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Research Article

Improving Naphtha Octane Number by using UV Rays under Atmospheric Pressure

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Abstract

The aim of this work is to study the feasibility of using UV rays to improve naphtha octane number. Naphtha fuel is exposed to the UV rays under atmospheric pressure with various conditions; UV exposure with cooling and catalyst, UV exposure with cooling, catalyst and oxidant O_2 and UV exposure with catalyst and oxidant O_2. Samples are prepared and exposed to UV rays in a cell unit under atmosphere pressure. The results show that naphtha octane number is improved when exposed to UV rays when ZnO catalyst and oxidant are used. Other exposing conditions either produces no change in octane number or reduces the octane number. The maximum rise in the octane number is 5.6 unit obtained under exposure duration of 4 hr. with O_2 feeding of 2.1 ml/min. Gas Chromatography Mass Spectrometry (GCMS) tests are conducted for samples before and after UV exposure to study the change in molecular structure of the sample (i.e. compounds that affect the octane number such as : Isooctane, Benzene, Toluene, P-xylene, O-xylene and M-xylene). Finally, Fourier Transform Infrared Spectroscopy (FTIR) tests are also conducted for the sample before and after exposure to know the eliminated and created bonds or functional groups.

Keywords: *Octane number, UV rays, Naphtha, fuel additives, photo-catalysis process.*

Introduction

Naphtha is a liquid fraction "cut" of crude oil which consists of a complex mixture of more than a hundred hydrocarbon compounds and has a boiling temperature range of (30°C - 200°C). It comprises (15 – 30%) by weight of the crude oil. These compounds contain (C_4 – C_{15}) carbon atoms. It represents the raw material necessary in petrochemical industries since it is used for producing a wide range of chemical products such as benzene, toluene, ethylene, propylene, xylenes, etc.(Reboucas, M. V. *et al*, (2003)). Specific gravity of naphtha at 15 °C is 0.694. It is volatile and flammable similar to gasoline in boiling point and carbon number range therefore it becomes a precursor to gasoline.

Many efforts are exerted to improve the octane number of fuel. **Thomas Midgley (1921),** (Groysman, A. (2014)) discovered that injection of small amounts of tetraethyl lead [TEL—(C2H5)4Pb] (150 mg Pb/l gasoline) into gasoline caused knocking elimination and higher octane gasoline. However harmful properties of TEL were detected since the nineteenth century and recognized as dangerous substances which could cause lead poisoning. TEL using had engine problems due to formation of harmful deposits in engines. These deposits were lead oxides produced from burning of gasoline with added TEL inside the combustion chamber and settled on the valves and spark plugs causing the engine damage. **Graham Edgar (1926),** (Groysman, A. (2014)) observed that after addition different amounts of normal heptane and iso-octane (2,2,4-trimethylpentane) to gasoline, the knock was eliminated when iso-octane addition was increased. This was the origin of searching for different compounds (anti-knock agents) by chemists and engineers to increase octane number of gasoline.

Adel S. Hamadi (2010), (Sharif, A. (2010)) tested multi blends of gasoline which reformulated from (30% light naphtha, 45% Reformate and 25% power formate) with different additives to improve octane number. The results exhibited that the mixture of additives which consists of (20% aniline, 54% iso-propanol, 10% oxinol and 16% xylene) in blend of (10.7%vol additives + 89.3%vol gasoline) lead to better increasing in RON of gasoline blend pool which reached to 11.5 or RON is raised from 84.5 to 96.

Mutaz M. *et al*. (2013), (Mutaz M. Elshiekh and Nazar A. Elnasri, (2013)) used synthetic zeolite to enhance the octane number of the gasoline portion of the Sudanese petroleum. They prepared four synthetic zeolites: Zeolite /Li, Zeolite /Na, Zeolite /Cu and Zeolite /Bi (in grams) and mixed them separately with the same amounts (in liter) of the gasoline portion which

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is called (blank). It was found that the best enhancing of the RON and the MON was by using Zeolite/Li. **Ali H. A. Rashed *et al*. (2013),** (Ali H. Ali Rashed, et. al. (2013)) improved the octane number for Al-Dura product pool which was a blend of (70% Reformate + 30% Light Naphtha) by using UV rays in photo-degradation process in the presence of ZnO catalyst, with different exposure times. They raised the RON by 5 units with 8 hr exposure. **Nibal H. AL-Mashhadani *et al*. (2014),** (Nibal H. AL-Mashhadani, et. al. (2014)) used organic compounds to improve the gasoline octane number instead of the lead additives. It was found that a significant improvement of RON was obtained due to these alternative additives and an important increasing of about 9.3 units in RON was obtained by adding a blend of 1.5 % vol alcohols and 1.5 % vol aniline to gasoline.

