Visbreaking Reaction of Atmospheric Residue (Part 4)

Structural Analysis and Reaction Mechanism for Taching Atmospheric Residue

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Atmospheric residue from Taching crude was subjected to thermal cracking at 420—460°C in the presence of a diluent, namely, nitrogen, hydrogen, or tetralin as a hydrogen donor. A significant decrease in the molecular weight of the product residue was observed. The feed and the product residues were separated into six fractions. The distribution of the fractions was dependent on the diluent used, whereas the distillate yield was but slightly affected. Taching crude is essentially paraffins, saturates, and monoaromatics with long alkyl side chains comprising about 70% of the residue. Although the residue contained no asphaltenes (*n*-pentane insolubles), a considerable amount of asphaltenes was formed by visbreaking. The yield and structural change in the fractions were accounted for by the mechanism consisting of unimolecular decomposition and radical chain reaction.

1. Introduction

Atmospheric residues from four topped crudes, namely, Arabian Heavy, Iranian Heavy, Taching, and Khafji were subjected to thermal cracking at 420—460°C in the presence of a diluent, nitrogen, hydrogen, or tetralin at 50 kg/cm². Details on the yields of cracked distillates (343°C-) and some physicochemical properties of the product residues have been reported elsewhere.¹⁾ Observations on Taching atmospheric residue are summarized as follows: Among the four crudes studied, Taching topped crude was the least susceptible to thermal cracking. The distillate yield was less than 14 wt% and but slightly affected by the diluent used. Significant changes in the physicochemical properties of the visbroken residues were observed, namely, the decrease in specific gravity and viscosity and the increase in Conradson carbon.

The present paper is the outcome of the results of detailed structural analysis of the feed and the visbroken residues from Taching crude, involving minute fractionation of the residues. It is hoped that this study will afford a specific insight into

the structure of Taching residue and its visbreaking reaction mechanism. Similar studies on Arabian Heavy²⁾ and Iranian Heavy³⁾ residues have been described in our previous papers.

2. Experimental

Inspection of the general properties of Taching feed oil, the apparatus and reaction conditions employed for visbreaking, details concerning the separation and structural analysis of the feed and product oils have been described previously.^{1),2)}

3. Results and Discussion

3.1 Molecular Weight

Taching topped crude was not susceptible to thermal cracking, the yield of distillates being less than 14 wt%. However, a significant decrease in the molecular weight of the product residue was observed. Gel permeation chromatography curves of atmospheric residues (AR) of the feed and several product oils are shown in **Fig. 1**. **Table 1** shows the average molecular weight of the residues calculated from the curves. It is noteworthy that the decrease is slightly larger in the presence of hydrogen or tetralin than in the presence of nitrogen.

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Solvent, CHCl_3 ; Flow rate, 1 ml/min; Calibrated with polystyrene standards

Fig. 1 GPC Chromatograms of AR of Taching Feed and Its Visbroken Products

Table 1 Average Molecular Weight of AR of Taching Feed and Its Visbroken Products

Sample	$\bar{M}_w$	$\bar{M}_n$
Feed	1,330	750
N_2 460°C	930	580
H_2 460°C	890	550
Tetralin 460°C	880	550

3.2 Distribution of Fraction

Atmospheric residues of the feed and the product were separated by solvent extraction and subsequent column chromatography as described elsewhere.²⁾ In **Fig. 2**, the proportions (wt% based on oil) of the fractions of Sa (saturates), MA (monoaromatics), DA (diaromatics), TA (triaromatics), PP (polyaromatics and polars), and As (asphaltenes) were plotted against the cracked distillate (D) yield.

In the presence of nitrogen, the yield of Sa, the main constituent of Taching AR, decreased with increasing cracking severity. In the presence of tetralin or hydrogen, however, it first increased and then decreased in the advanced stage of cracking. The increase in the yield of Sa was remarkable in the presence of tetralin. The yield of MA notably decreased in the initial stages of cracking. The decrease seemed to be enhanced by tetralin. The yields of DA and TA fractions remained virtually unchanged, whereas PP slightly decreased with increasing cracking severity. The decrease in

Fig. 2 Fraction Distribution in AR of Taching Feed and Its Visbroken Products

the yield of PP was slightly enhanced by tetralin or hydrogen. Taching AR is characterized by absence of the As fraction. However, a significant amount of As was formed by visbreaking. Its formation was suppressed by tetralin or hydrogen.

3.3 Structural Change of Fractions

Extensive structural analyses of AR fractions from the feed and the product oils were performed according to the procedures described elsewhere.²⁾ The carbon distribution in atoms per molecule was determined according to the Speight's method⁴⁾ with a minor modification,²⁾ where C_a =saturated carbon atoms at α -position to the aromatic ring; C_n =naphthenic carbon atoms other than α -position to the aromatic ring and methine carbon atoms in the paraffinic location; C_r =saturated carbon atoms other than C_a , C_n and C_m , C_m =methyl carbon atoms other than α - or β -position to the aromatic ring; C_s =total saturated carbon atoms, C_a =total aromatic carbon atoms, C_p =peripheral carbon atoms in an aromatic sheet, and C_i =internal carbon atoms in an aromatic sheet.

