals determines the subsequent chemical reactions, and it is important to quantify them in terms of amount and activity. Electron

spin resonance (ESR) or electron paramagnetic resonance (EPR) has been used to quantify radicals [11,12]. However, it should be noted that the radicals detected by ESR/EPR are actually those which have survived the cracking reaction and have a long life span. They are unreactive and are therefore termed “stable radicals” to be distinguished from the reactive radicals in this work.

Little work can be found in the literature on quantification of reactive radicals generated in cracking of heavy tars. However, a few studies quantified the reactive radicals generated in pyrolysis of coal, biomass and oil shale using hydrogen donor solvents (HDSs) [9,13,14]. Based on the quantities of H radicals (H) donated by a HDS, these studies have shown that the quantities of reactive radicals greatly exceed those of stable radicals; specifically, they are roughly three orders of magnitude higher. The fundamental principle of the method is that the reactive radicals abstract H radicals (i.e. atoms) from surrounding HDS during thermal cracking and are therefore stabilized [15,16].

Theoretically, quantities of cleavable bonds and reactive radicals generated from heavy tar cracking under the same conditions are constant because they are determined by the distribution and dissociation energy of the bonds. However, the quantities of reactive

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radicals abstracting H· from different HDSs may not be the same due to the different C–H bond dissociation energy (BDE) in different HDSs. If the activities of reactive radicals are sufficiently high, they would readily abstract H· from different HDSs and the differences in their quantities detected by different HDSs would be minimal. Conversely, if the activities of reactive radicals are low, the differences in quantities of reactive radicals detected by different HDSs would be large. Therefore, the quantities of H· abstracted from different HDSs may measure the activity of reactive radicals as well as the bonding structure of heavy tars.

Based on the above discussion, we quantified the reactive radicals generated in thermal cracking of two heavy tars at 250–400 °C using two HDSs with different C–H BDE, 9,10-dihydroanthracene (DHA) and tetrahydronaphthalene (THN). The kinetics of bond cleavage to generate reactive radicals and relationship between the reactive radicals and stable radicals measured by ESR were also established. Key factors influencing the generation of reactive radicals from the heavy tars were analyzed based on the tars' structural characteristics.

## 2. Experimental

### 2.1. Characterization of heavy tars

The heavy tar samples, black liquids of poor fluidity at room temperature, were provided by ExxonMobil Chemical Company. The samples, with density about 1100 kg/m<sup>3</sup> at 20 °C and viscosity about 150 mm<sup>2</sup>/s at 100 °C, are pyrolysis tar derived from steam cracking of hydrocarbons such as naphtha or even heavier hydrocarbon streams. Their elemental compositions were determined by ultimate analysis using an elemental analyzer (Vario EL cube). Their SARA fractions (Saturates, aromatics, resins and asphaltenes) were determined according to the Chinese national standards NBSHT 0509-2010, in which asphaltenes were precipitated out by n-heptane and the n-heptane soluble fractions were quantified by chromatograph separation with an alumina column.

The average molecular structures of the tars were determined with a cross-polarization magic angle spinning (CP/MAS) <sup>13</sup>C nuclear magnetic resonance spectrometer (<sup>13</sup>C NMR, Bruker AV-300) at a resonance frequency of 75.47 MHz at room temperature with the contact time of 1 ms, a MAS rotation speed of 12.0 kHz, and the recycle delay time of 0.5–1.5 s.

### 2.2. Cracking experiments

The heavy tars were heated to 110 °C and sampled 5.5 ± 1 mg with glass capillaries of 1.1 mm in diameter. The heavy tar sample, with or without HDS, was placed into a glass tube of 2 mm in diameter and 30 mm in length. When DHA (98.0% purity) or THN (99.5% purity) was used as a HDS, the mass ratio of the heavy tar to DHA and THN was 1:2.73 and 1:1, respectively. At these ratios, the theoretical amounts of H· donated by these HDSs are the same.

The cracking experiments were carried out by placing the sample-loaded glass tube into a furnace with 20 sample slots and preheated to 250, 300, 350 or 400 °C. After being heated for 1.0, 2.0, 3.0, 5.0, or 10.0 min, the glass tubes were removed from the furnace and cooled down to room temperature.

