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OXIDATION INFLUENCE ON THE CHEMICAL CONTENT AND SOME RHEOLOGICALY PROPERTIES FOR NATURAL ASPHALT TO ABU ALJEER _ ALANBAR

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Abstract:

Heating of natural asphalt at high temperatures for a long time lead to oxidation of the asphalt , which starting on the surface while with continuous mixing and heating leads to oxidation to all the asphalt molecules and the texture of oxidized asphalt becomes a solid , glossy, dark black of color. The rheological properties before and after oxidation were studied , the results showed that increase of oxidation time , Lead to reduce the degree of penetration(increased stiffness) and an increment in the softening degree, also the oxidation processes load to increase in the fractional Asphaltene compared with that of maltene parts, Which have been separated and estimated by using manual column liquid –solid chromatography and extraction in parallel with a solvent and precipitant the Asphaltene index I_A and Gastl index I_C were also calculated, the spectra of FT-IR , U.V-visible and HNMR showed a change in the physical properties of oxidated since there was Chemo - Physical relationship between a chemical content and Rheological properties of the oxidized asphalt .

تأثير الاكسدة على المحتوى الكيميائي للاسفلت وبعض الخواص الريولوجية للاسفلت الطبيعي لمنطقة أبو الجير- الانبار

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الكلمات المفتاحية : خواص جيولوجية ، إسفلت طبيعي ، الاكسدة الحرارية.

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المستخلص:

إن تسخين الإسفلت بدرجات حرارة عالية ولفترة زمنية طويلة تؤدي إلى اكسدتة ، فتبدأ بالسطح ومع التحريك والمزج المتواصل للاسفلت تؤدي الحرارة الى اكسدة جميع جزيئات الاسفلت فيصبح ذو لون اسود غامق لماع وصلب القوام . (بسبب زيادة التصلب) ،وزيادة درجة الليونة و قيم اللزوجة كما أدت عمليات الأكسدة إلى زيادة نسبة جزء الاسفلتينات ونقصان جزء المالتينات . والتي تم فصلها وتقديرها بطريقة الكروماتوغرافيا العمود السائل الصلب وطريقة الفصل بالإذابة والترسيب . وتم حساب معامل الاسفلتين I_A ومعامل جستل I_C وأعطت أطياف HNMRو FT-IR و uv-visible تغيراً واضحاً في مواقع حزم الامتصاص للمجاميع الفعالة مما يدل حصول تطور واضحاً في خواص الإسفلت بتأثير درجة الحرارة العالية ولفترة زمنية طويلة الامد. وأن هناك علاقة كيمو- فيزياوية بين تركيب الإسفلت والخواص الميكانيكية.

1-Introduction:

Natural asphalt consists of a mixture of high molecular weight hydro-carbons, and has a large number of carbon up to 150 atoms , which has a color between black and black-brown with the strength of viscous Fluid of special smell . there are two kinds of natural asphalt were found , the solid form which deposits mixed with asphalt Rocks (Masson,2008) .The other type comes out of the ground because of cracks resulting from the formative movements of the crust of the seismic movements forming lakes due to the asphalt with water (Yousefi,2008), The natural asphalt has a chemical structure similar to an asphalt of petroleum in chemical composite but differs in physical properties, asphalt of Abu-Aljeer area floating with water sulfur springs in several springs because of the cracks in the earth's crust because it is located on the fault, which caused the rush of the earth's crust to the top (Alobaidy, 2010) and the asphalt a companied the spring has Specifications (black fluid , gooey), Bad rheological properties of natural asphalt making it useless for industrial application , chemically the structures of asphalt have tow part (Villaneuva & Zanzolto,2008) the first is Asphaltene which are insoluble in normal heptane or normal hexane , and the other maltenes which are soluble. Asphaltene is composed of poly heterogeneous aromatic rings and substituted by the nitrogen and oxygen and sulfur atoms of high molecular weight, but it is soluble in carbon disulfide CS_2, maltenes part consists of saturated hydrocarbons and non-polarized aromatics, and the Resin (representing polarized aromatics) giving the molecules high adhesion, which causes attraction forces between the components of asphalt, and these affect the behavior of physical properties and when used for Industrial purposes(Havog,2010)**.**

Rheological properties of asphalt depend on the regularity of the physical particles within the composition. but change rapidly with temperature change(ASTM,2009). Thermal oxidation of natural asphalt under atmospheric pressure has a large impact on physical and chemical properties and gets a clear change in Penetration , Softening , Viscosity and Ductility (Kanabar,2010), (Zeng and Hung) indicated that ideal of thermal aging at laboratory and calculation the results of the change in properties of asphalt a heat oxidative asphalt compared with the properties of the original reference (Hung & Roth,1996). The decrease of the emissions, smell, and increasing of the hardness properties but occurs a decrease in the creep values , makes it more stable and hence more industrially viable (Cawe,2004) as there is a change in the packet absorption of the spectrum **UV& FT-IR** for oxidized asphalt, because of the high concentrations of acids (Carboxyl group - and esters - and ketones - and anhydrides) which all give the absorption due to (C=O) group and also the transformed of sulfur compounds to Sulfoxide which can be estimated by FT-IR Spectroscopy.

The objective of this study is to investigate chemical characteristics of narrow cut- fragments related periods with thermal oxidation high temperatures under atmospheric pressure and their effect on the rheological properties (Penetration - and Softening - viscosity) and the chemical content by calculating the asphaltene index $\mathbf{I_A}$ and Gaestal index $\mathbf{I_C}$. and fractionating oxidized asphalt to the its components by using liquid-solid column chromatography and compared that with original asphalt , **^{1}H-NMR ,FT-IR** and **UV-visible** spectral were selected to analyze of the oxidated asphalt which demonstrate its industrial applicability.

2-Experimental:

Raw materials

Sample of asphalt from sulfur spring of the area of Abu Aljeer which has a strength of viscous Fluid and black color Alumina $\mathbf{Al_2O_3}$ (**150µm - 200µm**) from the company Fluka ,without other purification solvents **99.5%** were used (normal heptane, toluene, carbon disulfide ,and hexane from Fluka).

Oxidation of asphalt:

After the expulsion of water from the asphalt by heating for total time of ((**5 hours**) , samples had been put in the oven (Japan sanyo), equipped with an air fan and samples of asphalt were inserted into metallic pot at **160 c** ^{o} and different periods (**5,10.25, 35, 55**) hour and total time of **55** hours according to American Society for Testing and Materials (**ASTM D36**) , The samples were taken out from the oven periodically and the rheological properties once were made measurements , the sample returned to the oven for completing the required oxidation time .

Measurement of rheological properties

Penetration Point was measured by using standard a needle which penetrates a form to a specified distance and time , according to **ASTM (D5-83)** , before and after the oxidation , Softening Point was measured according **ASTM (D36-72)** and they represent the fall of the metal ball of a particular for asphalt disk in certain distance **2.54 cm** under thermal and pressure the weight of the ball. Softening Point was measured periodically and different times, in addition to measurements of the kinematic viscosity of asphalt before and after the oxidation processes using viscometer type **(canon) at 135 c^0** according to the **ASTM (D2170-85).** (Zofta, 2004).

