Photo-degradation Effect on Naphtha Octane Number by Using UV Radiation

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الخلاصة

تم استخدام النفثا في هذا البحث كوقود اختبار حيث تم تعريضها الى الاشعة فوق البنفسجية تحت ظروف اختبار مختلفة (تعرض للاشعة فقط ، تعرض للاشعة بوجود التبريد ، تعرض للاشعة بوجود التبريد والعامل المحفز ، تعرض للاشعة بوجود التبريد والعامل المحفز والعامل المؤكسد ، تعرض للاشعة بوجود العامل المحفز والعامل المؤكسد) حيث تم تتبع عملية تكسير الاواصر ضمن تفاعلات التحلل الضوئي، فلوحظ تكسر اواصر عديدة نتيجة امتصاص الاشعة فوق البنفسجية ذات الطاقة العالية، ومن النتائج المتوقعة لهذا التحلل هو تغير العدد الاوكتاني للنفثا .

تم تحضير نماذج من وقود النفثا ومعاملتها تحت ظروف مختلفة باستخدام منظومتين :

- منظومة مفاعل الاشعة (Reactor Unit) : هذه المنظومة تعمل ضمن ضغوط مرتفعة نسبياً ، حيث لوحظ من خلال استخدام هذه المنظومة ان العدد الاوكتاني للنفثا يتناقص او يبقى ثابتاً تحت تأثير الاشعة فوق البنفسجية .
- منظومة خلية الاختبار الزجاجية (Cell Unit) : هذه المنظومة تعمل ضمن الضغط الجوي الاعتيادي حيث لوحظ من خلال استخدامها ان العدد الاوكتاني للنفثا يتغير بثلاث سلوكيات (ارتفاع ، انخفاض ، عدم تغير).

ومن خلال مجموعة الاختبارات تبين ان اكبر مقدار انخفاض في العدد الاوكتاني للنفثا تحت تأثير الاشعة يصل الى (-11) درجة ضمن ظروف تعرض النفثا الى الاشعة بوجود التبريد وثنائي اوكسيد التيتانيوم (TiO_2) كعامل محفز باستخدام منظومة الخلية الزجاجية ، بينما أعلى ارتفاع في العدد الاوكتاني للنفثا يصل الى (5.6) درجة ضمن ظروف تعرض النفثا الى الاشعة بوجود اوكسيد الزنك (ZnO) كعامل محفز و (2.1 ml/min) من تغذية الاوكسجين كعامل مؤكسد باستخدام منظومة الخلية الزجاجية . ولكي نفهم سلوك هذه التغيرات الحاصلة في العدد الاوكتاني للنفثا تم استخدام جهاز المطياف Gas chromatography Mass Spectrometry (GCMS) لتحليل عدة نماذج قبل وبعد التعرض للاشعة لرصد التغير الحاصل في نسب المركبات المؤثرة بشكل رئيسي على العدد الاوكتاني وهي :

(Isooctane , Benzene , Toluene , P-xylene)

بحيث لوحظ بعد التحليل حدوث زيادة في نسبها في بعض النماذج ونقصان في نماذج اخرى . أخيراً تم استخدام جهاز التحليل الطيفي Fourier transform infrared spectroscopy (FTIR) لتحليل عدة نماذج قبل وبعد التعرض للاشعة لمعرفة الأواصر الكيميائية المتكونة والملغية بفعل تأثير الاشعة وباقي ظروف الاختبار.

الكلمات الدالة: التحلل الضوئي ، النفثا ، العدد الاوكتاني البحثي ، الاشعة فوق البنفسجية ، عملية التكسر بتأثير الاشعة

Abstract

In this work naphtha is exposed to ultraviolet rays under various conditions namely; UV exposure only, UV exposure with cooling, UV exposure with cooling and catalyst, UV exposure with Cooling, Catalyst and Oxidant O_2 and UV exposure with Catalyst and Oxidant O_2 to investigate the bonds cracking process (Photo-degradation or photolysis reactions) and its effect on naphtha octane number where several bonds are to be broken due to absorption the high energy of UV radiation. It is expected that naphtha octane number should be changed as a result of the Photo-degradation effect. Samples are prepared and treated with various conditions in a UV Reactor unit under prevailing pressure (elevated pressure). No systematic change in octane number is noticed but the octane number is either decreases or remains constant. Another technique which the cell unit is used. Samples are prepared and treated in the cell unit under atmosphere pressure. Three different behaviors of the change in naphtha octane number are resulted (decreasing, no change and increasing). Maximum decreasing in octane number is (-11 unit) occurred when naphtha is exposed to UV rays with cooling & TiO_2 catalyst in the cell unit , while the maximum increasing is (5.6 unit) occurred when naphtha is exposed to UV rays with ZnO catalyst & (2.1 ml/min) O_2 feeding in the cell unit. In order to understand this behavior Gas chromatography Mass Spectrometry (GCMS) tests are conducted for some samples before and after UV exposure to study the changes in chemical composition of naphtha specially the changes in percentage of compounds that affect the octane number such as: Benzene, Toluene, Isooctane and P-xylene. It is noticed that the percentages of these compounds increased in samples in some tests and decreased in others. Also Fourier Transform Infrared spectroscopy (FTIR) tests are conducted for these samples before and after exposure to find the eliminated or created chemical bonds or functional groups of these bonds.

Keywords Photo-degradation , Naphtha , Research octane number (RON) , UV radiation , photolysis process.

Introduction

Ultraviolet radiation (UV) is part of the non-ionizing region of the electromagnetic spectrum and comprise approximately 8–9 % of the total solar radiation [1] .It is one portion of the electromagnetic spectrum which travel through space. UV radiation is used in many industrial applications such as photo-degradation of hydrocarbon compounds.

In all organic compounds which contain the C-H bond and the C-C bond, the values of their bond energies and octane number depend on the structures of their molecules. It is well known that hydrocarbon fuels with long straight chain molecules have low octane number while fuels with short chain, branched and cyclic molecules have high octane number.

Naphtha is one of hydrocarbon fuels which is produced from crude oil by several methods such as: fractionation of distillates or even crude petroleum, hydrogenation of distillates, solvent extraction, alkylation processes and polymerization of unsaturated olefinic compounds or may be a combination of them. [2]

It is a volatile and flammable fuel with specific gravity of (0.694) at 15C° and boiling range about (30°C - 200°C) . It consists of a complex mixture of more than a hundred hydrocarbon compounds with carbon atoms range between ($C_4 – C_{15}$). [3]

When naphtha is exposed to UV radiation it will undergo a Photolysis (Photo-dissociation) process [4]. This process causes changes in chemical composition of naphtha and then in its octane number which depends on nature of the contained compounds in naphtha.

There were attempts of subjecting catalysts to varied sources of radiation to enhance their activity. some of these attempts were concentrated on the study of UV rays on the catalyst activity in conversion of unsaturated hydrocarbons. They found that if a catalytic reaction occurs in the presence of UV radiation , substantially complete conversion of reactants is obtained. Thus, they proved that the UV radiation exposure enhances the catalyst activity [5].

Two advantages for using of UV rays with hydrocarbon compounds, one of them is cracking which relates to hydrocarbon bonds and the other is enhancing of the catalyst activity which relates to catalysts in photo-catalysis process [6].

Ali H. A. Rashed et al. (2013)[7], used UV rays to improve the Octane number for Al-Dura product pool (70% Reformate + 30% Light Naphtha) in photo-degradation process in the presence of ZnO catalyst, with different exposure times . They raised the octane number by (5 degrees) at (8 hours) exposure.

The main aim of the present work is to study the changes in naphtha octane number under UV radiation exposure based on idea of C-C and C-H bonds breaking and re-structuring.

Experimental Rig and Measurements

UV Reactor Unit : This unit is manufactured to study the effect of UV exposure on naphtha octane number at different operating pressures (relatively elevated pressures). It consists of the following parts, see figs.(1 & 2).

a) A cylindrical tank (0.26 m diameter, 1 m height with 50 L capacity) manufactured from stainless steel to obtain good reflection of UV rays from the tank inner walls.

b) A motor mounted on the top cover of the tank used to drive the mixer inside the tank at 20 RPM.

c) Three UV lamps each of (100 W/m^2) are inserted in three sleeves manufactured from quartz to obtain optimum transmissivity of UV rays. These sleeves are fixed by Teflon bushes and rubber O-rings in the holes through the top cover of the tank. The rubber O-rings are used to prevent pressure leakage between the sleeve wall and the Teflon bush.

d) Thermometer for temperature recording before and after the test.

e) Pressure gauge to record the tank pressure before and after the test.

f) Safety valve for pressure release.

g) Drainage valve at the base of the tank to empty a charge (a sample) after each test.

h) Cooling water tube (0.5 m × 0.5 m × 0.7 m) contain cooling water.

i) Submerged water pump (pumping height of 1.8 m) to pump the cooling water from cooling tub to the water distributor.

j) Water distributor which is a perforated tubular ring with 17 holes, each hole diameter of (3 mm). It is installed around the tank near the top cover at a height of (1.1 m) above the submerged water pump and used to distribute the cooling water on the outer surfaces of the tank for cooling if necessary.

UV Cell Unit : This unit operates under atmospheric pressure. It consists of the following parts and auxiliary tools:

a) Two concentric glass vessels are formed as a cell with annulus space used for cooling water, so that the fuel sample is put in the inner vessel.

b) Mixing capsule is immersed inside the cell for sample rotation.

c) Magnetic stirrer is used to rotate the mixing capsule inside the test sample under effect of magnetic field.

d) Cooling system is used to cool the cell during the test and to keep the sample temperature at required value.

e) UV lamp of (75 W/m^2) is fixed by standing over the cell. The lamp is partially enveloped to concentrate the rays in direction of a sample.

f) Air feeder with air flow rate of (10 ml/min) is used as an Oxygen source.

g) Filtering sheets, graduated cylinder, funnel, electronic balance, burette, thermometer and sample bottle are used. See figs. (3&4).

Sample Preparation and Test Procedure

Naphtha samples of 40 L for UV Reactor Unit or (500 ml) for UV Cell Unit are prepared. Each sample is mixed with catalyst for 20 min before UV exposure. The Octane number of the sample is measured either in CFR engine or SHATOX Octane meter, GCMS and FTIR analysis are also conducted for sample before exposure. The temperature of the sample is recorded initially and during the test. Also the pressure inside the UV Reactor tank is recorded initially and during the test. The sample is then exposed to UV rays for a specified period under various conditions. Octane measurement, GCMS and FTIR analysis are conducted after exposure to investigate the changes in the molecular structure caused by the UV exposure.

CFR Engine and SHATOX Octane Meter

Cooperative Fuel Research (CFR) engine is a 4-stroke, SI engine with a single-cylinder and variable compression ratio used to measure the fuel octane number, see fig. 5. Its Compression Ratio (CR) varies from 4.5 to 16 quickly and accurately by moving the cylinder head with respect to the piston [8] SHATOX Octane Meter is a portable device used to measure the fuel Octane number depending on comparison between characteristics of the test sample and these of standard gasoline stored in the internal memory of its microprocessor [9], see fig. (6). It is calibrated against the CFR engine as shown in fig.(7).

Gas Chromatography Mass Spectrometry (GCMS) Analysis

It is an apparatus used in the separation, identification and quantification of complex mixtures. The determination of these compounds is very difficult by the standard MS library. Therefore, the retention time was used as an index for the GC qualitative analysis [10]. The changes in the main effective compounds (i.e. compounds that affect the octane number) is determined by comparing the GCMS results before and after UV exposure. The octane number change may be interpreted according to the qualitative and quantitative changes in these compounds.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

This apparatus provides crucial information about the molecular structure of organic and inorganic components [11]. The FTIR technique is based on the absorption of IR radiation which occurs when photons transfer to sample molecules. These molecules are excited to a higher energy states [12] causing vibrations of molecular bonds (i.e. bending, stretching, rocking, twisting, wagging and out-ofplane deformation). Those excitations occur at varying frequencies (wavenumbers of range about 4000 – 400 cm^{-1}) in the IR region of the electromagnetic spectrum.

Results and Discussion

The results are divided into five groups according to the tests conditions:

1.Naphtha Exposed to UV Rays Only

The results of these tests are shown in table 1 & fig.8 .These results show a fluctuating response in the change of naphtha RON when exposed to UV rays only. It decreases to a minimum value of 51.3 after one hour exposure (initial RON 54.5) and then increases to 56 after two hours exposure and then decreases. This fluctuating in Octane number may be attributed to the effect of photolysis (Photo-dissociation) process.