In Iraq refineries, there is an excess quantities of naphtha. These quantities can be treated based on the idea of C-C bonds cracking and re-structuring to benefit from them as maximum as possible. The bond energy must be known to accomplish the required cracking. Since the energy of C-C bonds varies from (346 to 350 kJ/mol) an average value is used, 347 kJ/mol (Marten J. ten Hoor (2009)).

Experimental Apparatus and Measurements

The experimental work requires the manufacturing of glass UV cell unit. This unit operates under atmospheric pressure. It consists of the following parts and auxiliaries:

a) Two concentric glass vessels formed as a cell. The annular space is used for cooling water. The inner vessel has a capacity of (500 ml) and the outer vessel has a capacity of (1000 ml), as shown in fig. 1. The fuel sample is put in the inner vessel.
b) Mixing capsule is immersed inside the cell for sample rotation.
c) Magnetic stirrer used to rotate the mixing capsule inside the test sample under effect of magnetic field.
d) Water cooling used to cool the cell during the test and to keep the sample temperature at required value.
e) UV lamp with 75 W/m^2 is fixed by standing over the cell at a distance of 4 cm. The lamp is partially enveloped to concentrate the rays on the sample.
f) Air feeder with variable flow rates (5, 10 and 15 ml/min).
g) Filtering sheets, graduated cylinder, funnel, electronic balance, burette, thermometer and sample bottle are used.

Sample Preparation and Test

Samples of 500 ml of naphtha are prepared. The sample is mixed with 0.75 g (Al-gubury, H. Y., & Mohammed, Q. Y. (2016)) of catalyst either TiO_2 or ZnO for 20 min before UV exposure. Octane number measurement, GCMS and FTIR analysis are performed for each sample before exposure. The octane number is measured either in CFR engine or SHATOX Octane meter. The temperature of the sample is recorded 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 performed after exposure to know the occurred changes.

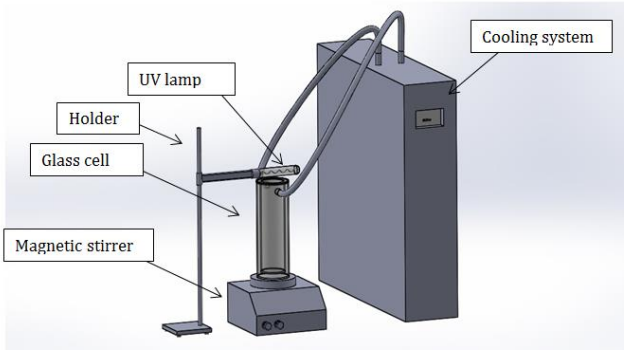
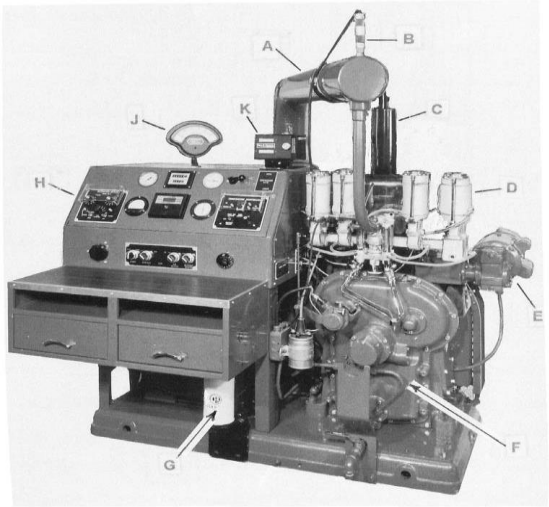


Fig.1 Schematic Cell unit

CFR engine and SHATOX Octane meter

The Cooperative Fuel Research (CFR) is a four-stroke, single-cylinder spark-ignition engine with a variable compression ratio. It is used to measure the fuel octane number (Genchi, G., & Pipitone, E. (2014)), see fig. 2. This engine is available in the laboratories of Al-Dura refinery.



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, K—C.R. digital counter

Fig. 2 CFR engine (An American National Standard, Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel, D 2699 – 04a)

The SHATOX Octane Meter operation depends on comparative measurement of dielectric characteristics of the test sample to the value of standard gasoline

stored in the internal memory of its microprocessor. The detector of octane number has a volume of 75 ml, see fig. 3.