Fractionation of asphalt:

The fractionation of asphalt were carried out using solvent extraction method via column liquid -solid chromatography . firstly the sample was fractionated into the precipitated asphaltene part and other was soluble (maltenes part) using n- hexane , the maltenes part was separated in to the ***SARA*** (Saturated ,Aromatic, Resin and Asphaltine) components within column liquid - solid chromatography **ASTM (D3279) , (**Michalico, 2008).

5 g of water free asphalt was put in to the **500 ml** flask and normal hexane was added then the solution was sharked at room temperature For **1.5** hour to ensure the full solubility of asphalt sample, then filtrated by using an ash less No (**42**) mm using a Buchner funnel the precipitate until less for the color drops ensure complete asphaltene separation In the form precipitate , the soluble are maltenes had been distilled to remove the solvent, Maltenes fractional separation on the three components (Saturates, Aromatics, and Resin) , maltenes part dissolved with a few amount of normal heptane ,transferred to the column chromatography of length **100 cm** , diameter **2** mobilizes in the activated alumina **Al_2O_3(80-100)** mesh,doping at **350 c^o** for two hours, first part of a saturated hydrocarbon was seperated using normal heptane as solvent second part of aromatic was separated by using toluene part and the third part of Resin separated using methanol, once separation processes was finished of the three part with chang color, during the follow-up phases for each of the three samples were collected and then distilled, dried and vaporized for measuring the weights of fractions and determined the kinds of **H%** by **HNMR** of every fractionated part of asphalt.

Spectral study:

The spectral study **FT-IR** were obtained by using PERKIN ELMER SPECTRUM **2000 FT-IR** spectrometer (in faculty of women education - anbar), and sample prepared in the form of film of asphalt while separated parts for the purpose of studying the physical changes taking place on sites and the degree of absorption of each part , **H-NMR (400MHz)** spectra were recorded by using a BRRUKER spectrometer and **($CDCL_3$)** as solvent (in Syria) Spectroscope (**UV-visible**) of the asphalt fractional was determine by **UV-visible** (100 varin Australian).

Coefficients I_A &I_C

Coefficient Asphaltene Index **(I_A)** and Gaestl Index **(I_C)** (represent the resin from) was calculated by using the following relationship .(Oyekunle,2006).

$$I_A = \frac{Asphaltenes + Resins}{Saturates + Aromatics}$$

$$I_C = \frac{Saturates + Asphaltenes}{Resins + Aromatics}$$

3-Results and discussions:

The natural asphalt to the area of Abu Aljeer - Anbar was exposed to the high temperatures for long times under atmospheric pressure , in the presence of oxygen to get changes in the the physical structure, its becomes darker , more shiny , strength of hardness. The oxidation of the asphalt as in (figure-1).

It also gets a change in the chemical content of the synthetic components by studying

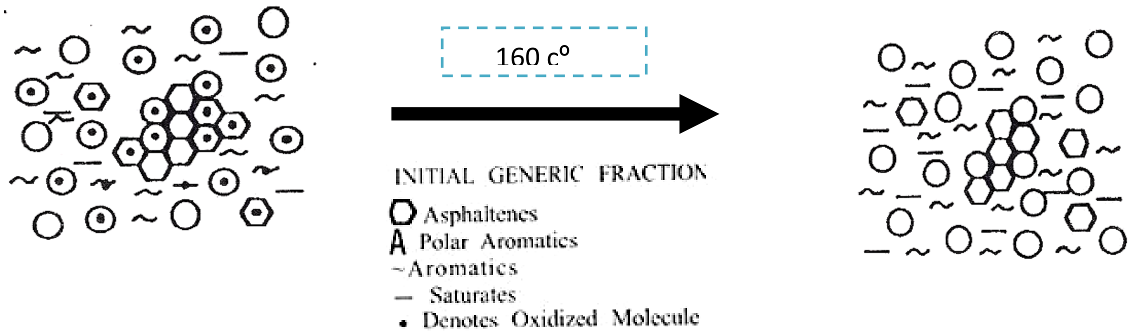

Figure-1: Impact oxidation time on asphalt

fractionated asphalt using solvent extraction method in tow part non soluble asphaltenes, and soluble part is the maltenes. were separated by liquid –solid chromatography column and measuring the weight that have been separated oxidated asphalt becomes more chemically stable than original asphalt, and can calculate in the values of asphaltene and determinate the coefficient **(I_A)** , which represents the spread of asphaltene into the asphalt and know the changing in asphaltene **%** before and after oxidation calculate **Gaestl** Index **(I_C)** (figure-3) , Resin plays an important role of colloidal stabilizing decrease that demonstrates the viability of the distribution or spread of maltenes compared to the spread of asphaltene (Alboundwarei & Jakher,2002) .

This study show that the oxidation process lead to an increase in the asphaltene **%** from **21.61 to 29.09** , aromatic **%** from **23.33 to 26.28** and decrease risen **%** from **18.09 to 9.31** and saturated **% 35.56 to 33.12** show (table-**1)** ,(fig**ure-4).** The asphalt of Abu-Aljeer is in **(Sol)** form because it has large proportion of saturated compounds and when asphalt oxidized asphalt will be changed nearly to **(gel)** form.

Rheological properties study of oxidized asphalt had been changed it , giving increase in the values of the degree of softening point with increasing of oxidation time (table-**2)** , it also gave a decrease in the values of penetration (increased stiffness) (fig**ure-5,6)** , and show the effected of Asphaltene index and **Gaestl** index on the Rheological properties in the **Sol** and **gel phase. (fig**ure-7,8,9,10**).** and The viscosity increased with increasing time of oxidation (table-**2)** , in comparison with the asphalt before and after oxidation (figure-12,13**).** The **I_A** and **I_C** , effected on rheological properties of the samples before and after oxidation and describes the statement of changes in the properties .

This can be explained that the oxidation processes cause the production of the totals of new heating facilitated due to free radicals generation .radical molecules are inter between twined chains hydrocarbon which makes the molecular structure of the asphalt more compact and the formation of bridges of the Common linkage with hydrogen bonds of associative forces Vander Waals leading to a sharp decrease in free volume. the strength of asphalt becomes more solid and more resistant to heat and to the operational circumstances, and the oxidative stress caused an increase in the proportion of asphaltene which works to increase the degree of flexibility (because they are large molecules size associated with each Vander Waals forces in the form of layers of chins by of hydrogen atoms of the multi-planar aromatic rings) and the other for overlap between the molecules asphaltene of the multi- planar aromatic ring while overlap between the molecules asphaltene with the basic strength of aromatic type **(π-π)**,also oxidative stress cause the production of effective groups (carboxylate , ketones ,and phenols) which increases the polarity of molecules consisting asphalt and attraction of with each other and give toughness to asphalt , as well as the works of oxidation stress to reduce the part of saturated hydrocarbon due to the consumption of hydrogen atoms . (figure-14,15,16,17), thermal oxidation has addition affect increase the values of softening point increased by time increase, and became more resistant to needle penetration and the reduce of penetration point values oxidized become largest hardness (table-**2)** show the values fractional parts of the oxidation sample.

The **U.V- Visible** spectra showing (figure-18,19**)** . was absorption different peak of asphalt after and before oxidation the adsorption of original asphalt (**2.35**) and after **55h** oxidation become (**2.55**) because the impact of oxidant to product new groups such (keton , aldehyde , and others).