It is known that the bonds of the branched compounds (iso-paraffin) are weaker than those in the straight chain compounds (n-paraffin) because the branched compound molecules are more compact with less surface area. This means that the intermolecular attractive forces of the branched compounds are smaller. Therefore, the broken bonds due to UV exposure are more in the branched compounds than in the straight chain compounds. In other words, the branches are broken and may be converted into small straight chain compounds. On the other hand, some of the UV energy may be used to break the bonds of straight chain molecules and converted them to branched molecules. As it is known that the RON of straight chain compounds (n-paraffins) is less than that of branched compounds (iso-paraffins), as shown in fig. (9) the net effect of these two restructuring processes may cause the fluctuation in Octane number changes.

2.Naphtha Exposed to UV Rays with Cooling

The results of these tests are shown in table (2) & fig. (10). These results indicate that no change occurs in the Octane number when naphtha is exposed to UV rays with the existence of cooling. An important fact may be concluded in these tests, that the cooling inhabits the Photolysis activity.

In other words, during the UV exposure with temperature rise process the interaction between photons and fuel molecules may occur causing the crack of the bonds of that molecules, whereas the cooling process inhibits that interaction and protects the molecules against the UV exposure effect.

3.Naphtha Exposed to UV Rays with Cooling and Catalyst

The results of these tests are shown in table (3) & fig. (11). These results exhibit that there is sever drop in the RON between (0.5 –1 hr) of UV exposure reaching to (-11 unit). After two hours exposure the drop becomes (-6.4 units) only.

When a catalyst is added to the fuel and exposed to UV rays the photo-catalysis process will occur (i.e. the acceleration of photoreaction in the presence of a catalyst) . In this process electrons of catalyst molecules are excited by UV photons and transferred from the valence band to the conduction band, leaving positive holes in the valence band, see fig. (12). The ultimate goal of the process is to have a reaction between the excited electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product [13]. If there is no capturer for the electrons in conduction band (active electrons), as in this test, they return quickly to their valence bands and react with the holes (Recombination process).

Titanium dioxide (TiO_2) and Zinc oxide (ZnO) are used as a suitable catalysts . They are both semiconductors each of them have a band gap energy of (3.2 eV) [14]. The fluctuation in the RON change that is exhibited in these results may be attributed to the recombination process which occurs in the absence of capturer. Therefore only the photolysis effect will be existed.

4.Naphtha Exposed to UV Rays with Cooling , Catalyst and Oxidant O_2

Oxygen is known to act as a capturer of electrons that exist in the conduction band to generate radicals which may lead to production of high RON compounds. Air is used as a source of oxygen in this work in the presence of catalyst to improve RON of naphtha. Two tests are carried out with air flow rate of 10 ml/min (oxygen flow rate of 2.1 ml/min). In the first test TiO_2 is used as catalyst and the results are shown in table (4) and fig. (13) while in the second test ZnO is used as catalyst and the results are shown in table (5) and fig. (14).

The results of TiO_2 test show a decrease in the RON, while the results of ZnO test show an increase in the RON value. This means that ZnO is more effective than TiO_2 in photo-catalysis process with the presence of O_2 oxidant which acts as a capturer for the active electrons in conduction band of catalyst molecules.

5.Naphtha Exposed to UV Rays with Catalyst and Oxidant O_2

To investigate the effect of cooling on the photo-catalysis process samples with ZnO catalyst and oxidant are exposed to UV rays in the absence of cooling. The oxidant (which oxygen) flow rate oxidant. 2.1 ml/min.

The results are shown in table (6) and fig. (15). These results show a fluctuating decrease in octane number initially until two hours exposure then the octane number begins to increase. A maximum increase in octane number of 5.6 units occurs at 4 hrs exposure. At longer exposure time the RON value decreases again. In these tests the oxidant reacts with the excited electrons in conduction band generating radicals (reduced product) in photo-catalysis process. These radicals may lead to production of high RON compounds.

GCMS Tests

Due to the large number of compounds contained in naphtha, it is difficult to follow all changes in the chemical composition of the sample. It is known that the aromatic compounds have high RON values in comparison with the other hydrocarbons groups [15] as shown in fig. (9). Therefore, the GCMS test is performed to understand the changes in aromatic group in addition to the iso-paraffin (Isooctane) which may be the cause of changes in the RON values.

The GCMS tests are performed on a sample of naphtha before and after (2 hrs) of exposure of UV rays as shown in figs. (16&17) tables (7&8). The RON change is (6.4 decrease) with the conditions mentioned in table (3).

Table (9) & fig. (18) Show the percentage change in the main effective four compounds. The results show that the Isooctane is generated after UV exposure test and the Toluene percentage is increased. Whereas, the percentages of Benzene is decreased and P-xylene is vanished. The RON decrease which happened in the sample after UV exposure test may be attributed to the changes of the effective compounds. Specially, after taking into account the RON values of these effective compounds as mentioned in table (10).

GCMS tests are also performed on a sample which shows an increase in octane number. The tests are performed before and after three hours exposure of UV rays and the result is shown in figs. (19 & 20) and tables (11&12). The RON change of this sample is 2.1 unit increase with the mentioned conditions in table (6).

Table (13) and fig. (21) show the percentage change in the main effective four compounds which are Isooctane, Benzene, P-xylene and Toluene . The results show that there are increases in the percentages of Isooctane, Benzene and P-xylene, while the Toluene is vanished completely. The increase in RON value which happened in this sample may be attributed to the increase in the percentage of the effective four compounds. specially, after taking into account the high RON values of these effective compounds.

FTIR Tests

FTIR tests are conducted before and after UV exposure for the sample which shows a decrease in RON which is the same as in the GCMS and the results exhibit the following changes shown in figs.22 & 23. The following changes are noted:

At frequency of (2175.5 cm^{-1}), (C ≡ C) bond from (alkynes) functional group is existed before UV exposure, but it is not apparent after the exposure.

At frequency of (2229.17 cm^{-1}), (C ≡ C) bond from (alkynes) functional group appears after the exposure.

This test is also carried out on the same RON increasing sample that mentioned in the GCMS test. Figs. (22 & 24) show the results of the FTIR test before and after UV exposure respectively. The results exhibited the following changes.

At frequency of (2175.5 cm-1), bond from (alkynes) functional group and at frequency of (1350.86 cm-1), bond from (alkanes) functional group are existed before UV exposure, but they are eliminated after the exposure.

At frequency of (1404.94 cm-1), bond from (aromatics) functional group and at frequency of (706.14), bond from (aromatics) functional group are created after the exposure.

Conclusions

The following conclusions can be drawn:

1. Photolysis effect under UV exposure only . This effect causes a fluctuating change in the octane number due to the difference in the broken bonds numbers between the straight chain and branched.
2. Cooling process inhabits effect under UV exposure. This effect causes no effect in the octane number.
3. UV exposure, cooling and catalyst also causes a fluctuating change in the octane number.
4. Using ZnO catalyst with UV exposure, cooling and oxidant gives positive octane number change as the results of photo-catalysis process while using TiO_2 catalyst gives negative change.
5. Photo-catalysis effect under UV exposure, ZnO catalyst and O_2 oxidant produces an increase in octane number due to production of high RON compounds.

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Fig. (1) Reactor Unit.

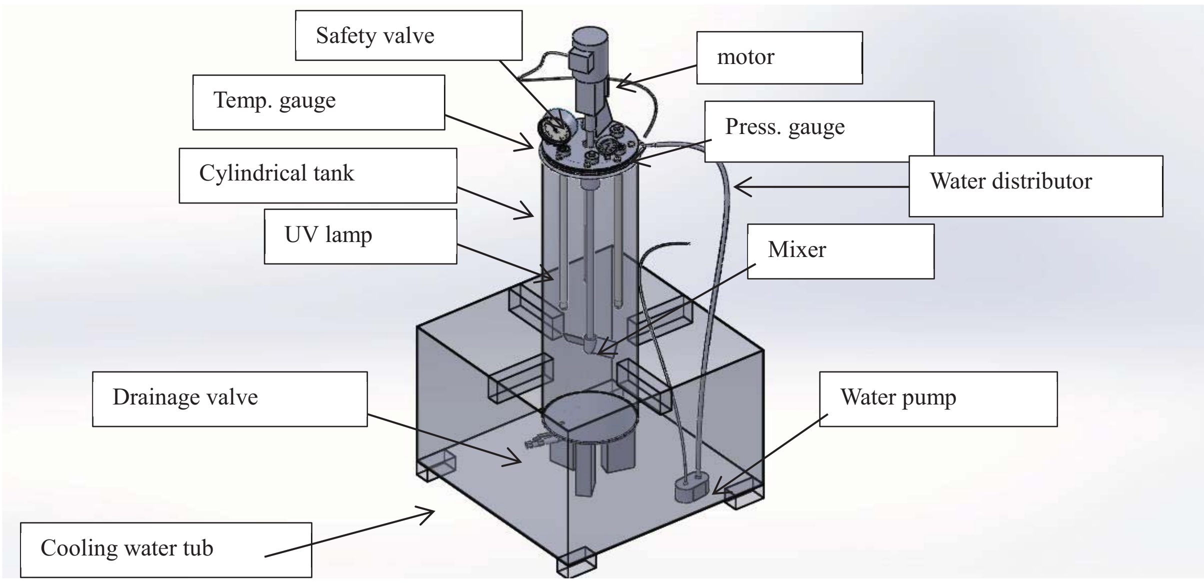


Fig. (2) Schematic Reactor Unit.

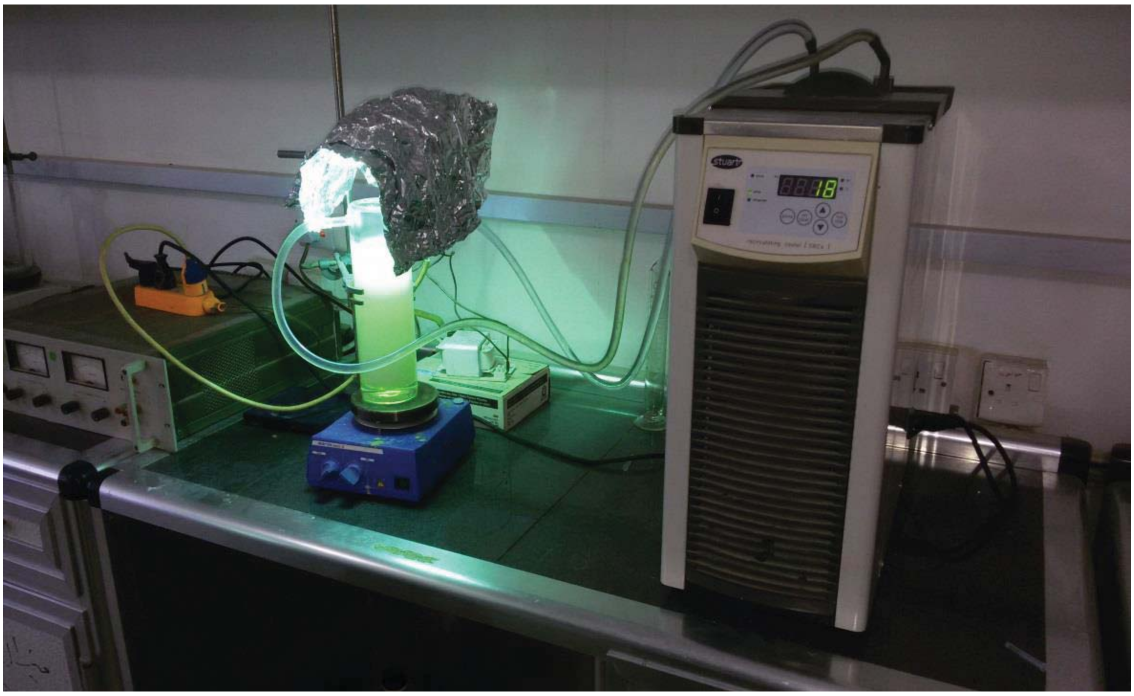


Fig. (3) The Cell Unit.