Fig. 3 SHATOX Octane meter

Gas Chromatography Mass Spectrometry (GCMS) Analysis

The system consists of two parts

Gas Chromatography (GC) separates blend to its components by using capillary column under temperature regulator based on the difference between their boiling points.
Mass Spectrometry (MS) identifies and quantifies the mixture components according to the mass spectra (Munther A. Mussa , 2016).

The change in the mainly effective compounds (i.e. compounds that effects on the octane number) is determined by comparison between the GCMS result before UV exposure and after it. Then, 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. The principle of the FTIR technique is based on the idea of sample molecules excitation to a higher energy states due to absorption of IR radiation which occurs when photons transfer to these molecules (Parikh, S. J., & Chorover, J., 2005).

Results and Discussion

Initially, calibration of SHATOX Octane Meter is done against the CFR engine using four measurements and the following calibration equation is obtained. The calibration is shown in fig. 4.

$$y = 0.5029\,x + 23.111 \quad (1)$$

where:

(x) represents RON value measured by SHATOX Octane meter.

(y) represents the converted RON value to CFR measuring.

For ease of presentation and discussion the results are divided into three groups according to the tests conditions.

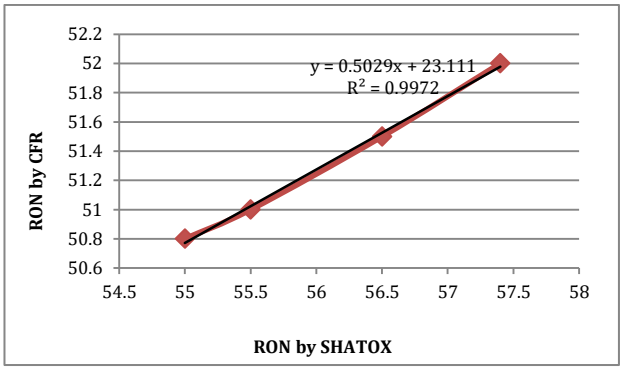


Fig. 4 Calibration of SHATOX Octane meter

1- Naphtha Exposed to UV Rays with Cooling and Catalyst

The result is shown in table 1 and fig. 5. It indicates that the RON decreases during the first half hour of exposure by 3.6 unit and more decrease in the RON occurs during the second half hour exposure until reach to 11 unit. During the second hour of exposure the RON starts to increase again. When the naphtha sample is exposed to UV rays in the presence of catalyst, the photo-catalysis process will occur. 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 (Carré, G. *et al* (2014)). Electron hole pairs are unstable and if there is no capturer for the active electrons (i.e. electrons in conduction band), they will return quickly to their valence bands and react with the holes (recombination process). The drop in the RON value in above results may be attributed to recombination effect in the absence of capturer which is only a Photolysis effect will remain (Photolysis or Photo dissociation process is a chemical reaction in which one or several bonds are broken due to the absorption of UV rays) (Mandal, A., 2015).

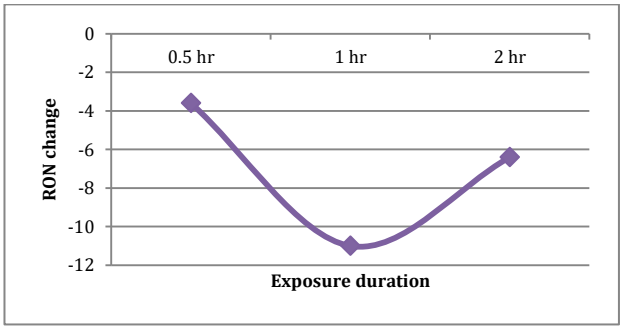


Fig.5 Results of naphtha exposed to UV rays with cooling & TiO2 catalyst

Table 1 Results of naphtha exposed to UV rays with cooling & TiO_2 catalyst

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 lamp of (75 W/m²) with cooling & TiO_2 catalyst	0.5	0	25	25	54.5	50.9	- 3.6
	1	0	25	25	54.5	43.5	- 11
	2	0	25	25	54.5	48.1	- 6.4

2- Naphtha Exposed to UV Rays with Cooling, Catalyst and Oxidant O_2

Table 2 Results of naphtha exposed to UV rays with cooling, TiO_2 catalyst & (2.1 ml/min) O_2

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/m²) 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

Oxygen is known to act as a capturer of electrons that exist in 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 (with 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 2 and fig. 6 while in the second test ZnO is used as catalyst and the results are shown in table 3 and fig. 7.

