



Changes in asphaltenes during thermal cracking of residual oils



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HIGHLIGHTS

- This study investigates the effects of thermal cracking on asphaltene molecules.
- An increase in cracking severity decreases the size of asphaltene molecules.
- An increase in cracking severity increases the aromaticity.
- An increase in cracking severity decreases the H/S ratio.
- An increase in cracking severity concentrates the metals in polyaromatic entities.

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ABSTRACT

This study attempts to understand how asphaltene molecules change under thermal stress. Asphaltene samples were precipitated from three crude oils and their atmospheric residues, vacuum residues, and pitch, using *n*-heptane. The pitch samples were obtained from the thermal cracking of vacuum residues at three operating temperatures (400, 415, and 430 °C) and three reaction times (30, 50, and 60 min). Asphaltene samples were characterized using gel permeation chromatography (GPC), ultraviolet spectroscopy (UV), metal content (Ni and V) analyses, and elemental analysis of C, H, N, and S. The experimental observations suggest that thermal cracking conditions influence the structure and the properties of asphaltene. An increase in cracking severity resulted in a notable decrease in the molecular size of asphaltene; a significant increase in aromaticity; a reduction in the H/S ratio, which indicates the presence of sulfur as a disulfide (–C–S–C–) and not as thiophenol or HS groups; and the concentration of metals in the core of smaller polyaromatic asphaltene molecules.

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1. Introduction

The demand for fuel and light products is increasing. To meet this demand, refinery operators constantly seek opportunities to convert their heavier fractions and residuals into lighter fractions [1]. Heavy oil fractions include the atmospheric residue (AR) and the vacuum residue (VR), which are the bottom products of atmospheric and vacuum crude distillation, respectively. These heavy residues are known to contain significant amounts of asphaltenes that can cause serious problems in petroleum refining operations [2].

Asphaltenes consist of highly condensed polyaromatic molecules bearing long aliphatic chains and alicyclic substituents with a high content of heteroatoms such as sulfur, nitrogen, and oxygen included as part of the aromatic system, as well as trace metals, mainly nickel and vanadium, included as porphyrins [3]. They are high-boiling-point, polar, aromatic, high-molecular-weight, and

low-API-gravity fractions of crude oil that are insoluble in alkanes (e.g., *n*-heptane or *n*-pentane) and soluble in aromatic solvents (e.g., benzene or toluene). The properties of asphaltenes render them the heaviest and the most problematic components in crude oil and residues. The main problems caused by asphaltenes during the upgrading of heavy oils, which are generally characterized by low API gravity (<20°API), are coke formation, fouling, rapid catalyst deactivation, and a decreased reaction rate [4–8]. These problems clearly indicate that some of the most important challenges in heavy oil processing include understanding the cracking behavior of asphaltenes and investigating their transformations during the various upgrading processes.

Petroleum residues cannot be utilized without being upgraded. The upgrading technologies for residues can be classified into two main categories: the hydrogen addition processes and the carbon rejection processes. The hydrogen addition processes normally utilize catalysts and hydrogen from an external source, which results in an increase in the H/C ratio of the product. The carbon rejection processes, in contrast, are normally based on a thermal treatment that redistributes the hydrogen among the various products, which

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increases the H/C ratio of some fractions and decreases the H/C ratio of others. The thermal cracking processes are more commonly used in processing vacuum residues because they normally have a high content of asphaltene that can cause rapid deactivation of catalysts. Examples of thermal cracking processes in the refining industry include delayed coking, visbreaking, fluid coking, Flexicoking, and Eureka process.

The Eureka process is a commercially proven thermal cracking process that produces valuable cracked oil and aromatic petroleum pitch from vacuum residues. The first Eureka processing plant was constructed in Japan by the Fuji Oil Company [9]. This process operates with a semi-batch reactor system in which the cracking reactions proceed at a lowered hydrocarbon partial pressure through the injection of steam into the reactor, which keeps the petroleum pitch in a homogeneous liquid state. Yield comparison between various thermal cracking processes indicate that Eureka has higher cracked oil yield and lower gas yield. The difference in yield distribution observed in Eureka products is mainly attributed to the continuous stripping of product, which prevent the successive cracking reactions. Takatusuka et al. [9] compared the yield distribution and the quality of products from Eureka process to other alternative coking processes, such as the delayed coking and the fluid coking, and reported advantages in term of cracked oil yield and quality of by-product.

Because asphaltenes cause numerous problems and make the process of upgrading difficult, the changes in asphaltenes' structure and properties during the upgrading of heavy petroleum fractions is an important topic of investigation. Asphaltene properties and structures have been investigated in many recent studies [2,10–12]. The characterization techniques that have been widely used to investigate the molecular structure and properties of asphaltenes include; elemental analysis, metal analysis (mainly nickel and vanadium), gel permeation chromatography (GPC), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and infrared spectroscopy. The elemental analysis helps in estimating the content of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in asphaltenes. GPC analysis, on the other hand, determines the molecular weight, whereas NMR provides important average structural parameters, such as the aromaticity factor, the average number of carbons per alkyl side chain, the percent of substitution of aromatic rings, and the aromatic ring number [5,8,13,14].