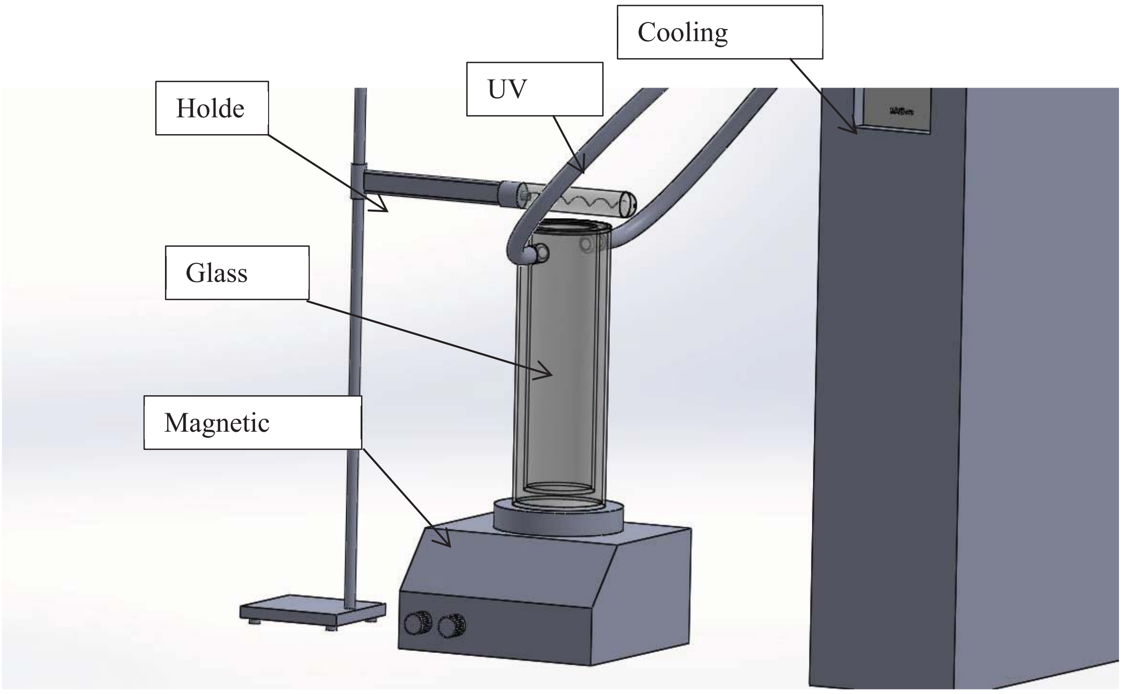
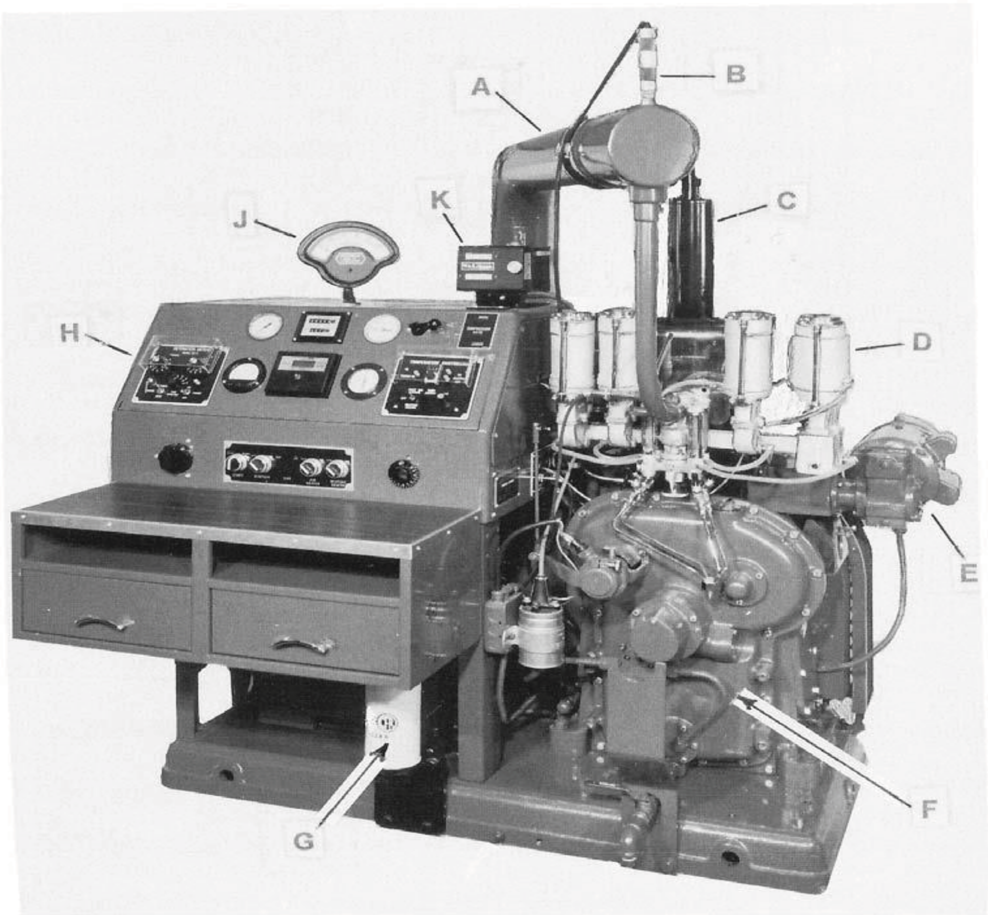


Fig. (4) Schematic Cell Unit.



A—Air humidifier tube
B—Intake air heater
C—Coolant condenser
D—Four bowl carburetor
E—C.R. change motor
F—CFR-48 crankcase
G—Oil Filter
H—Ignition Detonation meter
J—Knockmeter

Fig. (5) CFR Engine for RON & MON Testing [16].

Fig. (6) SHATOX Octane Meter

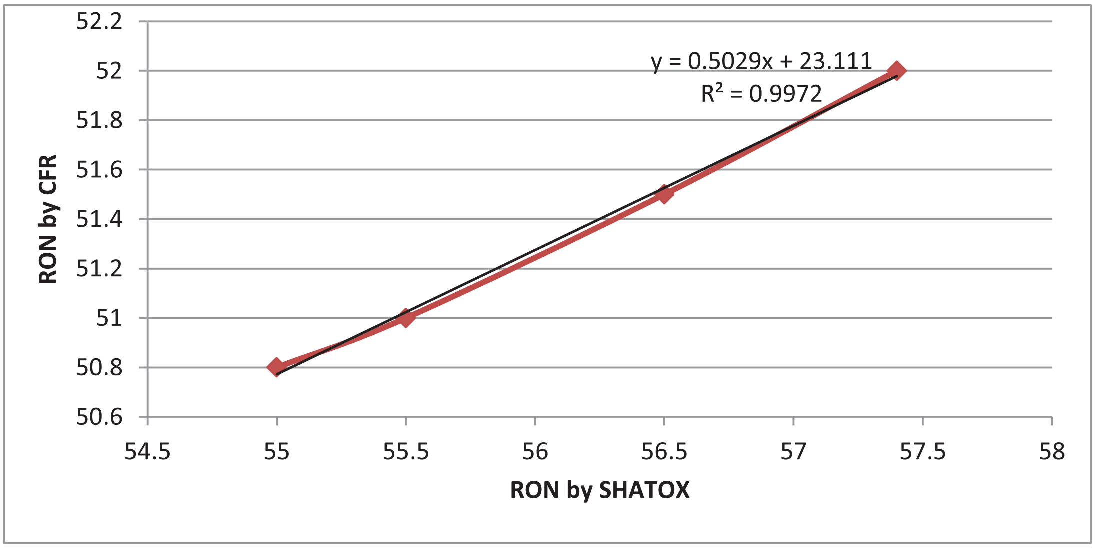


Fig. (7) Calibration of SHATOX Octane Meter.

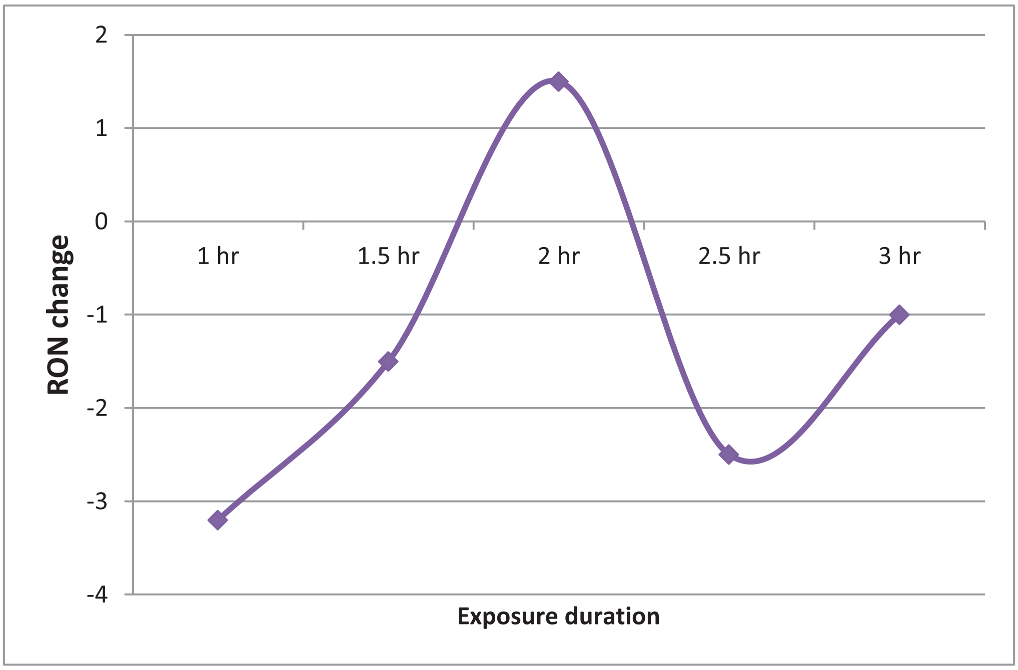


Fig. (8) Results Of Naphtha Exposed To UV Radiation.

Table (1) Results Of Naphtha Exposed To UV Radiation.

Conditions of test	Time of test (hr)	Pressure increase (bar)	Temperature (C°)		RON before test	RON after test	RON change
			Before test	After test			
Naphtha exposed to UV radiation only .	1	0.18	23	35	54.5	51.3	- 3.2
	1.5	0.21	24	35	54.5	53	- 1.5
	2	0.26	23	37	54.5	56	+ 1.5
	2.5	0.28	23	38	54.5	52	- 2.5
	3	0.31	22	38	54.5	53.5	- 1

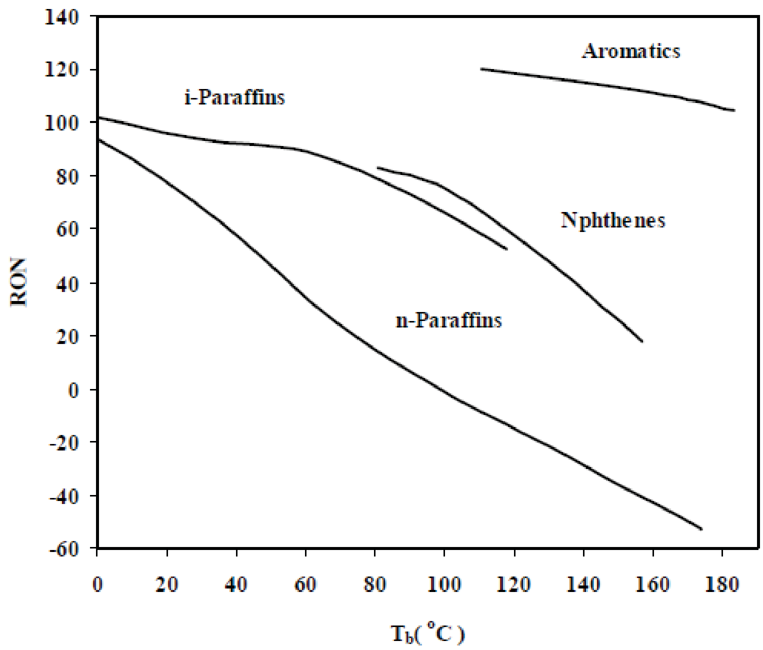


Fig. (9) Research Octane Number of Pure Hydrocarbons from Different Families [15].

