Aromatic Asphaltenes
Part II: Asphaltenes of Heavy Aromatics

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Heavy aromatics are produced as by-products from the thermal and catalytic cracking of petroleum distillates and the carbonization, gasification and liquefication of coal. Examples of heavy aromatics are: the catalytic cracker bottom (CCB) from the catalytic cracking of petroleum distillate, the steam cracker tar (SCT) produced from the steam cracking of naphtha or gas oil, and the coal tars (CT) from coal carbonization, liquefication or gasification.

Heavy aromatics produced from petroleum or coal processing vary in their chemical structure, molecular weight, aromatic ring distributions, thermal and coking characteristics. The variation in the characteristics depends on the feed, the process, and the conditions used for processing. Table 1 gives the key characteristics of various heavy aromatics.

Table 1. Characteristics of Heavy Feedstock

	Steam Cracker Tar: Gas/Oil Cracking	Steam Cracker Tar: Naphtha Cracking	Cat Cracker Bottom	Coal Tar Distillate
n-Heptane Insolubles (%)	20	12.5	1.0	1.0
Coking Value @ 550°C (%)	19	12.0	6.0	5.0
Viscosity @ 210 °F (cSt)	14	5.9	8.0	2.0
Aromatic Carbon (Atom %)	71	72	66	90
Aromatic Protons (%)	41	39	36	55
Benzylic Protons (%)	45	40	40	11
Aliphatic Protons (%)	14	16	24	34
Carbon/Hydrogen Atomic Ratio	1.07	1.01	0.95	1.50
Oxygen (Wt. %)	0.20	0.20	0.25	1.12
Nitrogen (Wt. %)				

Heavy aromatics are composed of two main fractions: a low molecular weight oil fraction (Mn = 150-200), and a high molecular weight solid (Mn = 600 -1,500) fraction insoluble in paraffinic solvents (asphaltene). Table 2 gives the average molecular weight, carbon/hydrogen atomic ratio (aromatic ring condensation), coking characteristics and aromaticity of the oil and the asphaltene fractions of SCT.

Table 2. Compositions of Heavy Aromatics

Composition of Heavy Aromatics	Total Feed	=	Oil	+	Asphaltene	+	Coke
Content (%)	100		95		5		0.1 - 1.0
Aromatic Rings	3 to 7+		3,4,5,6		7+		7+
Average Mol. Wt.	250		190		700		700+
Coking Yield (%) at 550°C	10		3		65		97
Aromaticity (% Aromatic Carbon)	65		61		68		85
Carbon/Hydrogen Atomic Ratio	0.97		0.90		1.19		2.1
Melting Point (°C)	Oil		Oil		190		>400

We used n-heptane to quantitatively determine the C_7-asphaltene content in heavy aromatics. Our method: reflux a mixture of the heavy aromatics and n-heptane for one hour, filter using Whatman filter paper, wash and dry. The aromatics/solvent ratio, the type of solvent and extraction temperature are important parameters in the extraction of asphaltenes from the heavy aromatics. Table 3 illustrates the effect of feed/solvent ratio on asphaltene yield and Table 4 illustrates the effect of the carbon number of the paraffinic solvent on the asphaltene yield.

Table 3. Effect of Solvent: Steam Cracker Tar Ratio on Asphaltene Content

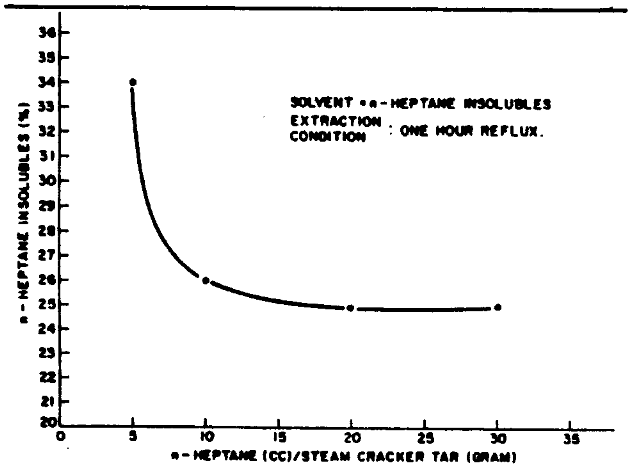
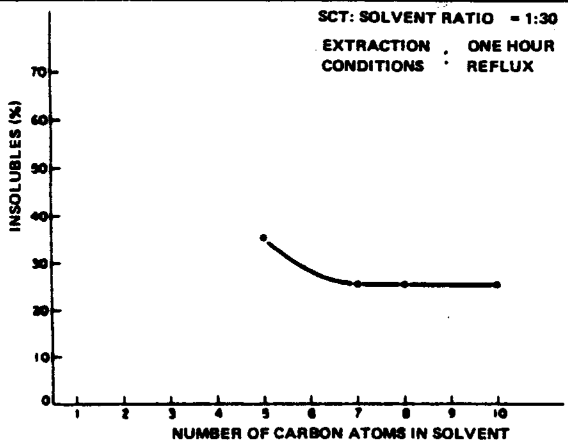