The **FT-IR** Spectra of oxidation asphalt showing (figure-20,21**).** a week band stretching **C = C - H** to aromatics ring in **3437 – 3400** and to **3300** cm^{-1} , the peak in **1550** to carbonyl group **C= O** it is become more sharp and longest in oxidation . and show band in **1378** to $CH_3 – CH_2$ reduce because the oxidations increase the aspheltene with high poly nucly aromatics ,the band of sulfoxide **C=O 1005** cm^{-1} the **FT – IR** Spectral demonstrates difference in physical properties of asphalt . **HNMR** spectral (fig**ure-22)** show the chemical shift of signal in **(6.5-8.5)** ppm to H_a aromatic hydrogen , signal in **(1.7-3.4)** ppm to H_α aromatic hydrogen in position **α** , signal **in (1.4-2.2)** ppm to H_n naphthenic hydrogen, signal in (**0.5-1,4**) ppm to H_{me} methyl aliphatic hydrogen and signal in **(0,9-1,8)** ppm to H_{my} methyl hydrogen in non α-substitution of aromatic ring , oxidation processes increase the H_n **%** from **4.89 to 5.28 also** H_{my} **%** increase from **52.86 to 54.12** but reduce in (**H_{me} , H_n , and H_a) %** (table-**3),** (figure-23**)** this study was achieved by using the area under the curve in **HNMR** spectral and demermine the type of the absorption of protons in the asphalt and also by used a feudal equations (Fridal,1976) .

Generally the asphalt oxidation processes lead to the improvement in the rheological properties resistance to penetration , increase softening , increase viscosity) also lead to increased values of I_A, I_C .for removal of hydrogen atoms and the formation of free radicals as it works to link the asphalt chains to gives a more solid

Table-1: fractions values of asphalt at different oxidation times

Sample	Time Aging (hrs) Oxidation	Asphalten %	Maltenes %		
			Saturated Comp.	Aromatic Comp.	Resins
Asphalt Abu Aljeer	0	21.61	35.56	23.33	18.08
	5	22.04	34.50	23.68	17.51
	15	23.28	33.05	24.01	15.36
	25	26.08	31.04	25.30	12.07
	35	28.13	32.60	25.85	11.06
	55	29.09	33.12	26.28	9.31

Table-2:chemical and rheological impact on properties of asphalt at different oxidation times

Properties	Oxidation time. (hrs)					
	0	5	15	25	35	55
I_A	0.661	0.690	0.688	0.692	0.697	0.701
I_C	1.376	1.384	1.430	1.524	1.646	1.747
Penetration	52.39	37.91	27.36	19.35	12.26	9.180
Softing	36.80	44.40	58.60	64.40	68.90	73.20
Viscosity. Cst	10850	13210	25670	65402	90873	125911

Table-3:distribution of hydrogen atom in asphalt of abu-aljeer before and after oxidation

Type of Hydrogen	H_{me}	H_{my}	H_n	H_α	H_a
Original Asphalt	28.41	52.86	6.65	7.09	4.89
Oxidation Asphalt	26.82	54.12	6.60	7.02	5.28

H_{me}	H_{my}	H_n	$H\alpha$	H_a
Hydrogen methane	Hydrogen methyl paraffin	Hydrogen naphtl	Hydrogen in alpha cyclo aromatic ring	Hydrogen Aromatic