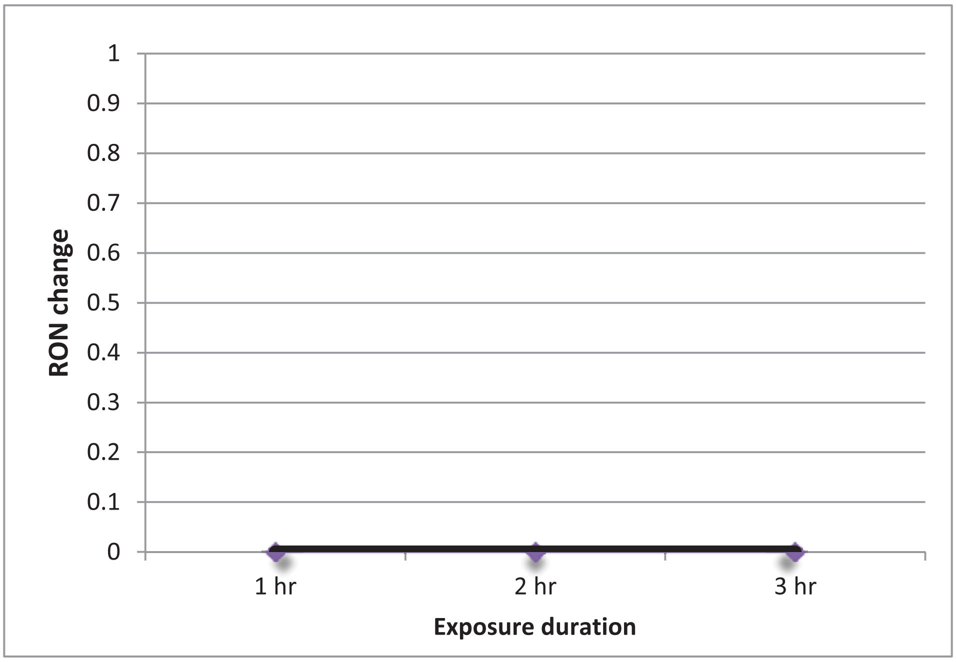


Fig. (10) Results Of Naphtha Exposed To UV Radiation With Cooling.

Table (2) Results Of Naphtha Exposed To UV Radiation With Cooling.

Conditions of test	Time of test (hr)	Pressure increase (bar)	Temperature (C^o)		RON before test	RON after test	RON change
			Before test	After test			
Naphtha exposed to UV radiation with cooling	1	0.16	24	25.5	54.5	54.5	No change
	2	0.17	24	25.5	54.5	54.5	No change
	3	0.19	24	25.5	54.5	54.5	No change

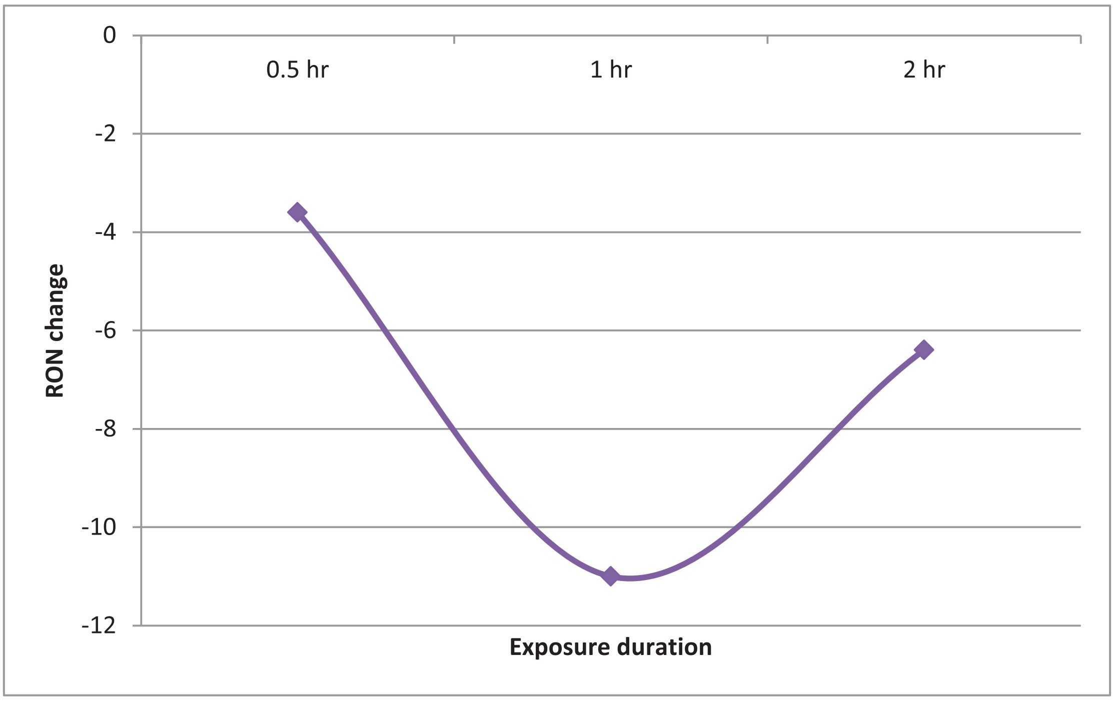


Fig. (11) Results of Naphtha Exposed To UV Radiation With Cooling & TiO_2 Catalyst.

Table (3) Results of naphtha exposed to UV radiation with cooling & TiO_2 catalyst.

Conditions of test	Time of test (hr)	Pressure increase (bar)	Temperature (C^o)		RON before test	RON after test	RON change
			Before test	After test			
Naphtha exposed to UV radiation with cooling & TiO_2 catalyst	0.5	0.11	25	25	54.5	50.9	- 3.6
	1	0.15	25	25	54.5	43.5	- 11
	2	0.17	25	25	54.5	48.1	- 6.4

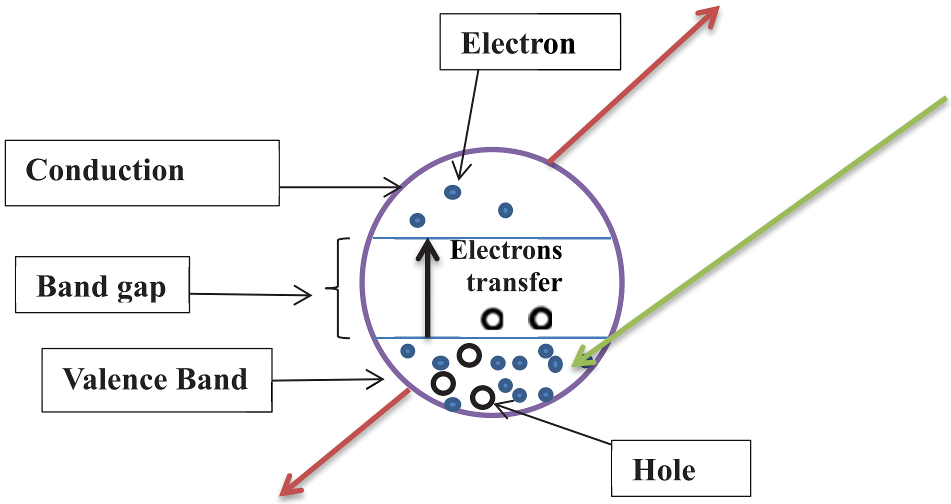


Fig. (12) Photo-Catalysis Process

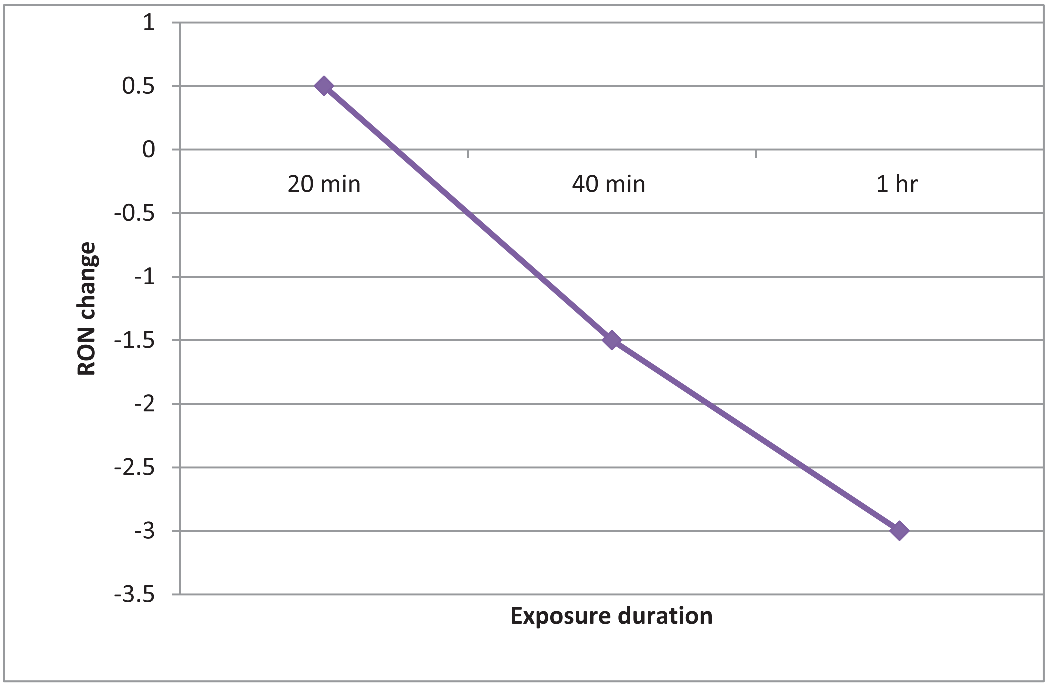


Fig. (13) Results of naphtha exposed to UV rays with cooling, TiO_2 catalyst & (2.1 ml/min) O_2 in the cell unit.

Table (4) Results of naphtha exposed to UV rays with cooling, TiO_2 catalyst & (2.1 ml/min) O_2 in the cell unit.

Conditions of test	Time of test	Pressure increase (bar)	Temperature (C°)		RON before test	RON after test	RON change
			Before test	After test			
Naphtha exposed to UV lamp of (75 W/m^2) with cooling, TiO_2 catalyst & (2.1 ml/min) O_2.	20 min	0	25	25	51.2	51.7	+ 0.5
	40 min	0	25	25	51.2	49.7	- 1.5
	1 hr	0	25	25	51.2	48.2	- 3

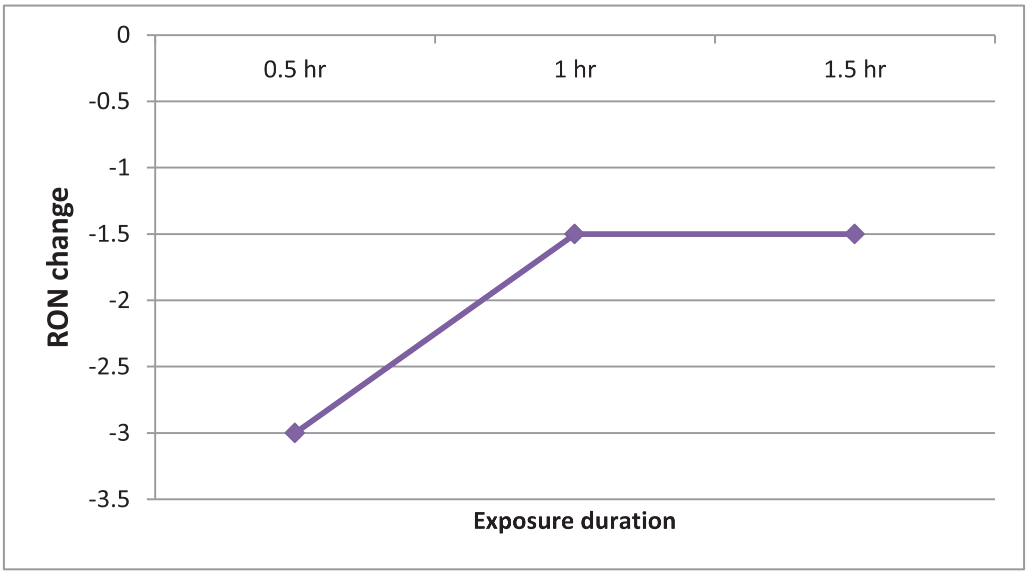


Fig. (14) Results of naphtha exposed to UV rays with cooling, ZnO catalyst & (2.1 ml/min) O_2 in the cell unit.

Table (5) Results of naphtha exposed to UV rays with cooling, ZnO catalyst & (2.1 ml/min) O_2 in the cell unit.