Table 4. Effect of Solvents: Carbon Number on De-Asphaltenation of Steam Cracker Tar (SCT)



The content of C_7-asphaltenes in heavy aromatics varies from 1 to 25% depending on the feed and the process conditions used when producing the heavy aromatics. Table 5 illustrated the effect of feed and process on the asphaltene content in the heavy aromatics.

Table 5. Effect of Process and Feed on Asphaltene Content

Process	Process and Feed	Asphaltene (n-Heptane Insolubles)
Steam cracking	Naptha	5-10
	Light Gas Oil	15-20
	Heavy Gas Oil	20-25
	Desulfurized Gas Oil	23-32
Catalytic cracking	High Severity	0.5-1.0
	Low Severity	1.0-4.0
Coal carbonization	Low Temp. Carbonization	30.0
	High Temp.Carbonization	9.0
Coal liquefaction	Exxon (EDS) Process	38.0

C_7-Asphaltenes in heavy aromatics vary in their average molecular weight and molecular distribution (MWD). We used two gel permeation chromatography (GPC) methods to determine the MWD of the asphaltene fraction of heavy aromatics. The first method require 1,2,4-trichlorobenzene at 93°C with a UV-spectrophotometer at 400 nm as a detector. In the second method, we use THF as a solvent at 20°C. Table 6 gives the molecular weight distributions of asphaltenes extracted from gas oil and naphtha-derived SCT, CCB and CT. Table 7 gives the MWD of three asphaltenes extracted from SCT (naphtha cracking) produced at three different steam crackers. The MWD of the three C_7-asphaltenes is similar.

The chemical structure of asphaltenes is measured by using carbon and proton Nuclear Magnetic Resonance Spectroscopy. We measured the aromatic, benzyllic and total parraffinic

Table 6. Molecular Weight Distribution of Asphaltenes Present in Heavy Aromatics GPC, THF Solvent, Room Temperature.

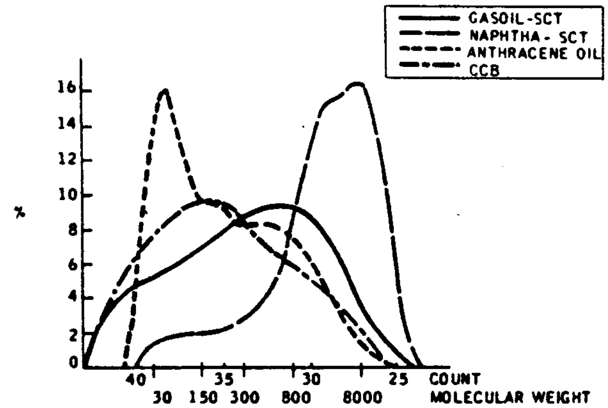
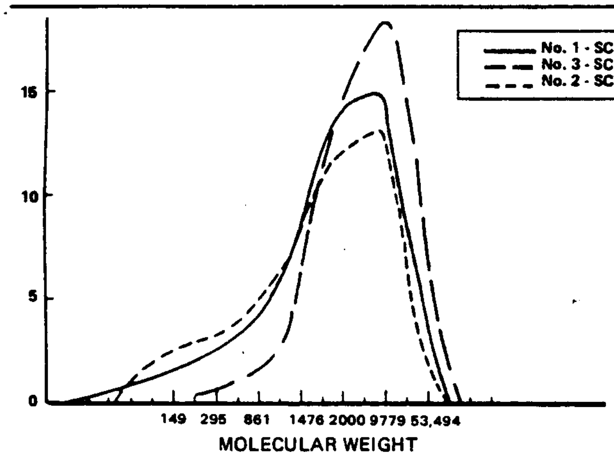


Table 7. Molecular Weight Distribution of Asphaltenes of Naphtha Steam Cracker Tars



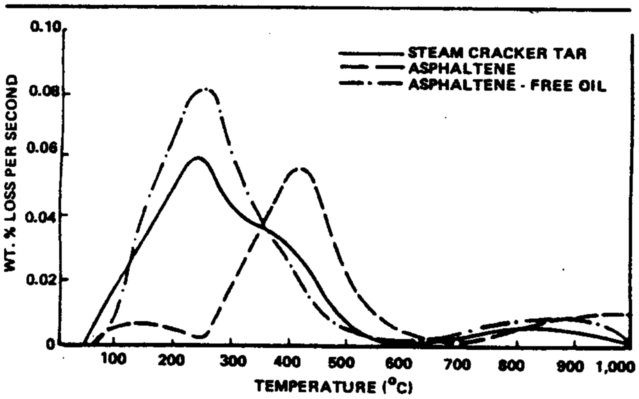
(aliphatic and cyclic aliphatic) protons and the aromatic carbon atom. Table 8 gives the average aromatic carbon atom and protons distribution of asphaltenes extracted from SCT in comparison to that of the total SCT (asphaltene and oil).