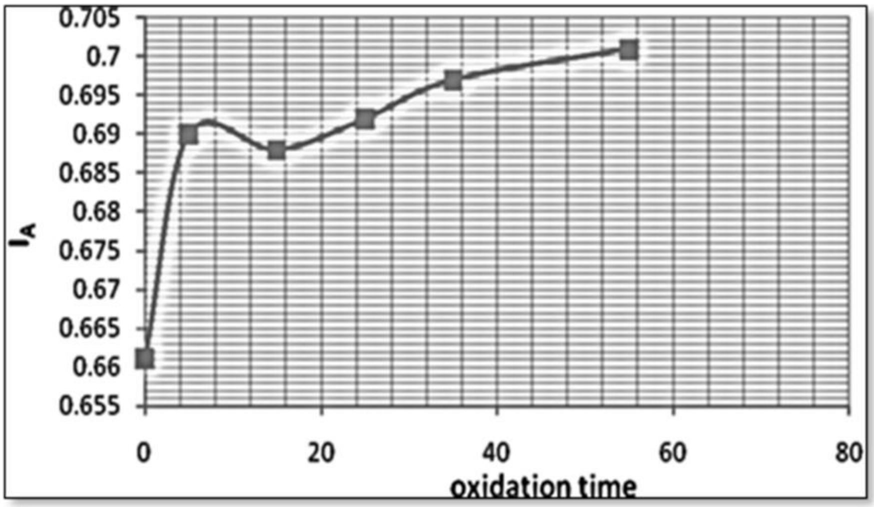

Figure-2: values of I_A at different oxidation times

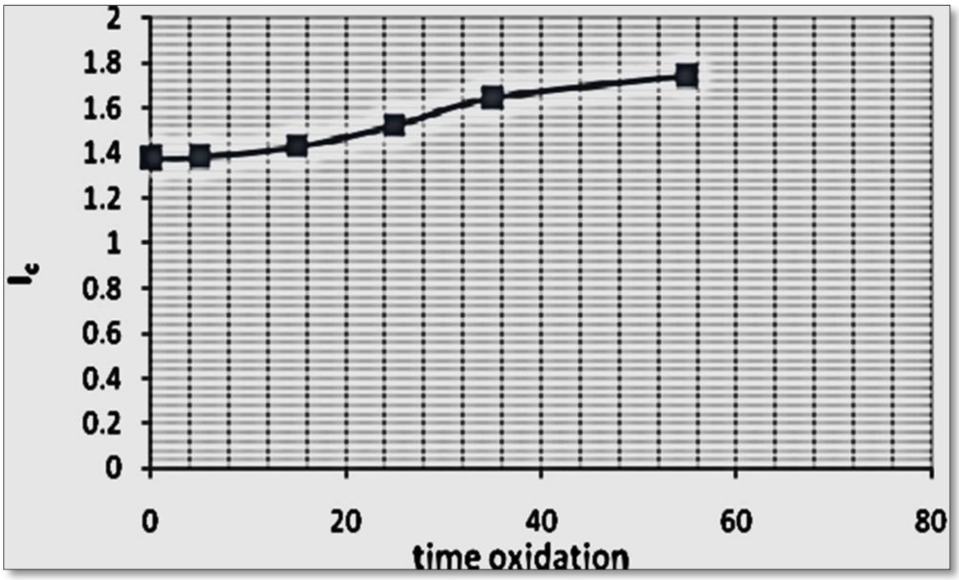

Figure-3: Values of I_C at different oxidation time

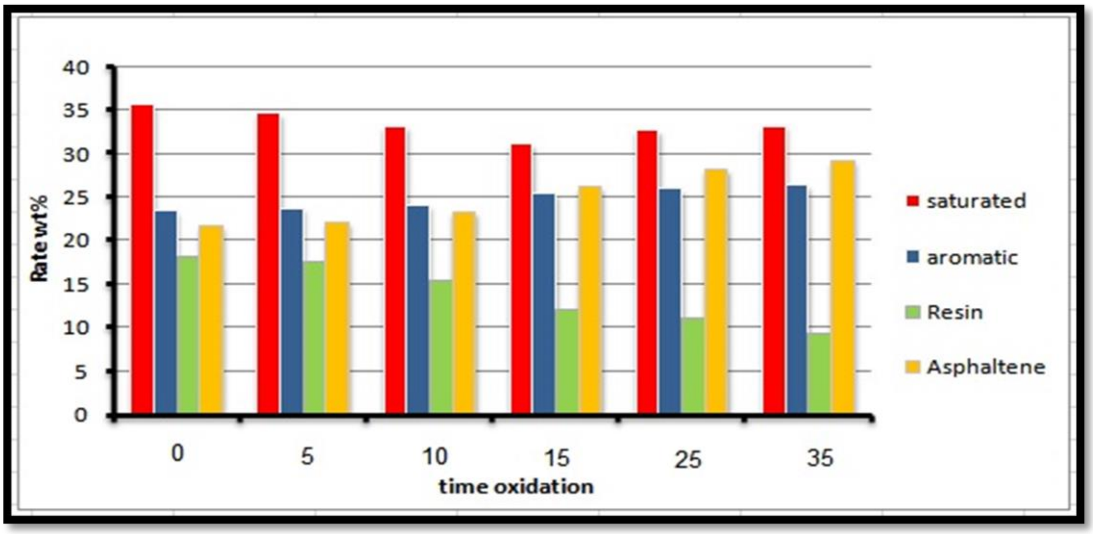

Figure-4:weight percentages of the fractions parts of asphalt at different times of oxidation

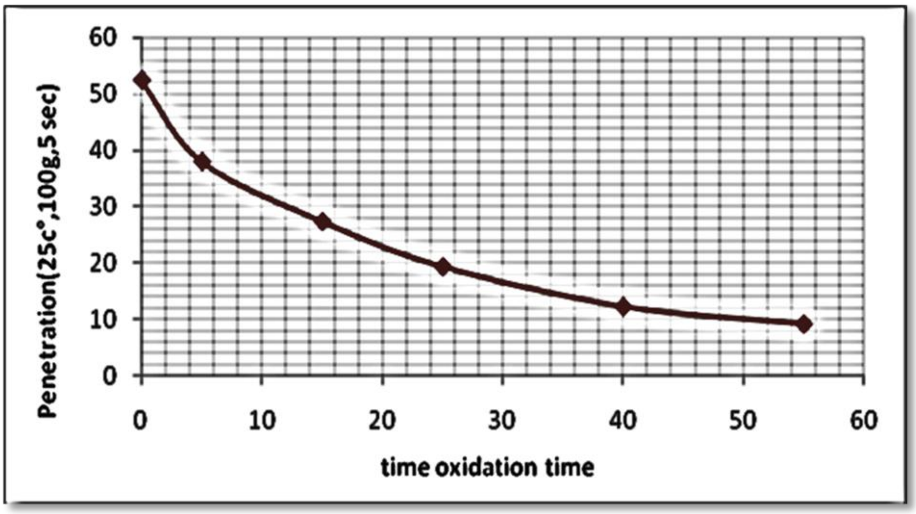

Figure-5: impact of aging on penetration (mm ,100gm,25c°,5sec) of asphalt

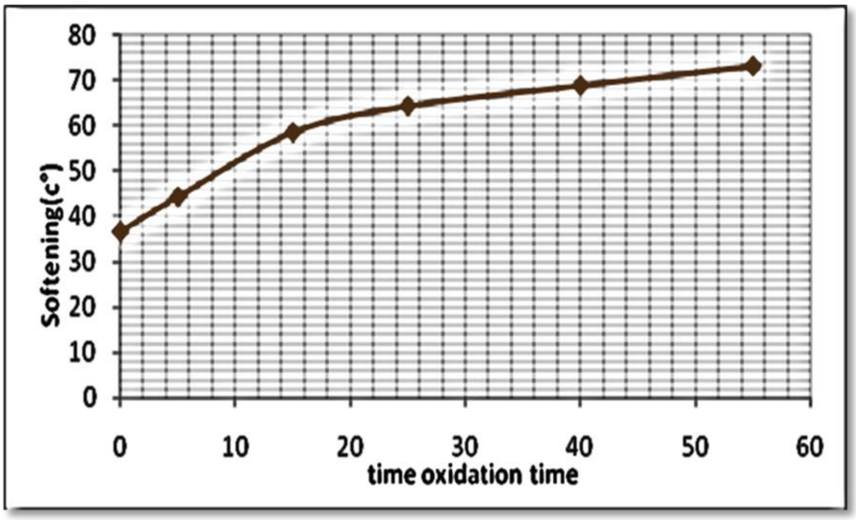

Figure-6:impact of aging on softening (c^o)of asphalt

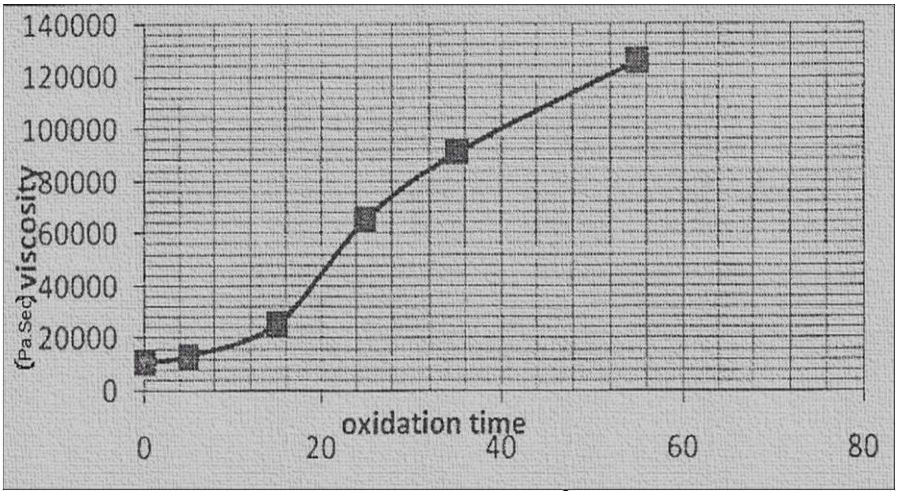

Figure-7: impact of oxadation aging on viscosity (cm^2\Sec,135$c^°$, centi- Stoke) of asphalt

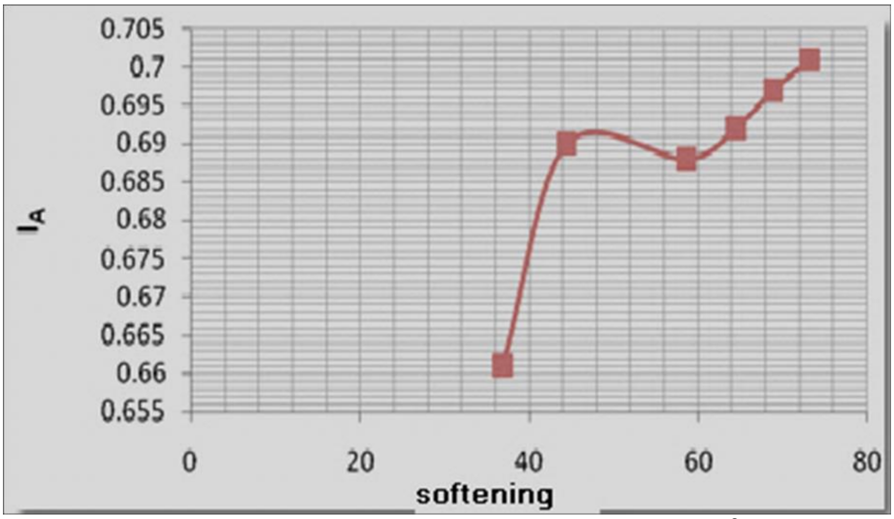

Figure-8: Relationship between I_A and Softening (c^o)