During visbreaking, no appreciable changes were observed in the average molecular weight ($\bar{M}_n$), the unsaturation number (USN), and the C_n/C_t ratio of Sa. The increase in the yield of Sa observed in the initial stages of cracking is peculiar to Taching AR. Saturate molecules are supposedly formed by cleavage of paraffinic substituents of the aromatic rings in the aromatic fractions. Dehydrogenation of naphthenes in the Sa fraction could occur to yield aromatics as is the case of Iranian Heavy Sa.³⁾ This reaction, however, would not occur to a great extent, since Taching feed Sa contains only a small amount of naphthenes. Thus, at low temperatures and in the presence of tetralin or hydrogen, the formation of saturates predomi-

Table 2 Structural Change of Taching As Fraction

	Feed	420°C		440°C		460°C		
		N ₂	H ₂	N ₂	Tetralin	N ₂	H ₂	Tetralin
As Yield (wt% on oil)	0	tr	0.2	3.9	1.7	4.7	3.2	2.7
USW				1,830	1,140	1,780	1,220	1,230
m				1.15	2.30	1.13	1.67	2.13
C_a/C_t				0.54	0.52	0.58	0.60	0.63
C_s/C_a				6.3	6.7	10.7	7.1	6.6
C_a/C_p				0.45	0.35	0.23	0.28	0.27
C_p/C_a				0.31	0.40	0.29	0.35	0.34
Recovery (wt% on oil)	91.3	88.5	91.9	93.7	94.2	97.7	96.4	94.5

Fig. 3 Structural Change of Taching TA Fraction

nates, resulting in the increase in the yield of Sa.

Aromatic fractions MA, DA, TA, and PP were similar in their structural changes during visbreaking. **Fig. 3** illustrates the changes in structural parameters of the TA fraction. The value of USN and C_p of the feed TA significantly exceeded the theoretical value for anthracene or phenanthrene derivatives, namely both 10. This evidently suggests that the feed TA contains some polymerized aromatic molecules in which carbon chains connect two aromatic rings or more. The C_s/C_a ratio, which represents the average length of alkyl side chains attached to an aromatic sheet, is much higher than that of the TA fraction of Arabian Heavy and Iranian Heavy, ranging from 3 to 4.

For $\text{Ph}(\text{CH}_2)_n\text{Ph}$ molecules, the bond dissociation energy depends on the length of the connecting methylene chain, n . Among the $\text{Ph}(\text{CH}_2)_n\text{Ph}$ type compounds, the weakest carbon-carbon bond is the β -bond in the dibenzyl type ($n=2$) compounds. With a bond dissociation energy of 55 kcal/mol, it is weak enough to dissociate at visbreaking temperatures.⁵⁾ The unimolecular decomposition is inherently unaffected by the co-existing diluent. On

the other hand, the β -bond in diphenylpropane and higher diphenylalkanes ($n \geq 3$) is ca. 10 kcal/mol stronger than that in dibenzyl, and it seems to be too strong to decompose unimolecularly at those temperatures. Thus, the cleavage of this type of bonds may proceed by a radical chain reaction mechanism and, therefore, is supposed to be suppressed in the presence of hydrogen or tetralin as a radical scavenger.

It may be deduced from the high C_s/C_a ratio that the TA fraction of the Taching feed consists mainly of polymeric aromatics with long bridging chains and monomeric aromatics with long alkyl side chains. There will be only a small share of bibenzyl type molecules. Furthermore, sulfur-containing weak bonds such as PhCH_2SPh and PhCH_2SR would be scarce, since the sulfur content of Taching AR is as low as 0.14%.¹⁾ This may account for the remarkable effect of the diluents on the structural parameters of the Taching aromatic fraction.

The Taching feed contained no As fraction. However, the presence of high molecular weight constituents was suggested by its GPC analysis as shown in **Fig. 1**. There exists a considerable amount of constituents whose molecular weights are higher than those of asphaltenes, ranging from 2,600 to 2,900^{2),3)} present in the crudes of Arabian Heavy and Iranian Heavy. Furthermore, they are inferred to be aromatic because of the high response of the ultraviolet detector to this region. Nevertheless, their alkyl side chains are so long that they cannot be precipitated from n -pentane solution. **Table 2** also shows the results of recovery in the separation. Recoveries from the feed and the product oils cracked at lower temperatures are rather low, which might be ascribed to the irreversible adsorption of such high molecular weight compounds on the alumina and silica gels. It should be noted that asphaltenes obtained in the presence of hydrogen or tetralin had smaller USW⁶⁾ and higher C_p/C_a ratio than those formed in the pre-

a, a' : Depolymerization
 b-1, b-1' : Cleavage of C-C bonds in alkyl groups
 b-2 : Cleavage of C-C bonds in paraffins
 c : Polymerization

Fig. 4 Visbreaking Pathways of Taching Atmospheric Residue

sence of nitrogen, consisting, thus, of less condensed polynuclear aromatics.