Thermo-gravimetric analysis (TGA) and differential thermo-gravimetric analysis (DTG) are used to determine volatilization, decomposition and coking characteristics. Heavy aromatics containing a large quantity of asphaltenes have a very broad DTG thermogram. All asphaltenes decompose at a higher temperature range (around 400°C) in comparison to the oil part which decomposes at around 250°C. Table 9 gives the DTG

Table 8. The Aromatic Carbon and Proton Distribution of SCT and its Asphaltene

	Total SCT	Asphaltene
Aromatic Carbon (Atom %)	72	68
Aromatic Protons (%)	39	39
Benzylic Protons (%)	40	38
Paraffinic Protons (%)	16	22

Table 9. Differential Thermo Gravimetric Analysis (DTG in Nitrogen) of Steam Cracker Tar, Asphaltene and Asphaltene-Free Oil



thermograms in nitrogen of total SCT, asphaltene and oil fractions.

Although the C_7-asphaltenes compose between 5 and 30% of the heavy aromatics, they play a major role in determining the coking characteristics of the total heavy aromatic. The coking characteristics of the C_7-asphaltene and the heavy aromatics vary significantly depending on the feed, process and conditions used to produce the heavy aromatics. Table 10 illustrate the relationship of the heavy aromatics process and the C_7-asphaltene characteristics.

Table 10. Relation of Heavy Aromatic and Process to C7-Asphaltene Characteristics

PROCESS	HEAVY AROMATICS C/H Ratio	HEAVY AROMATICS Coking Yield (%) @550 C	HEAVY AROMATICS Aromatic Carbon (Atom, %)	C7-ASPHALTENE IN HEAVY C/H Ratio	C7-ASPHALTENE IN HEAVY Coking Yield (%) @550 C	C7-ASPHALTENE IN HEAVY Average Molecular Weight
STEAM CRACKING						
NAPHTHA FEED	0.94	9.9	68	1.03	33	1.600
GAS OIL FEED	1.12	21.0	70	1.19	45	700
DESULFURIZED GAS OIL FEED	1.14	23.9	74	1.24	58	890
CATALYTIC CRACKING	0.96	10.0	62	1.26	60	670
COAL CARBONIZATION						
COAL LIQUIFICATION	0.94	2.1	63	0.98	6.0	180
HIGH TEMPERATURE COAL CARBONIZATION	1.33	3.1	83	1.41	13.0	220

We measured the coking characteristics of asphaltenes using two methods: a) a gravimetric coking method at 550°C (SMTPP Method PT-10-67); and b) a thermal balance, where the coke is determined quantitatively at any temperature between 500 °C to 1000 °C C_7-asphalenes of SCT (gas oil cracking) and CCB have very high coking characteristics, while asphaltene of SCT (naphtha-cracking) and CT have low coking characteristics. Table 11 gives the coking characteristics of the C_7-asphaltenes of SCT, CCB and CT using the two coking methods.

Table 11. Coking Characteristics of Various Types of Asphaltenes

PROCESS	FEED	THERMAL METHOD AT 1000°C(1)	STANDARD COKING METHOD AT 550°C(2)
Steam Cracking	Naphtha	10	33
	Gas Oil	29	45
	Desulfurized Gas Oil	31	60
Catalyst Cracking	Distillate	32	60
Coal Carbonization	Coal	3	13

(1) = Thermal Method Using a Thermal Balance at 1000°C, Nitrogen Rate 10 Liter/Min; Heating Rate 10°C/Min.

(2) = Standard Coking Method at 550°C; Standard Method for Testing Tar and Product, Method No. PT-10-67, Two Hours Coking at 550°C + 10°C.

Data indicates that C_7-asphaltene coking is responsible for the coking behavior of the total heavy aromatics. Actually, a direct relationship exists between the C_7-asphaltene content and the coking yield (at 550°C) of the total heavy aromatics. This relation is presented in Table 12.

Table 12. The Relation of C7-Asphaltene Content and Coking Value of Aromatic Feedstock