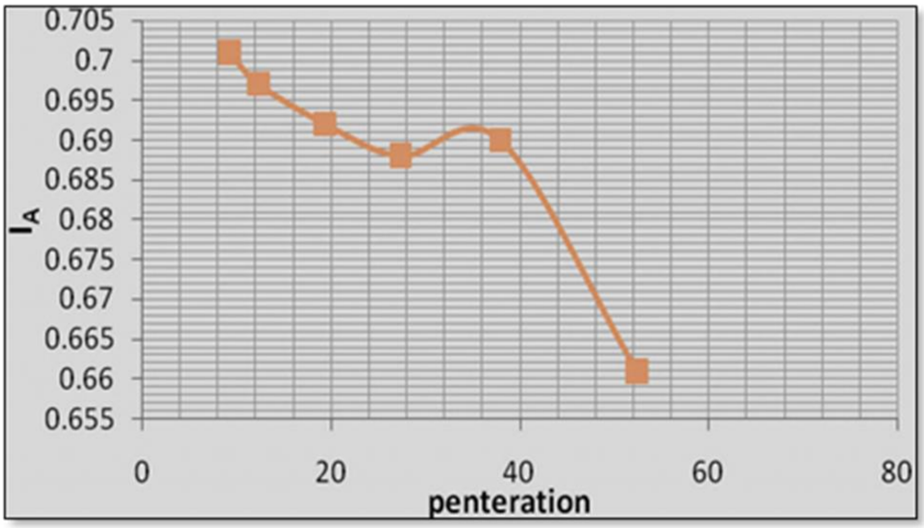

Figure-9: Relationship between I_A and Penetration(mm ,100gm,25c°,5sec)

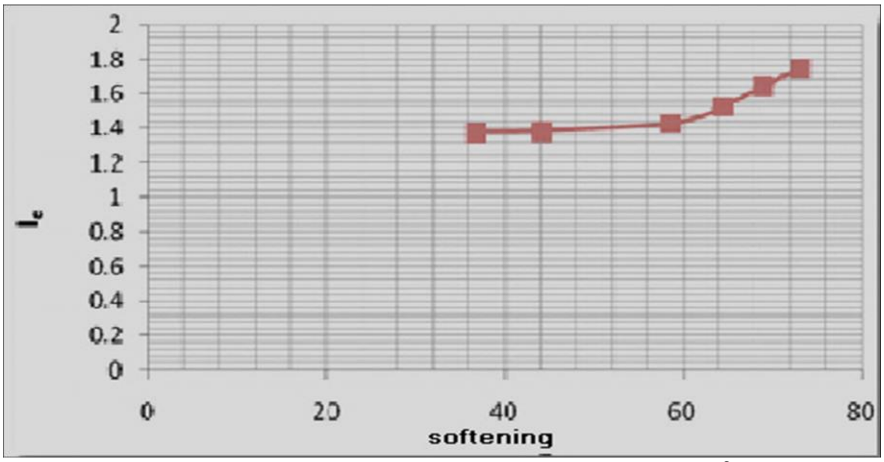

Figure-10: Relationship between I_C and Softening(c^0)

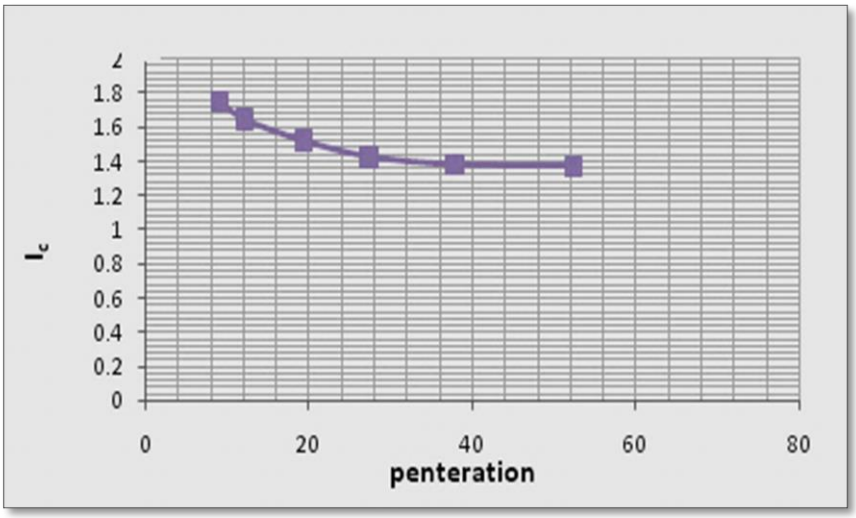

Figure-11: Relationship between I_C and Penetration (mm ,100gm,25c°,5sec)

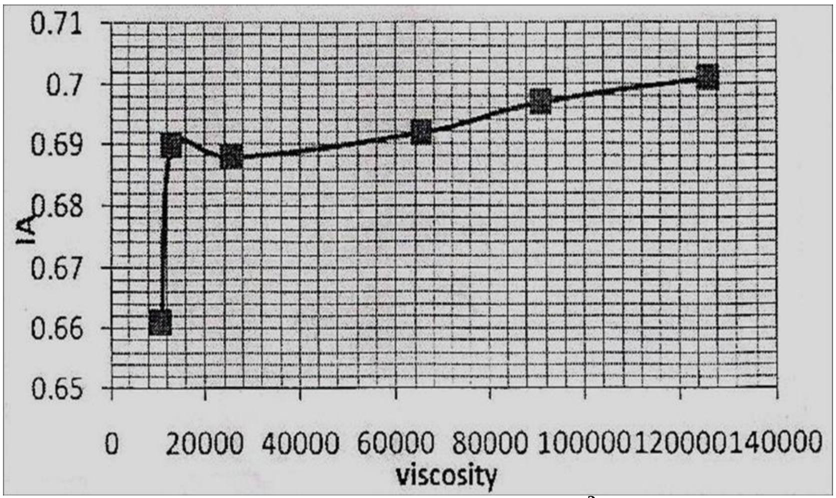

Figure-12: Relationship between IA and Viscosity (cm^2\Sec,135c°, centi- Stoke)