Conditions of test	**Time of test** (hr)	**Pressure increase** (bar)	**Temperature** (C^o)		**RON before test**	**RON after test**	**RON change**
			Before test	**After test**			
Naphtha exposed to UV lamp of (75 W/m^2) with cooling, ZnO catalyst & (2.1 ml/min) O_2.	0.5	0	25	25	51.2	48.2	- 3
	1	0	25	25	51.2	49.7	- 1.5
	1.5	0	25	25	51.2	49.7	- 1.5

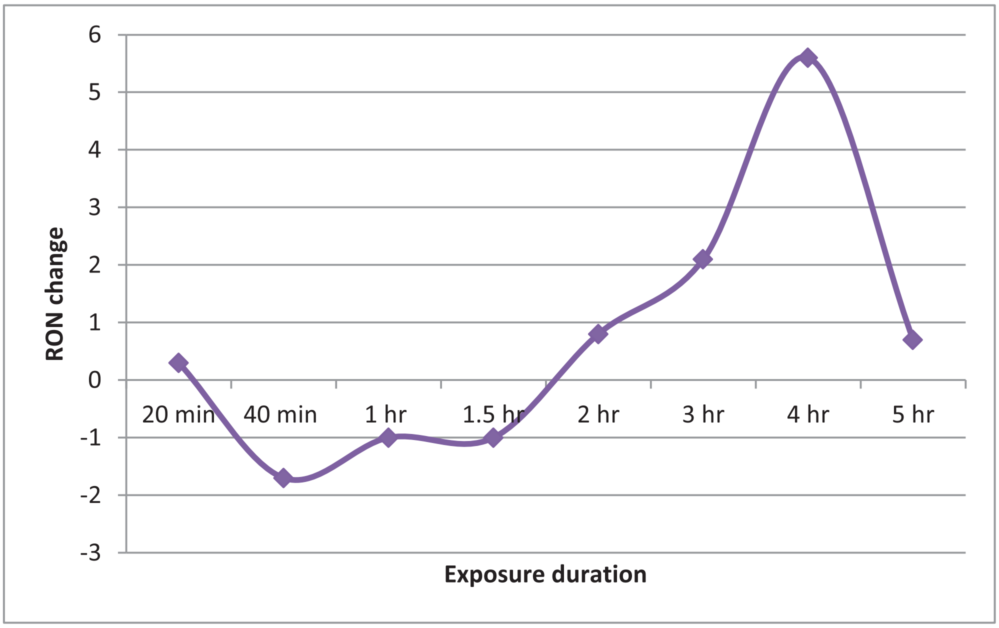


Fig. (15) Results of naphtha exposed to UV rays with ZnO catalyst & (2.1 ml/min) O_2 in the cell unit.

Table (6) Results of naphtha exposed to UV rays with ZnO catalyst & (2.1 ml/min) O_2 in the cell unit.

Conditions of test	Time of test	Pressure increase (bar)	Temperature (C°)		RON before test	RON after test	RON change
			Before test	After test			
Naphtha exposed to UV lamp of (75 W/m^2) with ZnO catalyst & (2.1 ml/min) O_2.	20 min	0	25.5	26	51.2	51.5	+ o.3
	40 min	0	25.5	26.6	51.2	49.5	- 1.7
	1 hr	0	25.5	27.1	51.2	50.2	- 1
	1.5 hr	0	25.5	27.7	51.2	50.2	- 1
	2 hr	0	25.5	28.1	51.2	52.0	+ 0.8
	3 hr	0	25.5	28.7	51.2	53.3	+ 2.1
	4 hr	0	25.5	29.4	51.2	56.8	+ 5.6
	5 hr	0	25.5	29.9	51.2	51.9	+ 0.7