Numerous studies have been conducted on the changes and transformations in asphaltenes during hydrotreating processes [4,7,8,15–20]. However, studies related to asphaltene behavior during thermal cracking are limited, and most of the previous efforts are related to coke formation and the development of kinetic models [1,21,22]. The main objective of this study is to investigate the changes in the structure and properties of asphaltenes during thermal cracking.

2. Experimental

2.1. Thermal cracking experiments

The thermal cracking experiments were performed using a pilot plant emulating a Eureka cracking unit. The Eureka process is a commercially proven thermal cracking process that produces cracked oil and aromatic petroleum pitch from vacuum residues [9,23]. Thermal cracking experiments were performed on three vacuum residues obtained from three Kuwaiti crude oils: Ratawi–Burgan (RB), Lower-Fars (LF), and Eocene (EC). The properties of the RB, LF, and EC vacuum residues are listed in Table 1.

The thermal cracking runs of vacuum residues were performed in a 2 L semi-batch pilot-scale reactor that emulates the commercial Eureka process. A schematic diagram of the pilot plant is

Table 1
Properties of RB, LF, and EC vacuum residues.

Property	Method	Unit	RB-VR ^a	EC-VR ^b	LF-VR ^c
TBP cut range		°C	550	550	550
Yield on crude		wt.%	31.2	40.2	36.3
Yield on crude		vol.%	26.6	40.8	32.4
Density at 15 °C	D 5002	g/cc	1.0497	1.0583	1.0659
Gravity	D 1250	°API	3.2	2.1	1.2
Molecular weight		g/mol	1174	1256.1	1045.3
CCR	D 4530	wt.%	25.98	29.17	31.76
C	D 5291	wt.%	83.6	83.2	82.5
H	D 5291	wt.%	9.9	9.6	9.1
N	D 5762	wt.%	0.6	0.7	0.5
S	D 5453	wt.%	5.9	6.5	7.9
H/C			1.42	1.38	1.32
V	D 5708	ppm	139.1	153.5	277.9
Ni	D 5708	ppm	69.9	75	106.4
Distillation (simdist ^d) (wt.%)	D 7169				
IBP		°C	489.5	483.0	487.0
5 (wt.%)		°C	535.5	534.5	534.5
10%		°C	551.0	550.0	549.5
20%		°C	574.5	574.0	572.5
30%		°C	594.5	594.0	592.0
40%		°C	613.5	612.5	610.5
50%		°C	632.0	631.0	629.0
60%		°C	650.0	649.0	647.5
70%		°C	666.5	664.0	663.0
80%		°C	689.5	687.0	686.0
90%		°C	712.0	710.5	710.0
FBP		°C	745.5	745.5	745.0

^a RB-VR: Ratawi–Burgan vacuum residue.

^b LF-VR: Lower-Fars vacuum residue.

^c EC-VR: Eocene vacuum residue.

^d Simdist: Simulated distillation.

shown in AlHumaidan et al. [24]. The reactor is loaded with 500 g of vacuum residue and heated using a two-zone electrical furnace (bottom and side electrical heaters) that can be controlled by the skin and bed temperatures of the reactor. The reactor is equipped with a mixer (300 rpm) and a nitrogen injector (1 NL/min) to introduce the preheated nitrogen used for stripping the cracked products. Continuous stripping of the products prevents over-cracking and reduces the hydrocarbon partial pressure in the reactor, which shifts the reaction equilibrium toward product formation. The vapor, which is stripped out of the reactor with nitrogen, is condensed at 50 °C, and most of the cracked oil is separated from the non-condensable gas. The condensed cracked oil is collected in a round-bottom flask, whereas the non-condensed vapor is passed through a 2 °C condenser to recover the light fractions of the cracked oil. The non-condensable gas, which is mainly composed of light hydrocarbons and inert carrier gas, is passed through a mist trap and a dry gas counter before being collected in a 150 L gas sampling bag for analysis. Each experimental run produced three products: cracked oil, off-gases, and pitch. The thermal cracking experiments were conducted at three cracking temperatures (400, 415, and 430 °C) and three reaction times (30, 50, and 60 min). Measurement of the reaction residence time was started from the moment when the liquid temperature in the reactor reached 380 °C, which is the temperature at which thermal cracking starts [25–27].

2.2. Precipitation of asphaltene samples

Asphaltenes were extracted from three crude (C) samples, three atmospheric residue (AR) samples, three vacuum residue (VR) samples, and 27 pitch (P) samples obtained from the thermal cracking of the vacuum residues at different operating temperatures and reaction times. Therefore, asphaltenes were extracted from a total of 36 samples according to the method described in

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