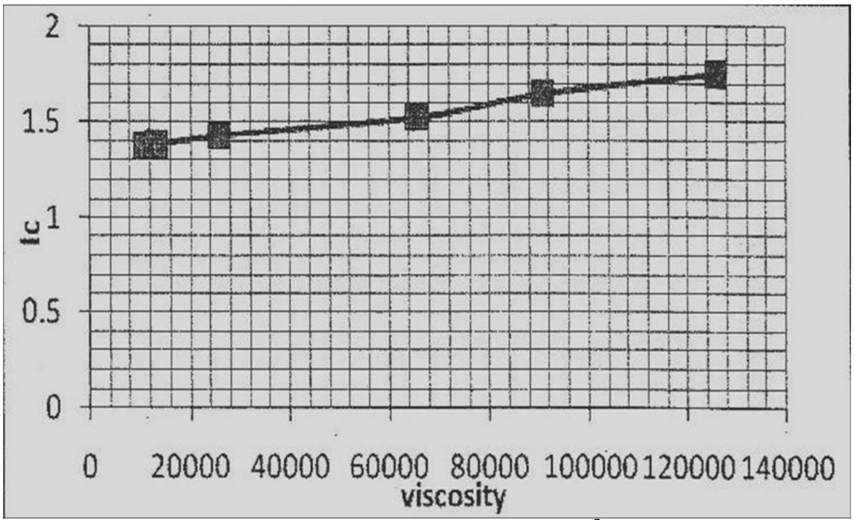

Figure-13: Relationship between IC and Viscosity (cm^2\Sec,135c°, centi- Stoke)