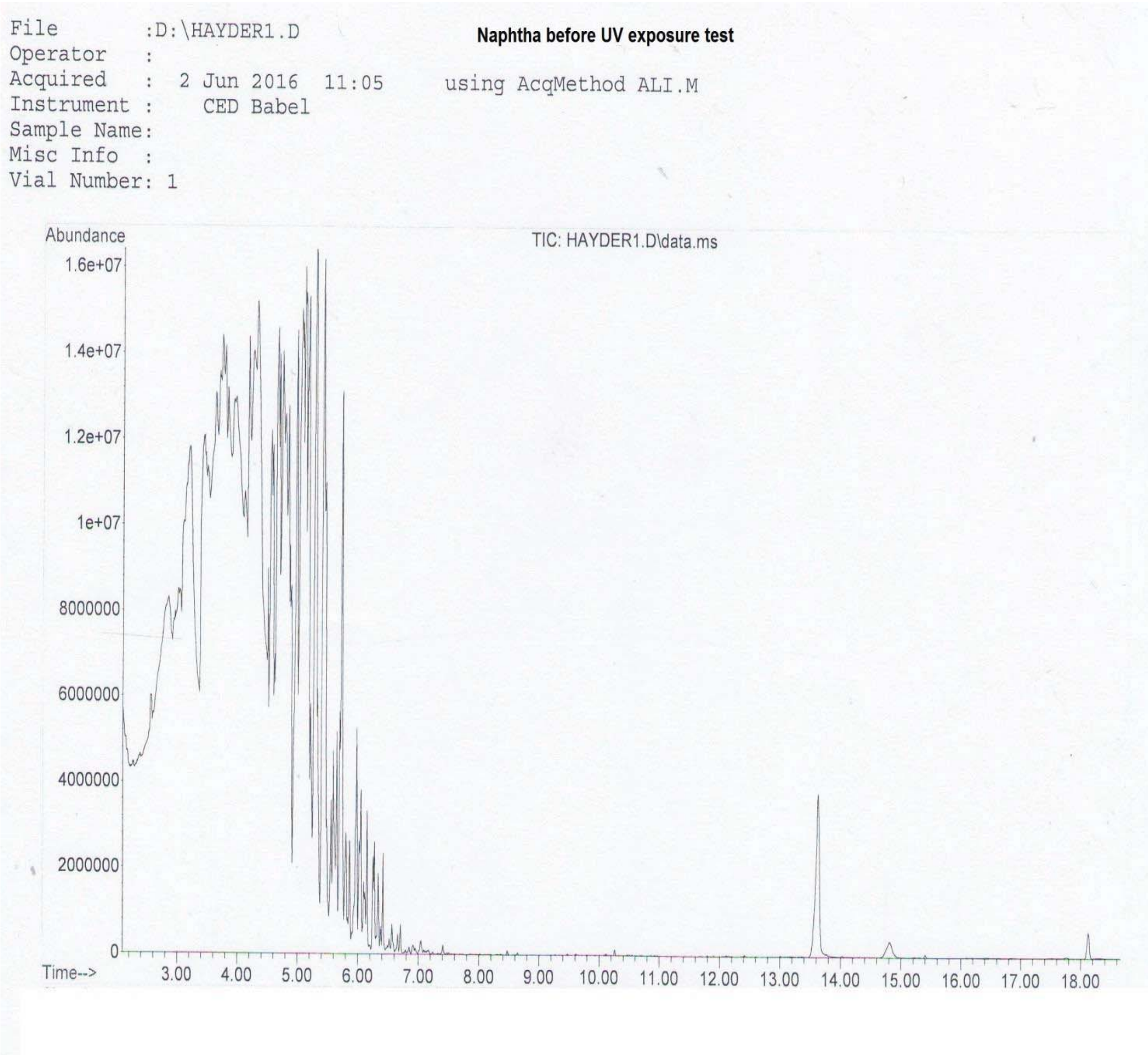


Fig. (16) GCMS Curve Of Sample Before Test

Table (7) Area percent report of sample before test

Area Percent Report

```
Data Path : D:\
Data File : HAYDER1.D
Acq On    :  2 Jun 2016   11:05
Operator  :
Sample    :
Misc      :
ALS Vial  : 1   Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method    : C:\MSDCHEM\1\METHODS\ALI.M
Title     :

Signal     : TIC: HAYDER1.D\data.ms
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	2.273	16	25	27	BV 2	167559	3058917	0.30%	0.021%
2	2.381	27	40	44	VV 2	466352	21089482	2.07%	0.142%
3	2.567	44	65	67	VV	2080204	107849575	10.57%	0.725%
4	2.597	67	69	70	VV	1693774	21299733	2.09%	0.143%
5	2.847	70	103	112	VV 5	4641700	645322485	63.26%	4.337%
6	3.014	112	125	127	VV 6	5029338	298274611	29.24%	2.004%
7	3.037	127	128	132	VV	5017827	105306809	10.32%	0.708%
8	3.101	132	137	138	VV 2	6689917	176880798	17.34%	1.189%
9	3.203	138	151	173	VV 7	8542180	938689343	92.01%	6.308%
10	3.443	173	183	188	VV 7	9068612	538974697	52.83%	3.622%
11	3.497	188	190	195	VV 2	8373462	251907110	24.69%	1.693%
12	3.633	195	209	213	VV 7	10266958	719026947	70.48%	4.832%
13	3.700	213	218	220	VV 4	10814365	327367087	32.09%	2.200%
14	3.744	220	224	227	VV 6	11703234	338326247	33.16%	2.274%
15	3.791	227	230	234	VV	11483634	302811241	29.68%	2.035%
16	3.835	234	236	243	VV 3	10584536	427592694	41.91%	2.873%
17	3.939	243	250	251	VV 4	10439125	349817917	34.29%	2.351%
18	3.967	251	254	270	VV 4	10534478	794866603	77.91%	5.342%
19	4.117	270	274	279	VV	8497178	301640582	29.57%	2.027%
20	4.182	279	283	287	VV	12172794	373198901	36.58%	2.508%
21	4.259	287	293	298	VV 3	11929701	545051449	53.43%	3.663%
22	4.323	298	302	324	VV 3	13157228	1020175901	100.00%	6.856%
23	4.506	324	327	329	VV 3	6872182	109401703	10.72%	0.735%
24	4.555	329	333	335	VV 2	10313950	253974226	24.90%	1.707%
25	4.583	335	337	340	VV 2	10116790	162692544	15.95%	1.093%
26	4.664	340	348	350	VV 3	12925661	403768650	39.58%	2.713%
27	4.692	350	352	354	VV	12191741	180788594	17.72%	1.215%
28	4.743	354	359	362	VV 2	12337728	386651515	37.90%	2.598%
29	4.790	362	365	369	VV 3	10995592	278506571	27.30%	1.872%
30	4.842	369	372	377	VV 2	11352838	329835217	32.33%	2.217%
31	4.887	377	378	382	VV 3	7113665	99888122	9.79%	0.671%
32	4.984	382	391	394	VV 2	13094312	394432905	38.66%	2.651%
33	5.062	394	402	406	VV 4	13712431	597221164	58.54%	4.013%
34	5.116	406	409	413	VV	14369611	363934107	35.67%	2.446%
35	5.182	413	418	421	VV 2	14833727	385959984	37.83%	2.594%
36	5.214	421	422	427	VV 4	4702052	88022380	8.63%	0.592%
37	5.298	427	433	444	VV 2	15436156	539014313	52.84%	3.622%
38	5.422	444	450	464	VV 3	15129706	560523108	54.94%	3.767%
39	5.556	464	468	471	VV 4	2657895	42178801	4.13%	0.283%
40	5.593	471	473	478	VV 2	3715934	72084412	7.07%	0.484%
41	5.652	478	481	484	VV	4337211	57234649	5.61%	0.385%
42	5.698	484	488	489	VV	4897930	60209428	5.90%	0.405%
43	5.731	489	492	497	VV	12939620	217857701	21.35%	1.464%
44	5.802	497	502	507	VV 3	2309786	48842661	4.79%	0.328%
45	5.864	507	510	513	VV	2236839	27867252	2.73%	0.187%

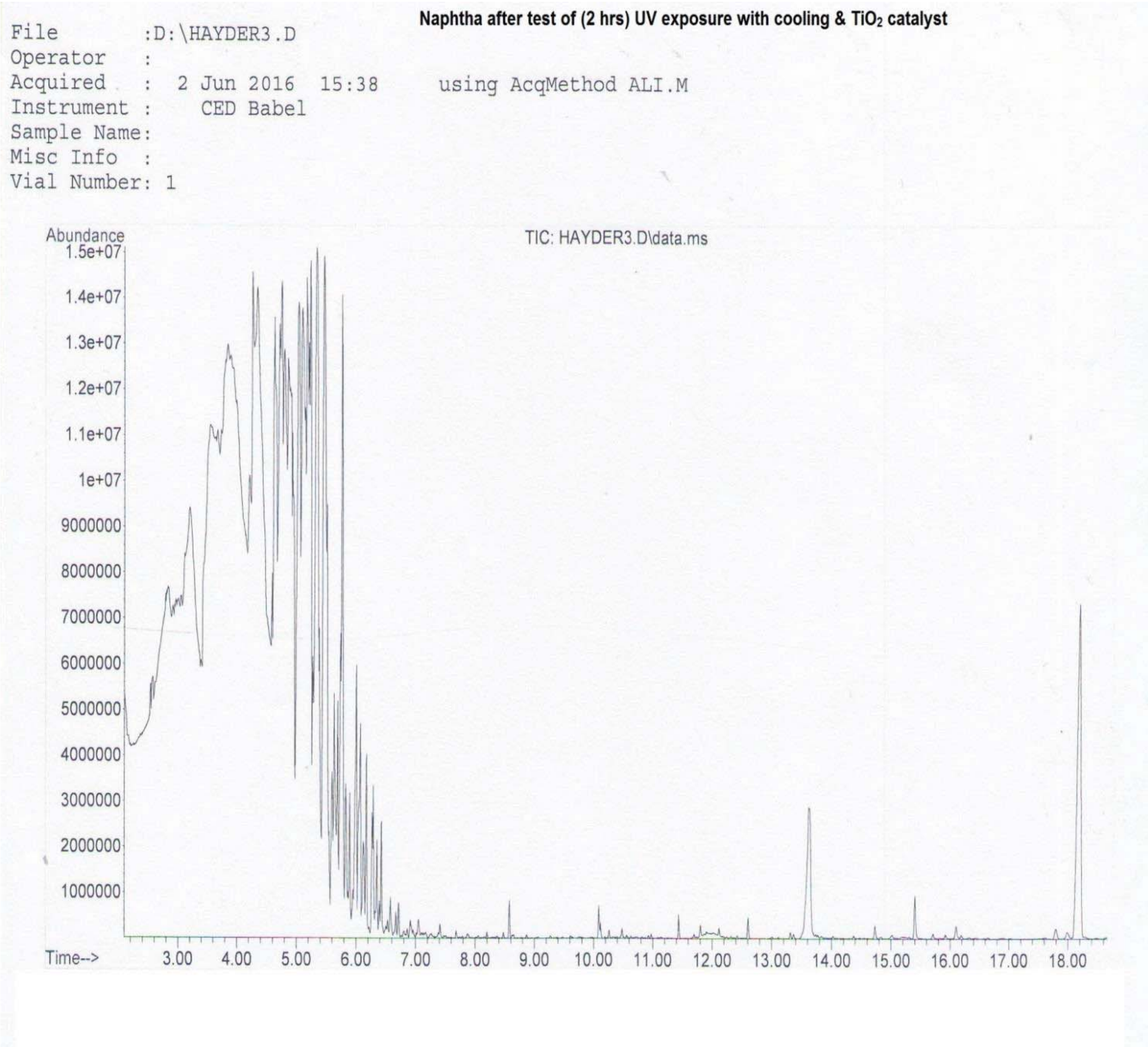


Fig. (17) GCMS Curve Of RON Decreasing Sample After Test

Table (8) Area Percent Report Of RON Decreasing Sample After Test

Area Percent Report

Data Path : D:\
Data File : HAYDER3.D
Acq On : 2 Jun 2016 15:38
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\ALI.M
Title :

Signal : TIC: HAYDER3.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	2.367	24	38	40	PV	354692	12550776	0.83%	0.086%
2	2.539	40	61	62	VV 3	1639626	73523730	4.87%	0.501%
3	2.573	62	66	68	VV	1841590	39274868	2.60%	0.268%
4	2.831	68	100	108	VV 6	4040493	525768404	34.83%	3.584%
5	2.914	108	112	114	VV 2	3713122	96523544	6.39%	0.658%
6	2.967	114	119	120	VV 3	3909971	106099726	7.03%	0.723%
7	3.007	120	124	128	VV	3967340	128572870	8.52%	0.876%
8	3.055	128	131	133	VV	4092040	98405738	6.52%	0.671%
9	3.115	133	139	140	VV 3	5074224	133645332	8.85%	0.911%
10	3.202	140	150	174	VV 3	6167588	728756436	48.28%	4.968%
11	3.392	174	176	179	VV 3	3030002	54934986	3.64%	0.374%
12	3.554	179	198	211	VV 8	8337502	1037412726	68.73%	7.072%
13	3.673	211	214	219	VV 3	8333211	267893729	17.75%	1.826%
14	3.737	219	223	224	VV 3	8411306	185544931	12.29%	1.265%
15	3.846	224	237	242	VV 4	10392947	762806469	50.54%	5.200%
16	3.894	242	244	282	VV 10	10194961	1509409776	100.00%	10.289%
17	4.212	282	287	290	VV	7908322	262367884	17.38%	1.789%
18	4.268	290	294	298	VV 2	12399211	336066966	22.26%	2.291%
