UV-Visible Analysis of Asphalt and Crackates from Asphalt

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Summary: The present paper demonstrates the UV-VIS analysis of various products obtained from thermal and catalytic cracking of asphalt in a micro autoclave under nitrogen atmosphere. Absorption bands correspond to conjugated benzene rings in the virgin sample indicate aromatic character. It is evident that the peaks correspond to aromatic conjugated system, unsaturation and heteroatoms are almost a feature of every spectrum which confirms that the products of cracking are unsaturated and need further hydrogenation in a separate step before their marketable use.

Introduction

Petroleum and its products are complex mixtures of hydrocarbons in which aliphatic; saturated and unsaturated, naphthenic and aromatic compounds occur abundantly. Unsaturated hydrocarbons usually absorb UV-VIS radiation when irradiated. UV-VIS studies of petroleum products and UV-VIS coupled with other techniques have been well documented in the literature [1-4]. This technique is enjoying popularity in the analysis of petroleum in a variety of samples [5,6].

In the present work, asphalt conversion in to distillate products was investigated in the presence of some catalysts. The products obtained were analyzed by Ultraviolet -Visible spectroscopy (UV-VIS)

Results and Discussion

a. Whole asphalt

Pentane soluble fraction of whole asphalt

The UV-VIS spectrum of virgin asphalt is displayed in (Fig. 1a). There are three major bands seen at 214, 232 and 254 nm. Band at 214 nm shows the presence of unsaturation as conjugated double bonds. Second band at higher wavelength (232 nm) shows the presence of conjugation of unsaturation due to π-π^* transition. Third band at still higher wavelength (254 nm) shows the presence of further conjugation of nonbonding system due to n-π^* transitions of some heteroatoms like O, S or N etc.

Benzene soluble fraction of whole asphalt

The UV-VIS spectrum of the benzene soluble fraction of the virgin asphalt (Fig. 3a) indicates an intense peak at 296 nm, which shows the presence of conjugation in the form of accumulated benzene rings, and some non-bonding system, which have shifted the characteristics absorption for benzene rings to higher wavelength due to π-π^* and n-π^* transitions.

b. Crackate obtained using no catalysts

The distillate obtained as a result of thermal cracking was fractionated in to benzene solubles (BS) and pentane solubles (PS) before undertaking UV-VIS analysis on the basis of solubility in benzene and pentane.

The UV-VIS spectrum of pentane soluble fraction is pictured in (Fig. 1b) which shows two bands, one intense band at 229.5 nm shows the conjugated C=C bonds. Another band just close to 252 nm with low intensity can be seen. The band is broadened over long range up to 300 nm showing further unsaturation and some n-π^* transition, in conjugation with C=C bond. It is inferred that the sample understudy is enriched with hydrogen deficient sites or condensed aromatic molecules.

The UV-VIS spectrum of benzene soluble fraction (Fig. 3b) shows an intense peak at 295 nm

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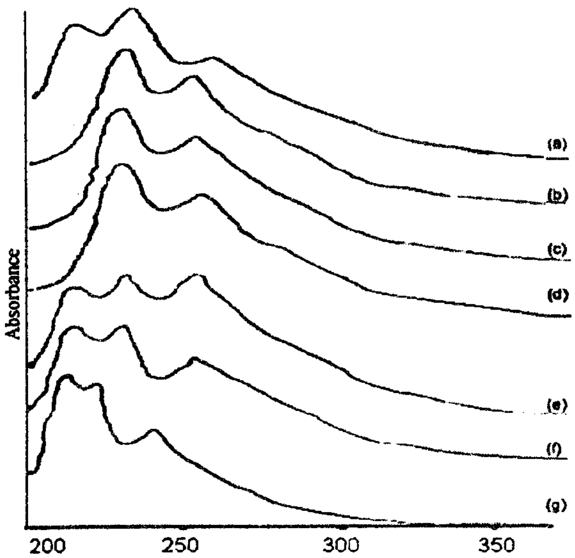

Fig. 1: UV-VIS Spectra of Pentane Soluble Fractions of Virgin, Thermal & Catalytically racked Asphalt

a. Pentane Soluble (virgin)
b. PS of Thermal Crackate at 300 °C
c. PS of Crackate loaded with UTIMAC (catalyst) at 300 °C
d. PS of Crackate loaded with HZSM-5 at 300 °C
e. PS of Crackate loaded with Silica at 300 °C
f. PS of Crackate loaded with Sodium Silicate at 300 °C
g. PS of Crackate loaded with Phosphotungstic acid at 300 °C

broadening towards the higher wavelength shows the presence of C=C bond conjugated with higher degree of unsaturation.

c. Crackate obtained with some clay type catalysts

Crackate obtained with UTIMAC

The UV-VIS spectrum of the liquid fraction obtained with Utmanzai Clay (UTIMAC) as catalyst is displayed in (Fig. 1c). The spectrum evidents peaks at 230 nm and 252 nm. The spectrum also shows absorption at 242 nm. The band at 230 nm suggests C=C conjugation. The other peak also shows further unsaturation. The peak at 252 nm shows unsaturation and conjugation with non bonding system.