### 2.3. Quantification of stable radicals

The stable radicals in the samples before and after cracking experiments were measured by ESR (Bruker JES-FA200) at room temperature. The ESR was operated at 9.5 GHz and 1.578 mW with a central magnitude field of 3485 G, a modulation amplitude of 1.0 G, a sweep width of 100 G, sweep time of 20.97 s, and a time constant of 0.04 s. The radical concentration was calibrated by DPPH (1,1-Diphenyl-2-picrylhydrazyl, purity over 98%). The control experiment

indicated that DHA or THN alone showed no radical signals under the cracking experiment conditions.

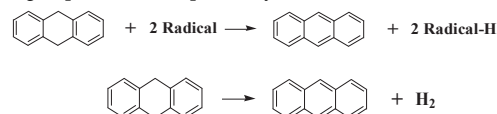
The stable radical concentration ( $N_{SR}$ , mol/g) is determined by Eq. (1), where  $M_{SR}$  is the amount of radicals (mol) in the sample and  $m$  is the mass (g) of the heavy tar. Repeated experiments have shown experimental errors of less than 5%.

$$N_{SR} = M_{SR}/m \quad (1)$$

### 2.4. Quantification of reactive radicals

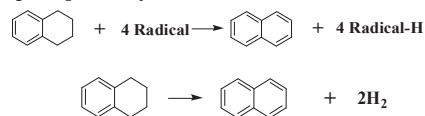
During the thermal cracking experiment, DHA may convert to anthracene (ANT) through four possible routes: (1) donating two H· to heavy tar generated radicals as shown in Re. (1); (2) dehydrogenation to form hydrogen molecule (H<sub>2</sub>) as shown in Re. (2); (3) hydrogen transfer from DHA to the aromatic rings in tars; and (4) hydrogen transfer from DHA for hydrodesulfurization of tars to form H<sub>2</sub>S.

The amount of H<sub>2</sub>S produced during the thermal cracking experiments was quantified by a GC-FPD and the results indicated that the maximum value was  $0.67 \times 10^{-3}$  mmol/g-tar (see Fig. S1 in the supplementary material). Therefore, the fourth route can be ignored. To verify whether the third route occurs, reaction of DHA and pyrene, a model compound of tars, was performed under the same conditions as the cracking experiment, with the products analyzed by GC-MS. The results indicated no hydrogenated product of pyrene, (see Fig. S2 in the supplementary material), confirming no hydrogen transfer from DHA to the aromatic rings. Therefore, the amount of H· donated by DHA to the heavy tar radicals (termed as  $N_{H-DHA}$ ) can be determined by Eq. (2), where  $N_{ANT}$  and  $N_{H_2}$  are the amounts of ANT and H<sub>2</sub> generated during the cracking experiment, respectively.



$$N_{H-DHA} = 2 \times (N_{ANT} - N_{H_2})/m_{tar} \quad (2)$$

Similarly, hydrogen transfer from THN to the aromatic rings and S-containing groups in tars was also not observed. THN converts to naphthalene (NAP) through H· donation as shown in Re. (3) and self-dehydrogenation as shown in Re. (4). Therefore, the amount of H· donated by THN (termed as  $N_{H-THN}$ ) can be determined by Eq. (3), where  $N_{NAP}$  and  $N_{H_2}$  are the amounts of naphthalene and H<sub>2</sub> generated in the cracking, respectively.



$$N_{H-THN} = 4 \times (N_{NAP} - N_{H_2})/m_{tar} \quad (3)$$

The amounts of DHA, ANT, THN and NAP were quantified by high-performance liquid chromatograph (HPLC) with an external standard method. The samples were dissolved in 0.5 mL CS<sub>2</sub> and then diluted 300 times with n-hexane before being injected into the HPLC. The HPLC was Waters e2695 equipped with a Waters 2998 diode array detector operated at a wavelength of 240 nm for DHA, 220 nm for ANT and 210 nm for THN and NAP. The column is a Waters Spherisorb NH<sub>2</sub> column (4.6 mm × 250 mm/5 μm), the column temperature is 35 °C, and the mobile phase is n-hexane (99.9%) at a flow rate of 1.0 mL/min. Preliminary results shown in Fig. 1 indicated that DHA and ANT, as well as THN and NAP, can be efficiently separated by this method with little interference of baseline, which confirms reliability of this method.

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