19	4.347	298	305	335	VV 7	12147900	1372107136	90.90%	9.353%
20	4.636	335	344	350	VV 5	11610832	536558186	35.55%	3.658%
21	4.721	350	356	357	VV 4	11639673	308146090	20.42%	2.101%
22	4.756	357	360	363	VV	12681465	297096282	19.68%	2.025%
23	4.800	363	366	372	VV 3	11256917	424086193	28.10%	2.891%
24	4.866	372	375	383	VV 4	11172556	507066980	33.59%	3.457%
25	4.936	383	385	390	VV 4	9103854	204084272	13.52%	1.391%
26	5.042	390	399	403	VV 2	12534803	492282329	32.61%	3.356%
27	5.103	403	407	413	VV 5	12473137	472556625	31.31%	3.221%
28	5.151	413	414	416	VV 2	10389703	135744512	8.99%	0.925%
29	5.185	416	418	424	VV 3	12905391	422040291	27.96%	2.877%
30	5.243	424	426	429	VV	13688759	233515404	15.47%	1.592%
31	5.278	429	431	432	VV	4960995	63713964	4.22%	0.434%
32	5.345	432	440	450	VV 2	14017232	608634068	40.32%	4.149%
33	5.470	450	457	470	VV 2	13985827	606448461	40.18%	4.134%
34	5.600	470	474	477	VV 3	2774771	46060442	3.05%	0.314%
35	5.638	477	479	484	VV	4274917	86053525	5.70%	0.587%
36	5.694	484	487	489	VV	4595605	64957734	4.30%	0.443%
37	5.773	489	498	502	VV	13104244	315715137	20.92%	2.152%
38	5.831	502	505	511	VV 3	2770993	54251872	3.59%	0.370%
39	5.897	511	514	518	VV 2	2503125	32043734	2.12%	0.218%
40	5.951	518	522	523	VV 3	629548	7596624	0.50%	0.052%
41	6.005	523	529	532	VV 2	5315404	102318163	6.78%	0.697%
42	6.072	532	538	541	VV 4	4307598	97146962	6.44%	0.662%
43	6.125	541	545	549	VV 3	1938427	38204633	2.53%	0.260%
44	6.176	549	552	560	VV	3889544	48101335	3.19%	0.328%
45	6.271	560	565	571	PV	2547463	65393072	4.33%	0.446%

Table (9) The Changes In Percent Of The Effective Compounds According To The GCMS Tests.

No.	Effective compound	Retention time (min)	Percentage before test %	Percentage after test %
1	Isooctane	3.347	0	0.374
2	Benzene	4.724	2.598	2.101
3	Toluene	3.021	0.708	0.876
4	P-xylene	4.154	2.508	0

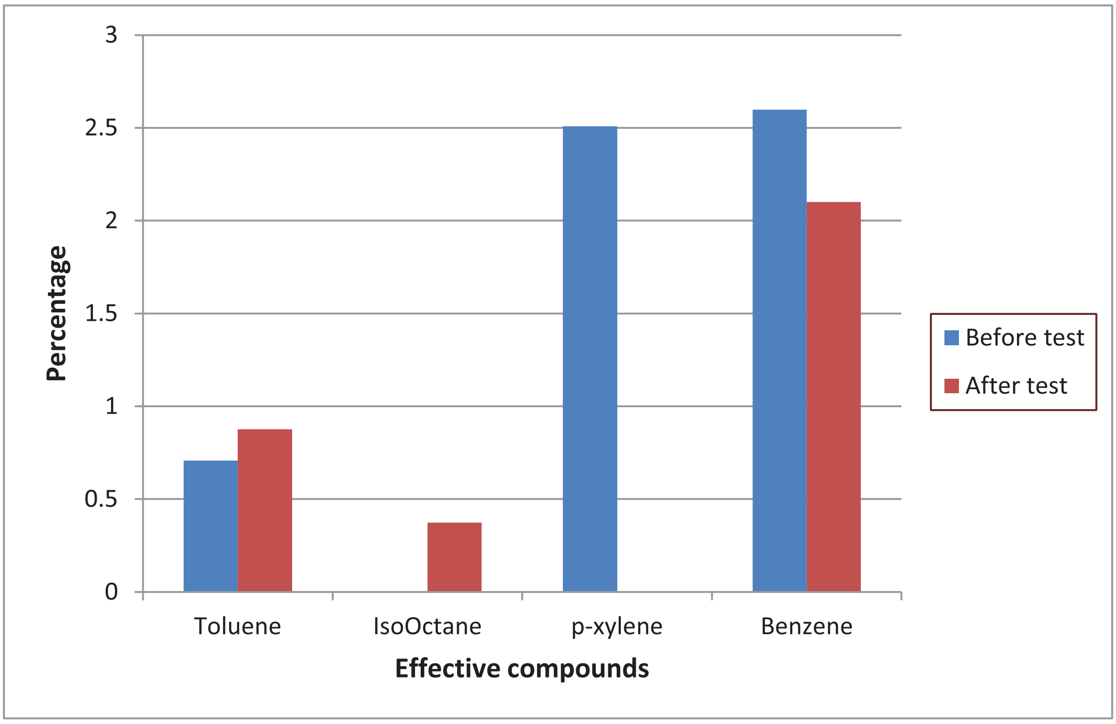


Fig. (18) The Changes In Percents Of The Effective Compounds According To The GCMS Tests.

Table (10) RON Of The Important Aromatic Compounds And Isooctane [17].

Compound	RON
Isooctane	100
Benzene	99
Toluene	124
P-xylene	146

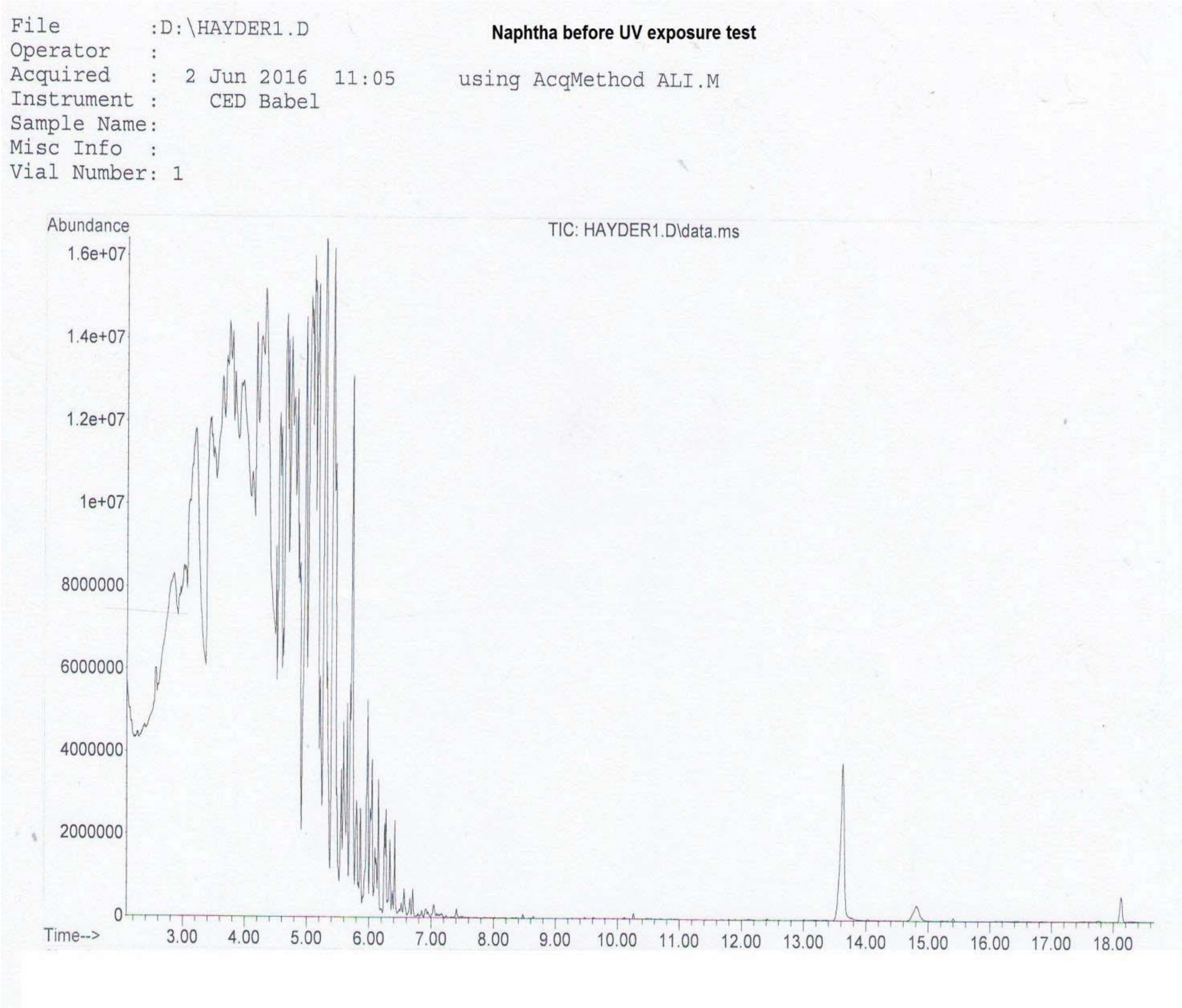


Fig. (19) GCMS curve of sample before test

Table (11) Area percent report of sample before test

Area Percent Report

Data Path : D:\
Data File : HAYDER1.D
Acq On : 2 Jun 2016 11:05
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\ALI.M
Title :

Signal : TIC: HAYDER1.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	2.273	16	25	27	BV 2	167559	3058917	0.30%	0.021%
2	2.381	27	40	44	VV 2	466352	21089482	2.07%	0.142%
3	2.567	44	65	67	VV	2080204	107849575	10.57%	0.725%
4	2.597	67	69	70	VV	1693774	21299733	2.09%	0.143%
5	2.847	70	103	112	VV 5	4641700	645322485	63.26%	4.337%
6	3.014	112	125	127	VV 6	5029338	298274611	29.24%	2.004%
7	3.037	127	128	132	VV	5017827	105306809	10.32%	0.708%
8	3.101	132	137	138	VV 2	6689917	176880798	17.34%	1.189%
9	3.203	138	151	173	VV 7	8542180	938689343	92.01%	6.308%
10	3.443	173	183	188	VV 7	9068612	538974697	52.83%	3.622%
11	3.497	188	190	195	VV 2	8373462	251907110	24.69%	1.693%
12	3.633	195	209	213	VV 7	10266958	719026947	70.48%	4.832%
13	3.700	213	218	220	VV 4	10814365	327367087	32.09%	2.200%
14	3.744	220	224	227	VV 6	11703234	338326247	33.16%	2.274%
15	3.791	227	230	234	VV	11483634	302811241	29.68%	2.035%
16	3.835	234	236	243	VV 3	10584536	427592694	41.91%	2.873%
17	3.939	243	250	251	VV 4	10439125	349817917	34.29%	2.351%
18	3.967	251	254	270	VV 4	10534478	794866603	77.91%	5.342%
19	4.117	270	274	279	VV	8497178	301640582	29.57%	2.027%
20	4.182	279	283	287	VV	12172794	373198901	36.58%	2.508%
21	4.259	287	293	298	VV 3	11929701	545051449	53.43%	3.663%
22	4.323	298	302	324	VV 3	13157228	1020175901	100.00%	6.856%
23	4.506	324	327	329	VV 3	6872182	109401703	10.72%	0.735%
24	4.555	329	333	335	VV 2	10313950	253974226	24.90%	1.707%
25	4.583	335	337	340	VV 2	10116790	162692544	15.95%	1.093%
26	4.664	340	348	350	VV 3	12925661	403768650	39.58%	2.713%
27	4.692	350	352	354	VV	12191741	180788594	17.72%	1.215%
28	4.743	354	359	362	VV 2	12337728	386651515	37.90%	2.598%
29	4.790	362	365	369	VV 3	10995592	278506571	27.30%	1.872%
30	4.842	369	372	377	VV 2	11352838	329835217	32.33%	2.217%
31	4.887	377	378	382	VV 3	7113665	99888122	9.79%	0.671%
32	4.984	382	391	394	VV 2	13094312	394432905	38.66%	2.651%
33	5.062	394	402	406	VV 4	13712431	597221164	58.54%	4.013%
34	5.116	406	409	413	VV	14369611	363934107	35.67%	2.446%