The UV-VIS spectrum of benzene soluble fraction (Fig. 3c) shows an intense peak at 301 nm which shows that C=C bond is in conjugation with further unsaturation and some non-bonding system due to the presence of sulfur as heteroatom.

Crackate obtained with HZSM-5

The UV-VIS spectrum of the pentane soluble fraction of the sample (Fig. 1d) shows two major bands at 230 and 254 nm. A band at 230 nm shows the presence of unsaturation as conjugated double bonds (C=C). Second band at 254 nm shows the presence of conjugation of non bonding system due to n-π* transitions. The UV-VIS results show that the crackate of sample consists of lighter products and hence proves the better efficiency of the catalyst for scission of the condensed aromatic structures in to lighter products.

The UV-VIS spectrum of the benzene soluble fraction (Fig. 3d) shows a prominent peak at 296 nm, which indicates high degree of conjugation of aromatic rings and non bonding transition together [7].

Crackate obtained with silica

The UV-VIS spectrum of pentane soluble fraction is pictured in (Fig. 1e) gives three intense peaks centered at 214, 231 and 253 nm. Peak at 214 nm shows conjugation and unsaturation. Some more pronounced bands at 231 and 253 nm further shows the complex conjugation and presence of heteroatoms. The band at 214 shows the presence of conjugation of about two conjugated π systems, a band at 231 nm also shows the presence of conjugation between 2 π systems having heteroatoms because of its greater intensity as compared to 214 nm. The band at 253 nm shows that there are three unsaturated systems in conjugation to one of the carbon. The heteroatom might be sulfur due to its greater intensity [8].

The UV-VIS spectrum of the benzene soluble fraction (Fig. 3e) features a band at 295cm^{-1} showing a complex conjugation of unsaturated compounds with extension in the benzenoid absorption.

Crackate obtained with sodium silicate

The UV-VIS spectrum of the pentane soluble fraction shows three peaks (Fig. 1f). Two intense peaks at 214 and 229 nm show the presence of C=C

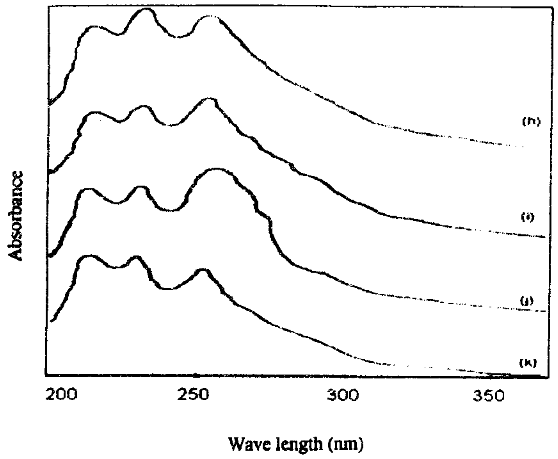

Fig. 2: UV-VIS Spectra of Pentane soluble fractions of Virgin, Thermal & Catalytically racked Asphalt

- h. PS of Crackate loaded with $AlCl_3$ at 300 °C
- i. PS of Crackate loaded with NiO_2 at 300 °C
- j. PS of Crackate loaded with Ammonium heptamolebdate at 300 °C
- k. PS of Crackate loaded with Hangu Coal at 300 °C

conjugated double bond accompanied by conjugation of more unsaturation due to π-π* transition. The third peak of low intensity shows the presence of unsaturation due to nonbonding system present as a result of some heteroatoms *i.e.* n-π* transitions.

The UV-VIS spectrum of the benzene soluble fraction (Fig. 3f) shows an intense band at 295 nm, which projects the same information like that obtained in case of HZSM-5, i.e. the presence of condensed aromatics conjugation and non bonding systems as the absorption for the benzene rings is shifted towards higher wave length.

d. Crackate obtained with some acid type catalysts

Crackate obtained with phospho-tungstic acid

The UV-VIS spectrum of the pentane soluble fraction (Fig. 1g) shows the same pattern like that of the virgin asphalt. Spectrum featuring three distinct peaks, two intense peaks at 215 nm show the presence of C=C conjugated double bond and at 229 nm shows conjugation of more unsaturation due to π-π* transition. The third band at higher wavelength indicates the presence of unsaturation due to nonbonding system of some heteroatoms i.e. n-π* transitions.