3.4 Reaction Mechanism

The observations and discussions described above lead to the formulation of a reaction scheme presented in **Fig. 4**. In the scheme, "Polymeric Aromatics" denotes the aromatic molecules in which carbon chains bridge two or more aromatic rings, including asphaltenes.

At relatively low temperatures or in the initial stages of cracking, the polymeric aromatics with weak bonds depolymerize to yield radical fragments. The radicals are stabilized by abstracting the hydrogen atoms from hydrogen-donating compounds. Some of the stabilized fragments are transformed directly into D fraction (a), but the majority remains in the residue as "Monomeric Aromatics" because of their relatively long alkyl side chains (a').

Some of the radicals may abstract a hydrogen atom from the alkyl side-chains of aromatics. The

alkyl side-chains from which hydrogen has been abstracted then decompose successively. If molecular weights of the paraffins produced are low, they should be included in D (b-1). Relatively large molecules remain in the Sa fraction (b-1'). The former is typical for reactions under nitrogen. In the presence of tetralin or hydrogen or at low temperatures, the paraffinic radicals may be stabilized by hydrogen donors before they are decomposed to smaller ones. Thus, the Sa yield first increases in the presence of tetralin or hydrogen. The decomposition of polymeric aromatics connected with long methylene chains may proceed in the same manner as cracking of alkyl side chains of aromatics.

Paraffins, the major constituents of the Taching feed, may decompose via the radical chain mechanism in the advanced stages of cracking (b-2). Undesirable polymerization and/or condensation of aromatics (c), may take place to form stable polymeric aromatics when hydrogen-donating compounds are deficient; thus, the formation of asphaltenes in the advanced stages of cracking proceeds extensively under nitrogen.

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要 旨

常圧残油のビスブレーキング反応（第4報）大慶常圧残油の構造解析と反応機構

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大慶常圧残油のビスブレーキング反応を行い、生成油の構造解析にもとづいて、反応の機構や共存する水素、テトラリンの効果について検討を加えた。原料および生成油は前報で述べたように、留出油 (D)、残油 (343°C⁺, AR) に分別後、AR を飽和分 (Sa)、単環芳香族分 (MA)、二環芳香族分 (DA)、三環芳香族分 (TA)、多環芳香族および極性分 (PP)、アスファルテン (As) に分離した。大慶常圧残油は熱分解されにくく、本実験の条件下では留出油収率も 14% を越えなかった。しかし、生成油の残油分においては分子量の減少が観察され、水素もしくはテトラリンの共存下でその傾向がやや大きかった (Fig. 1, Table 1)。

AR の主成分は Sa であるが、水素もしくはテトラリンの共存下では、反応初期に増加する。これに対し、MA は反応初期に大きく減少し、テトラリン共存下において顕著である。DA および TA の収率は反応によってあまり変化しないが、PP は反応の進行とともにわずかに減少する。原料油には As は含まれていないが、反応後期には As が生成する。テトラリンおよび水素は As の生成を若干抑制する傾向がうかがえる (Fig. 2)。

AR の各フラクションの構造解析によると、原料 Sa にはナ

フテンは少なく、その構造の反応による変化はほとんどない。芳香族分の構造変化については TA を代表として Fig. 3 に示した。原料 TA はアルキル側鎖の鎖長が7程度と長いことが特徴で、芳香環を炭素鎖がブリッジした重合体構造も含むが、平均鎖長が長いことからビベンジルの β -結合タイプの弱い結合が少なく、遊離基連鎖機構による分解が支配的となるため、構造パラメーターに対して希釈剤が大きく影響する。生成する As の構造についても希釈剤による影響が見られ、水素もしくはテトラリン共存下では単位構造の小さい、縮合度の低い As が生成する。

構造解析の結果をもとに、Fig. 4 に示すような反応スキームを推定した。すなわち、反応初期には解重合が起こるが、留出油を生成する (a') よりも側鎖が長い残油中に留まる (a) 部分が多い。またアルキル側鎖の分解により、パラフィンが生成し、留出油に含まれる (b-1) が、残油中に飽和分として留まる (b-1') が、水素、テトラリンの共存下では後者が多い。反応後期においては、パラフィンの分解 (b-2) の他に、重縮合によるアスファルテンの生成が見られ、特に窒素共存下の場合に顕著である。

Keywords

Chromatography, Hydrogen donor, Structural analysis, Taching crude, Thermal cracking, Visbreaking