35	5.182	413	418	421	VV 2	14833727	385959984	37.83%	2.594%
36	5.214	421	422	427	VV 4	4702052	88022380	8.63%	0.592%
37	5.298	427	433	444	VV 2	15436156	539014313	52.84%	3.622%
38	5.422	444	450	464	VV 3	15129706	560523108	54.94%	3.767%
39	5.556	464	468	471	VV 4	2657895	42178801	4.13%	0.283%
40	5.593	471	473	478	VV 2	3715934	72084412	7.07%	0.484%
41	5.652	478	481	484	VV	4337211	57234649	5.61%	0.385%
42	5.698	484	488	489	VV	4897930	60209428	5.90%	0.405%
43	5.731	489	492	497	VV	12939620	217857701	21.35%	1.464%
44	5.802	497	502	507	VV 3	2309786	48842661	4.79%	0.328%
45	5.864	507	510	513	VV	2236839	27867252	2.73%	0.187%

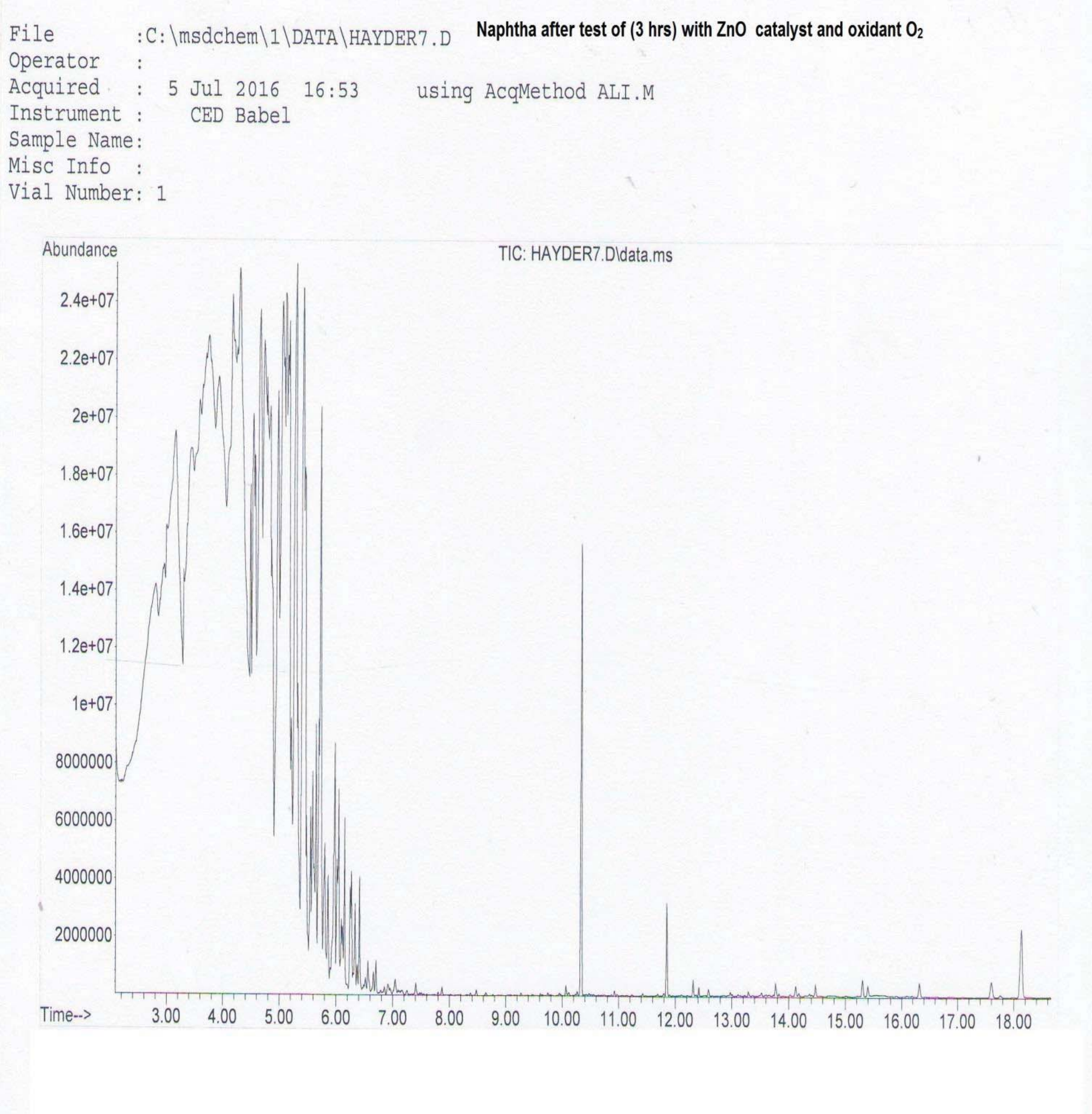


Fig. (20) GCMS curve of RON increasing sample after test

Table (12) Area percent report of RON increasing sample after test

Area Percent Report

Data Path : C:\MSDCHEM\1\DATA\
Data File : HAYDER7.D
Acq On : 5 Jul 2016 16:53
Operator :
Sample :
Misc :
ALS Vial : 1 Sample Multiplier: 1

Integration Parameters: events.e
Integrator: ChemStation

Method : C:\MSDCHEM\1\METHODS\ALI.M
Title :

Signal : TIC: HAYDER7.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	2.298	18	28	30	PV	691226	19608238	1.05%	0.077%
2	2.798	30	96	102	VV 5	7924225	1358718384	72.44%	5.331%
3	2.949	102	116	119	VV 3	8887170	596412964	31.80%	2.340%
4	2.994	119	122	124	VV	10341258	240299984	12.81%	0.943%
5	3.147	124	143	161	VV 6	13900809	1756566173	93.65%	6.891%
6	3.300	161	164	165	VV	9286702	156183286	8.33%	0.613%
7	3.431	165	181	188	VV 6	13823212	1229499779	65.55%	4.824%
8	3.580	188	201	205	VV 5	15749900	1078014847	57.47%	4.229%
9	3.633	205	209	210	VV 2	16361194	337268044	17.98%	1.323%
10	3.692	210	217	218	VV 4	17545369	628034848	33.48%	2.464%
11	3.741	218	223	238	VV 6	18284583	1563551365	83.36%	6.134%
12	3.918	238	247	266	VV 6	17185905	1875717621	100.00%	7.359%
13	4.159	266	280	288	VV 4	20322999	1696890709	90.47%	6.657%
14	4.241	288	291	292	VV	18759692	328066552	17.49%	1.287%
15	4.287	292	297	320	VV 4	21654108	1846945748	98.47%	7.246%
16	4.481	320	323	326	VV 3	14278014	250757439	13.37%	0.984%
17	4.530	326	330	332	VV 2	17008928	419584365	22.37%	1.646%
18	4.561	332	334	338	VV 2	15615474	325534451	17.36%	1.277%
19	4.651	338	346	351	VV 3	20802944	965557759	51.48%	3.788%
20	4.722	351	356	366	VV 7	19888410	1202449710	64.11%	4.717%
21	4.829	366	370	380	VV 3	17718664	766815544	40.88%	3.008%
22	4.965	380	389	393	VV	18537707	650250632	34.67%	2.551%
23	5.044	393	399	405	VV 4	21811453	989179454	52.74%	3.881%
24	5.106	405	408	411	VV	22297105	555324690	29.61%	2.179%
25	5.169	411	416	420	VV 2	21335717	663223574	35.36%	2.602%
26	5.206	420	421	425	VV 3	7635826	135148938	7.21%	0.530%
27	5.288	425	432	443	VV 2	23518219	897394064	47.84%	3.521%
28	5.413	443	449	452	VV	23082912	631390612	33.66%	2.477%
29	5.451	452	454	463	VV 3	16789673	320486878	17.09%	1.257%
30	5.550	463	467	470	VV 2	4936055	74590609	3.98%	0.293%
31	5.586	470	472	478	VV 2	6188018	129421610	6.90%	0.508%
32	5.647	478	481	483	VV	7868783	105517150	5.63%	0.414%
33	5.724	483	491	497	VV 2	19561047	450004203	23.99%	1.765%
34	5.799	497	501	506	VV 3	4337078	87703745	4.68%	0.344%
35	5.858	506	509	513	VV	3341525	43561696	2.32%	0.171%
36	5.977	513	525	528	PV 2	7820698	159616495	8.51%	0.626%
37	6.018	528	531	532	VV 3	4150962	57597625	3.07%	0.226%
38	6.046	532	535	538	VV	6214133	85808440	4.57%	0.337%
39	6.096	538	541	546	VV 3	2196175	54089567	2.88%	0.212%
40	6.149	546	548	553	VV	5197929	66524068	3.55%	0.261%
41	6.270	558	565	568	PV	3979463	90007675	4.80%	0.353%
42	6.334	568	573	576	VV	2699019	42668432	2.27%	0.167%
43	6.374	576	579	581	VV	838973	10460585	0.56%	0.041%
44	6.413	581	584	590	VV	3771562	48556570	2.59%	0.190%
45	6.518	590	598	601	VV 3	448014	10570390	0.56%	0.041%

Table (13) The changes in percents of the effective compounds according to the GCMS tests.

No.	Effective compound	Retention time (min)	Percentage before test %	Percentage after test %
1	IsoOctane	3.347	0	0.613
2	Benzene	4.724	2.598	4.717
3	Toluene	3.021	0.708	0
4	P-xylene	4.154	2.508	6.657

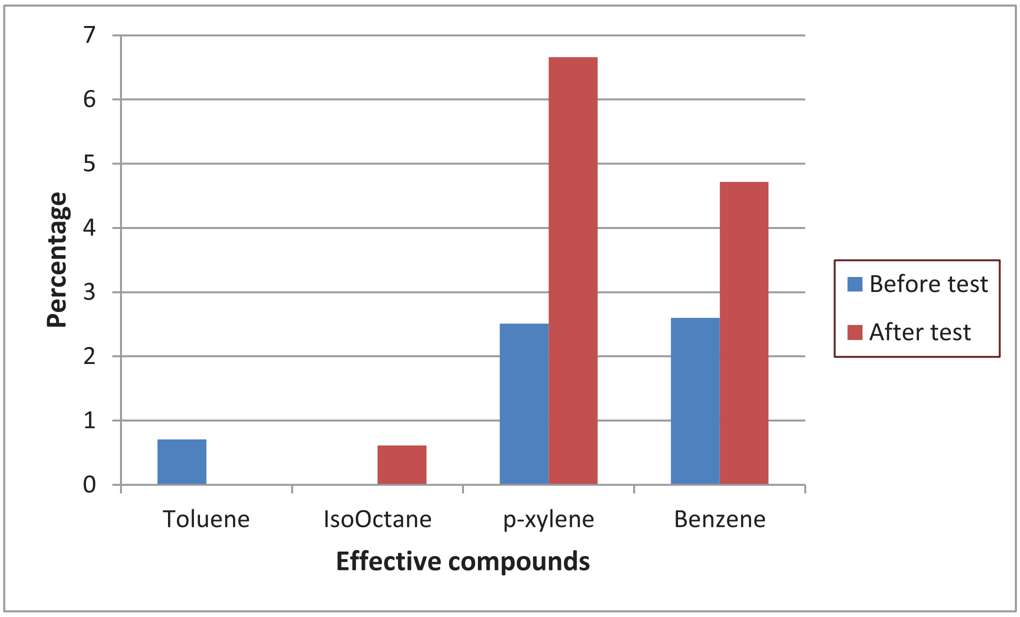


Fig. (21) The changes in percents of the effective compounds according to the GCMS tests.

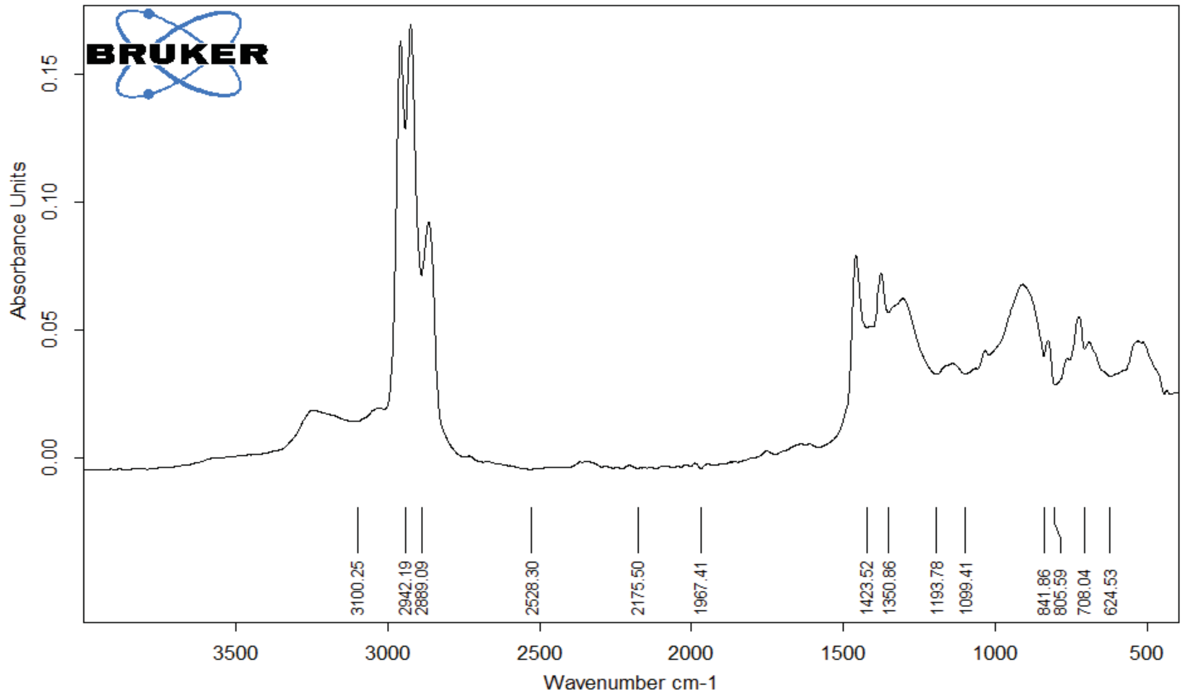


Fig. (22) FTIR Curve of RON increasing sample before test

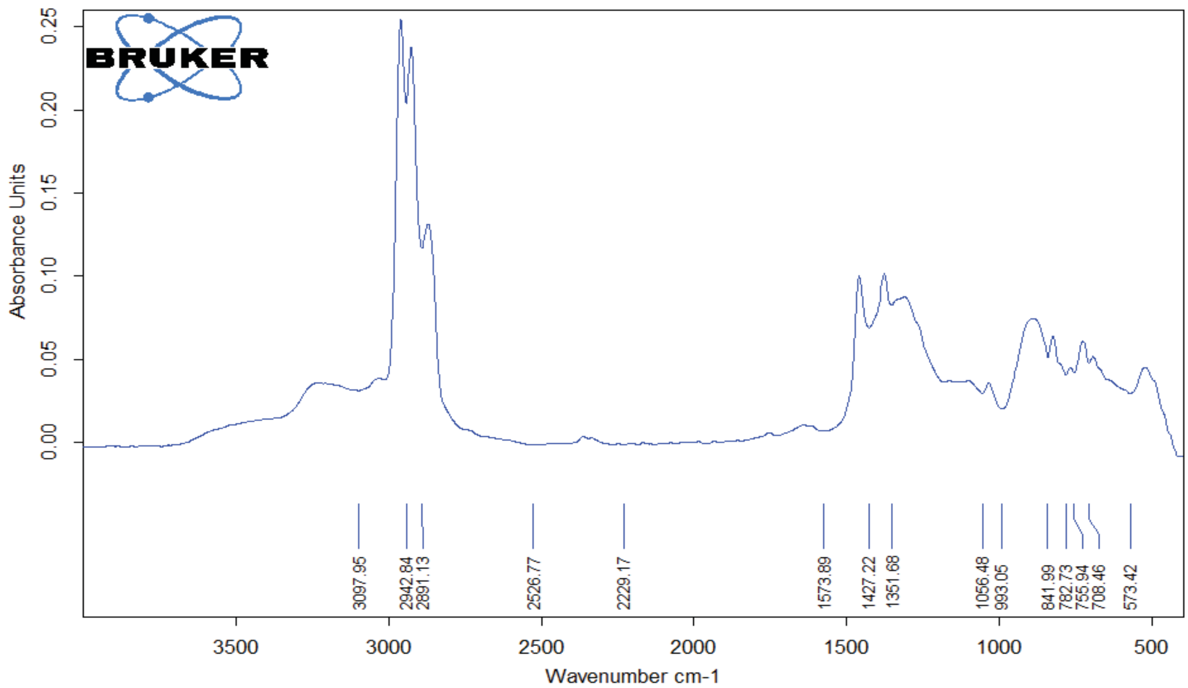


Fig. (23) FTIR Curve Of RON Decreasing Sample After Test

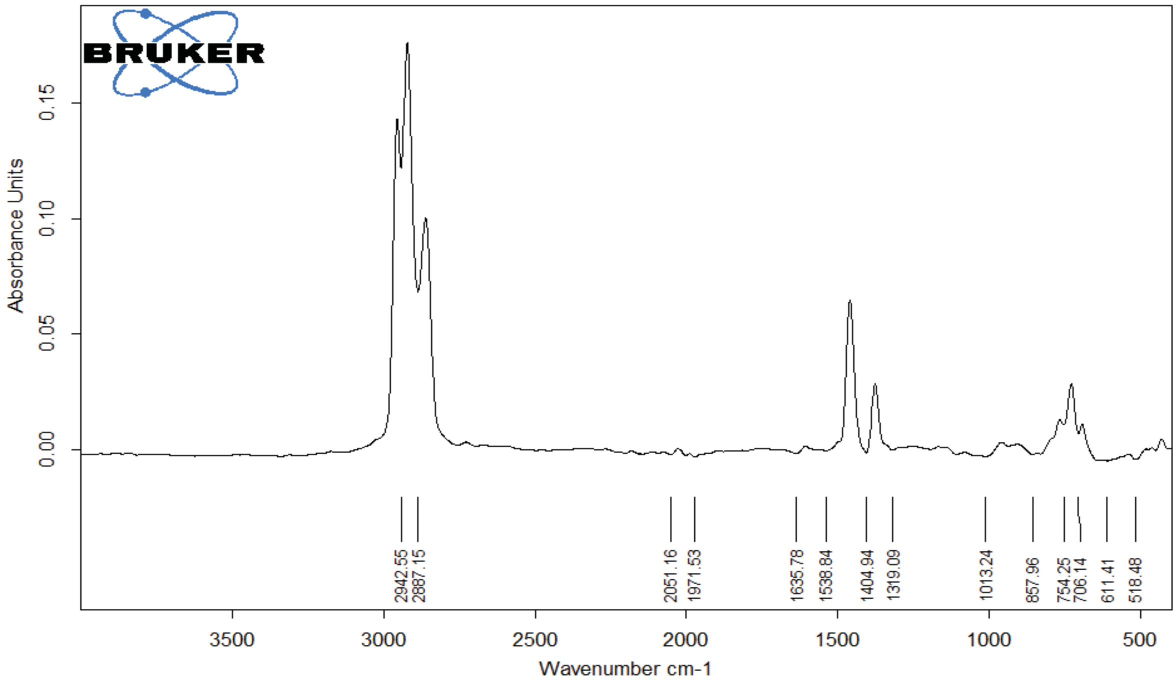


Fig. (24) FTIR curve of RON increasing sample after test