The UV-VIS spectrum of the benzene soluble fraction (Fig. 3g) shows an intense band at 297 nm, which shows the presence of conjugation of aromatic rings and non bonding configuration by some heteroatoms as the absorption for the benzene rings is shifted towards higher wavelength in the same way as in the other samples.

Crackate obtained with $AlCl_3$

The UV-VIS pattern of pentane soluble fraction is displayed in (Fig. 2h). The spectrum of this PS fraction portrays three peaks at 215, 231 and 254 nm. Peak at 215 nm shows conjugated double bonds, which is shifted to higher wavelength of 231nm, suggests long chain hydrocarbons and further conjugation, while the third intense peak at 254 nm suggests the n-π* transition, due to the presence of sulfur atom.

UV-VIS spectrum of the crackate obtained with $AlCl_3$ is provided in (Fig. 3h). The spectrum of benzene soluble fraction indicates high degree of unsaturation, an intense peak at 295 nm suggestive of conjugated double bonds shifting.

e. Crackate obtained with some oxide catalysts

Crackate obtained with NiO_2

The UV-VIS profile of PS fraction is provided in (Fig. 2i). The spectrum shows three peaks at 214 nm, 231.5 and 253 nm. Absorption at 214 nm shows C=C configuration, at 291 nm shows C=C in conjugation with non bonding system, i.e. n-π* transition due to S, O etc. and 253nm shows hemicyclic C=C conjugation.

The UV-VIS spectrum of benzene soluble fraction (Fig. 3j) shows an intense peak at 301 nm which exhibits the presence of C=C conjugation with non-bonding system i.e. n-π* transition.

Crackate obtained with ammonium heptamolybdate

The UV-VIS spectrum of the pentane soluble fraction of the sample cracked with ammonium heptamolybdate also shows the same pattern (Fig. 2j) as like that of the virgin asphalt. The spectrum portrays three major absorption bands. An intense

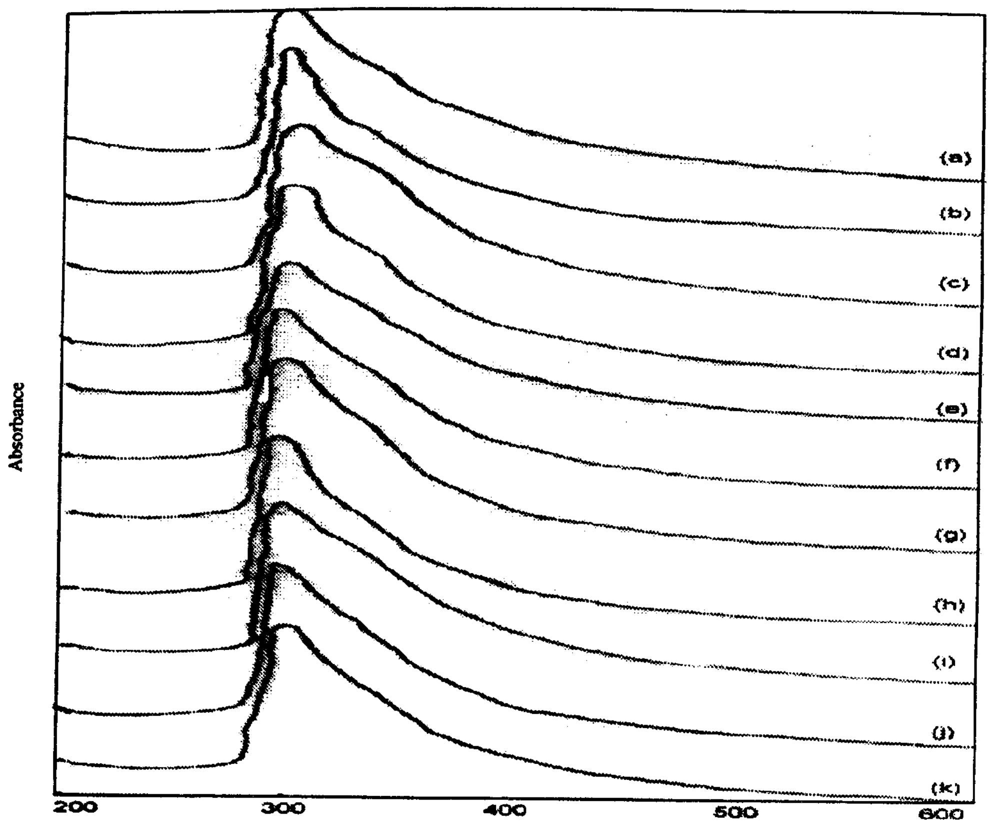

Figure 3: UV-VIS Spectra of Benzene Soluble Fractions of Virgin, Thermal & Catalytically Cracked Asphalt