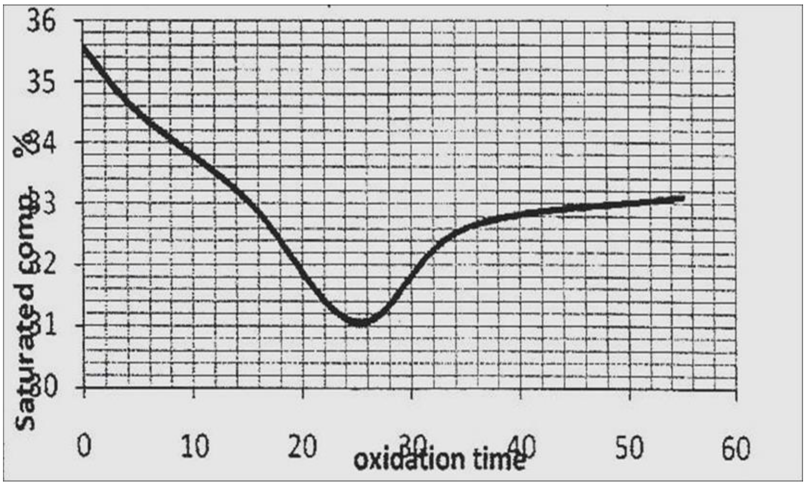

Figure-14: Saturated comp. % at different oxidation times

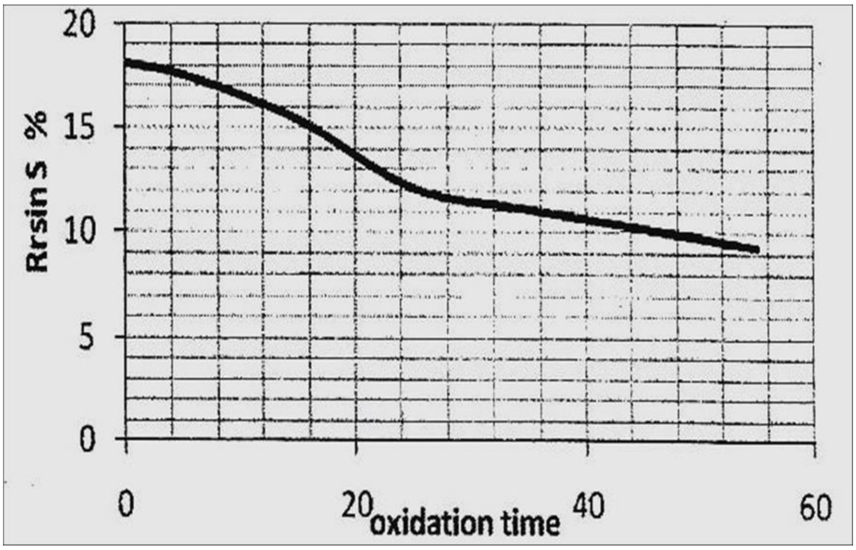

Figure-15: Resins % at different oxidation times

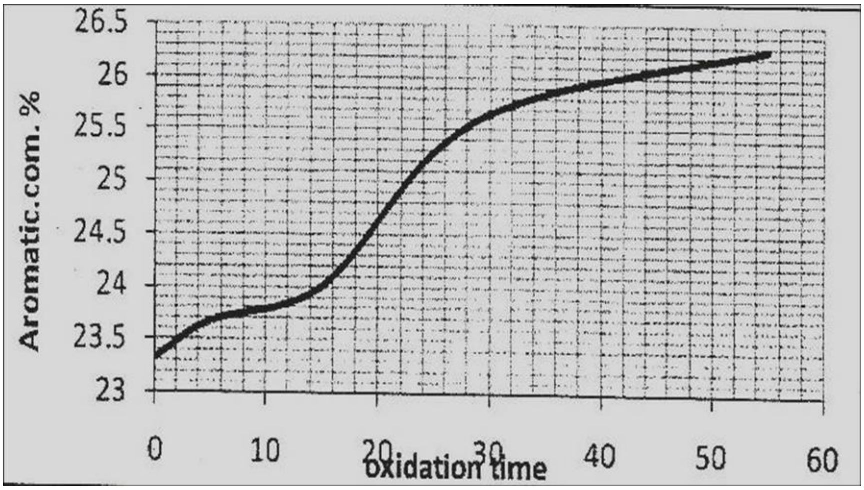

Figure-16: Aromatics % at different oxidation times

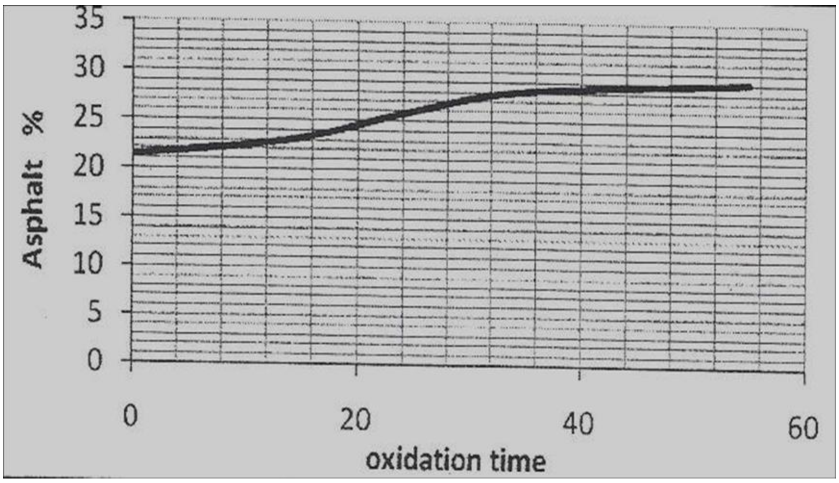

Figure-17: Asphaltens % at different oxidation times

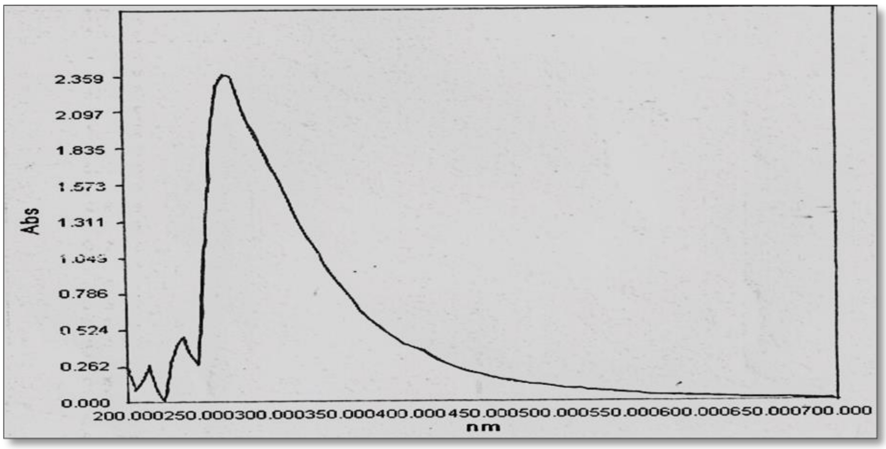

Figure-18: uv spectrum asphalt before oxidation

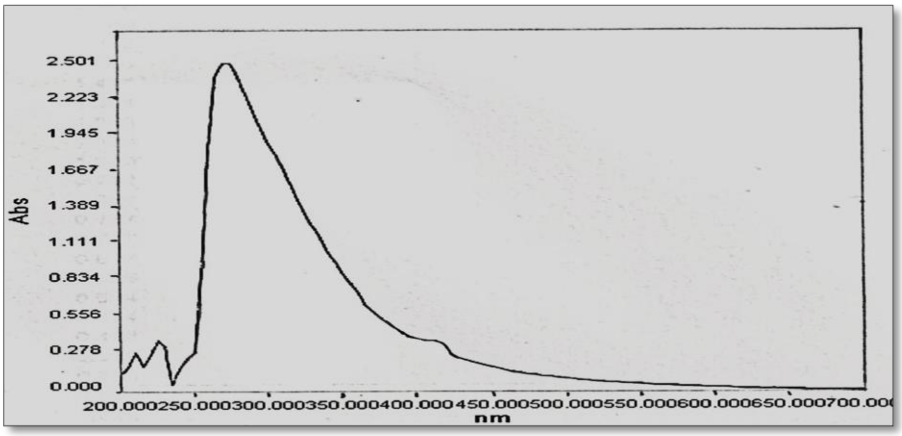

Figure-19: uv spectrum of asphalt after oxidation

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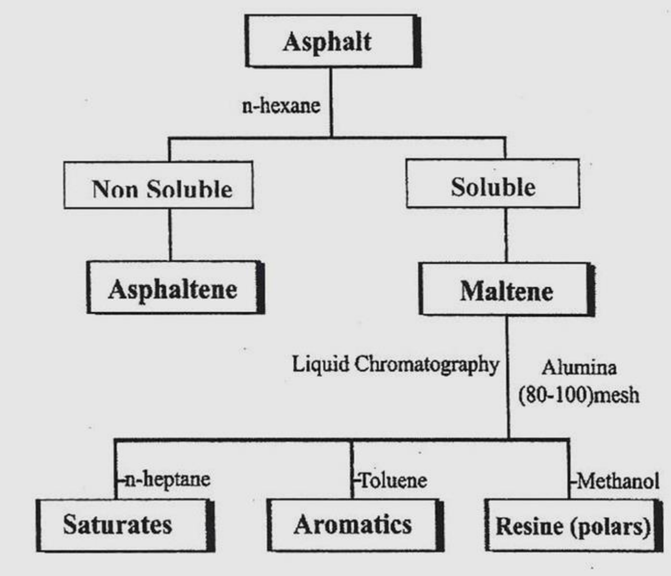

Schematic (1) of Separation Asphalt (SARA)