a. Benzene Soluble (virgin)
b. BS of Thermal Crackate at 300°C
c. BS of Crackate loaded with UTIMAC (catalyst) at 300°C
d. BS of Crackate loaded with HZSM-5 at 300°C
e. BS of Crackate loaded with Silica at 300°C
f. BS of Crackate loaded with Sodium Silicate at 300°C
g. BS of Crackate loaded with Phospho-tungstic acid at 300°C
h. BS of Crackate loaded with $AlCl_3$ at 300°C
i. BS of Crackate loaded with NiO_2 at 300°C
j. BS of Crackate loaded with Ammonium heptamolebdate at 300°C
k. BS of Crackate loaded with Hangu Coal at 300°C

band at 214 nm shows the presence of C=C conjugated double bond and at 229 nm shows additional conjugation of unsaturation by π-π* transition. A band at higher wave length 256 nm shows n-π* transitions by nonbonding system due to some heteroatoms.

The UV-VIS spectrum of the benzene soluble fraction (Fig. 3j) shows a prominent peak at 295 nm, exhibiting the presence of the conjugation of aromatic rings and non-bonding system as the band is at higher wavelength than that of normal benzene absorption.

f. Crackate obtained with modifiers

Crackate obtained with hangu coal

The pentane soluble fraction gives three peaks at 214, 229.5 and 252.5 nm (Fig. 2k). Band at 214 nm indicates the presence of conjugated double bonds i.e. C=C due to π-π* transition, which is shifted to higher wavelength at 231 nm, suggesting long chain hydrocarbons and further conjugation of C=C, while the third intense peak at 254 nm suggests the n-π* transition, due to the presence of heteroatom like sulfur. This proposition is supported by IR studies of the sample to be reported in the next paper.

UV-VIS spectrum of the benzene soluble fraction (Fig. 3k) shows an intense band at 295 nm, which shows the presence of conjugation of aromatic rings and non bonding configuration, as the absorption for the benzene rings has been shifted towards higher wavelength in the same way as is in the other samples.

Table-1: Properties of Asphalt used

Penetra-tion	Density	Carbon Residue	Ash	Acid No.	Pentane Insoluble
Grade	(gm/cm^3)	(%)	(%)	(mg KOH)	(%)
80/90	0.987	24.458	0.512	0.370	45

Table-2: Experimental Conditions used for Carbonization of Asphalt under Study

Parameter	Level
Temperature	300 ± 20 °C
Nitrogen Pressure (cold)	10 atm
Residence time	1.0 hrs
Rate of stirring	250-300 rpm
Heating rat	5 °C/minute

Experimental

Sample collection

The sample was collected from Attock Oil Refinery Rawalpindi, Pakistan. The physicochemical characteristics of the sample used is provided in Table-1.

Carbonization protocol

Asphalt was carbonized under the conditions provided in Table-2. Ten grams portion of asphalt was placed in a Pyrex brand glass insert fitted tightly in the autoclave. The autoclave was bolted tightly and pressure tested with nitrogen at room temperature after purging twice to remove air, then pressure tested to 10 atm with N_2 The furnace temperature was increased incrementally (heated at 5 °C min$^{-1)}$ to the desired temperature in order to avoid the shrinkage in the product as a result of catastrophic collapse, held there for one hour, and cooled to room temperature over night (18 hrs). The residual asphalt along with distillates was collected and the cake (carbonized asphalt) was subsequently soxhletly extracted with n-pentane till clearance in the thimble compartment. The extracts were analyzed by UV-VIS spectrophotometry

UV-Visible spectrophotometry

Pentane and benzene soluble fractions of virgin and crackates of asphalt (both thermal and catalytic) were analyzed by a double beam UV-VIS spectro-photometer [Shimadzu 160 A, Japan].

Conclusions

It is evident from the aforementioned discussion that the peaks correspond to aromatic conjugated system; unsaturation and heteroatoms are almost a feature of every spectrum. This confirms that the products are aromatic in nature and need further upgrading before being used for marketable purpose. Further, hydrocracking is suggested to eliminate sulfur and to further reduce the chain length of the molecules as well as to saturate the hydrogen deficient sites.

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