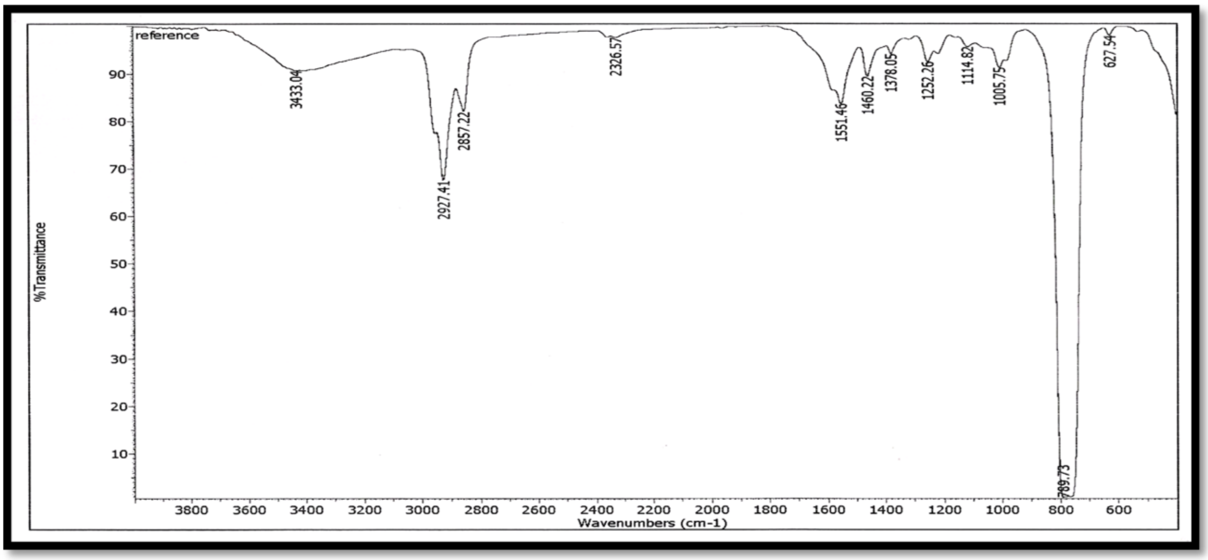

Figure-20: FT-IR spectra asphalt before oxidatio

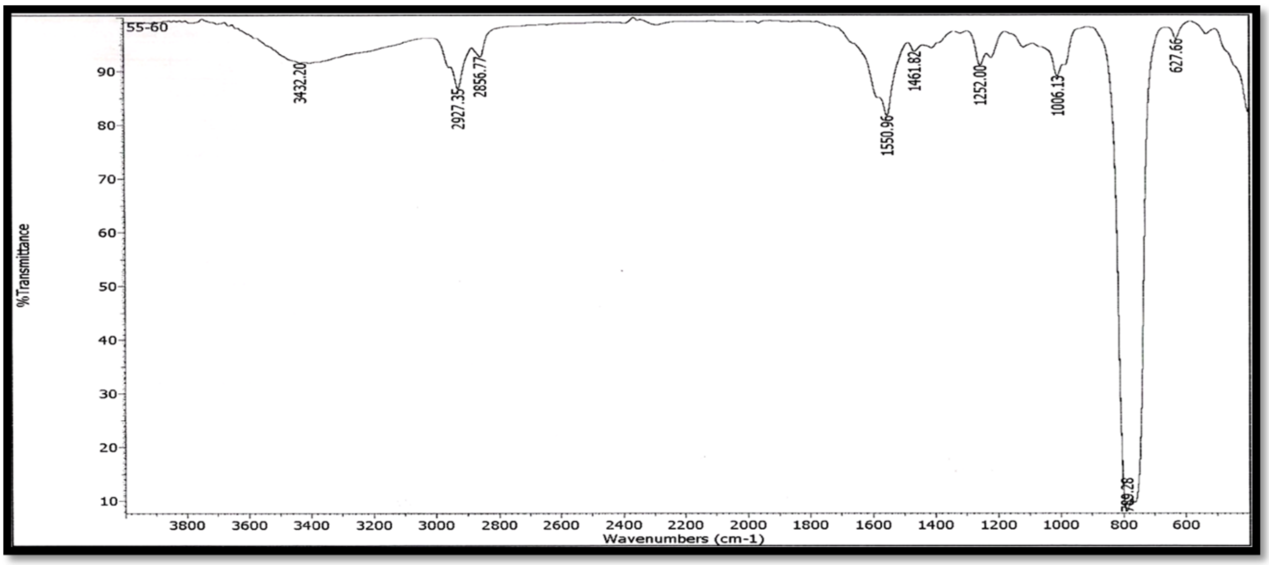

Figure-21: FT-IR spectra asphalt aftere oxidation

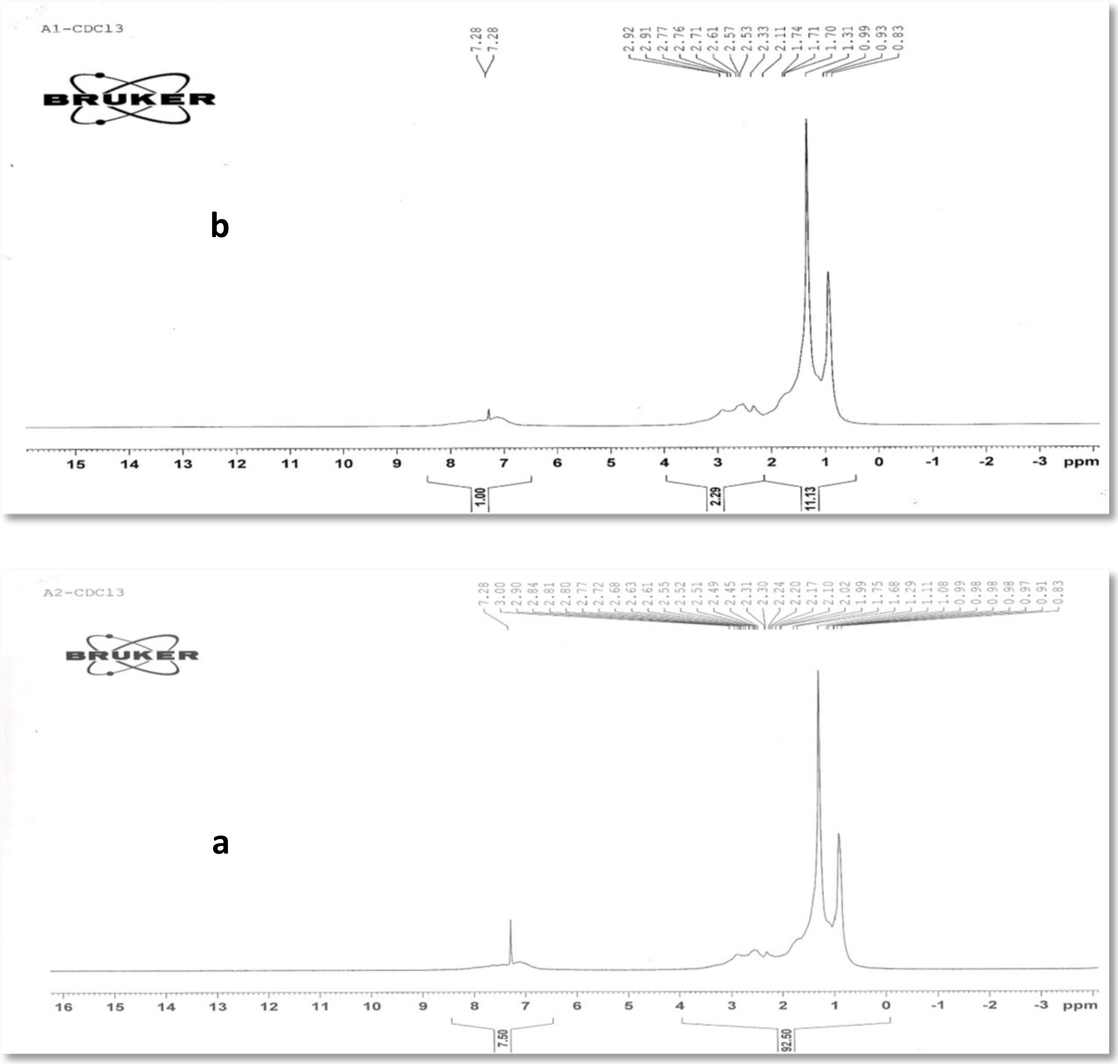

Figure-22: HNMR Spectral Asphalt of abu – aljeer : (a-before b- after) oxidation

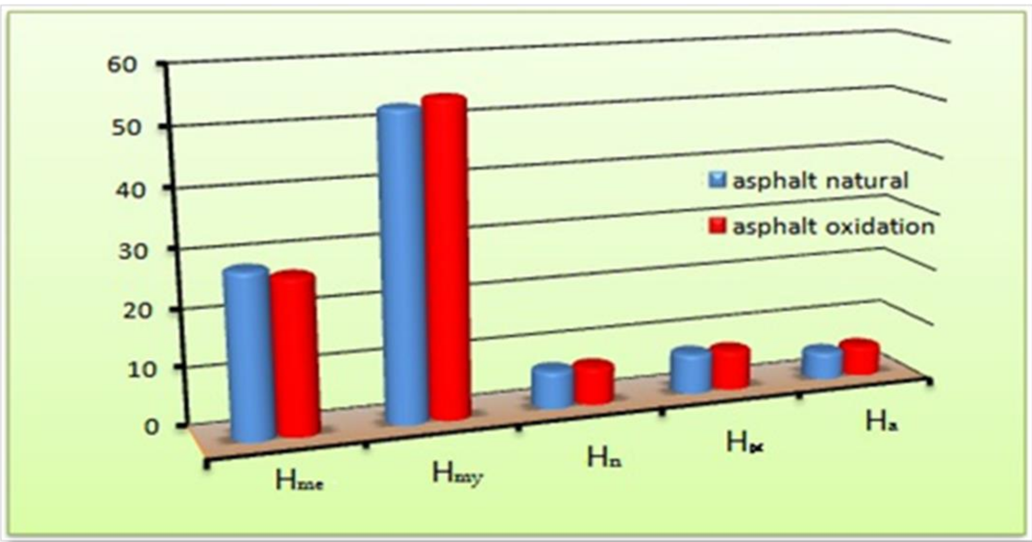

Figure-23: the proton relative distribution of measured parts with HNMR spectral

4 – Conclusion:

This study showed that thermal oxidation of (Abu Aljeer) asphalt in high temperature under air atmospheric was gives improvement in the chemical and physical properties and increase in the ratio of asphaltene and aromatic parts **(I_A, I_C)** , but decrease in the ratio of saturated and resins part, the study also showed that there is a relationship between the chemical content of asphalt and oxidation processes , and increase the stability of colloidal state when the less content asphaltene in the asphalt.

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