The results of TiO_2 test show a decrease in the RON, while the results of ZnO test give 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.

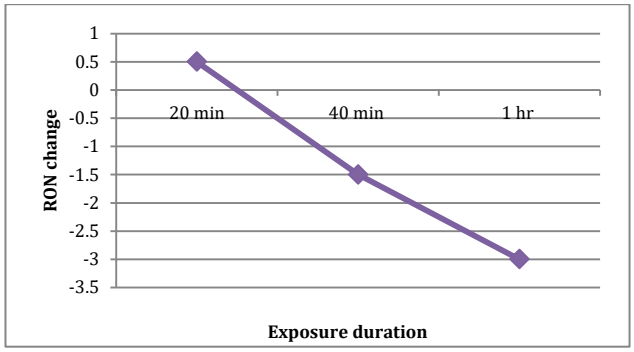


Fig.6 Results of naphtha exposed to UV rays with cooling, TiO_2 catalyst & (2.1 ml/min) O_2

Table 3 Results of naphtha exposed to UV rays with cooling, ZnO catalyst & (2.1 ml/min) O_2

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 lamp of (75 W/m²) 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

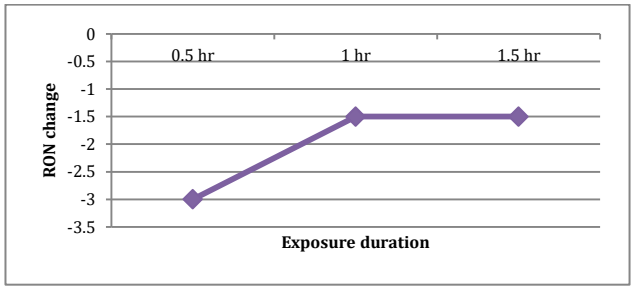


Fig. 7 Results of naphtha exposed to UV rays with cooling, ZnO catalyst & (2.1 ml/min) O_2

3-Naphtha Exposed to UV Rays with Catalyst and Oxidant O_2

To investigate the effect of cooling on the photo-catalysis process the same test is repeated without cooling in the presence of oxidant. Now, three air flow rates are used, 5 ml/min, 10 ml/min and 15 ml/min,

(oxygen flow rates of 1.05 ml/min, 2.1 ml/min and 3.15 ml/min).

The results with 1.05 ml/min are shown in table 4 fig.8.

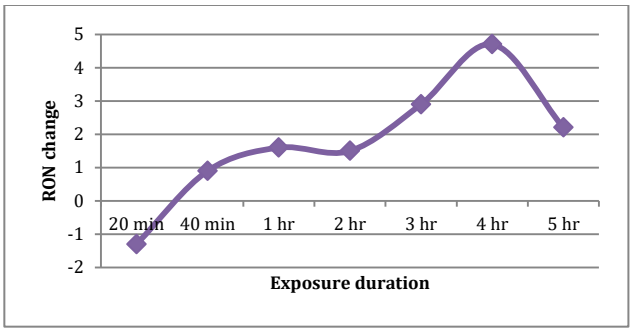


Fig.8 Results of naphtha exposed to UV rays with ZnO catalyst & (1.05 ml/min) O_2

Table 4 Results of naphtha exposed to UV rays with ZnO catalyst & (1.05 ml/min) O_2

Conditions of test	Exposure duration	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/m²) with ZnO catalyst & (1.05 ml/min) O_2 .	20 min	0	25.5	26.5	51.2	49.9	- 1.3
	40 min	0	25.5	26.8	51.2	52.1	+ 0.9
	1 hr	0	25.5	27	51.2	52.8	+ 1.6
	2 hr	0	25.5	**27.7**	51.2	52.7	+ 1.5
	3 hr	0	25.5	**28.3**	51.2	54.1	+2.9
	4 hr	0	25.5	**28.9**	51.2	55.9	+ 4.7
	5 hr	0	25.5	**29.4**	51.2	53.4	+ 2.2

The results indicate that if naphtha is exposed to UV rays without cooling in existence of ZnO catalyst and oxidant, 1.05 ml/min O_2, under atmospheric pressure there is an increase in the RON as the exposure time increase from 20 min – 4 hr. The maximum increase of 4.7 units is obtained at 4 hr exposure time. Then the RON change decreases to 2.2 units at 5 hrs exposure time. 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.

The same test is repeated with different oxygen flow rate, 2.1 ml/min and 3.15 ml/min to investigate the effect of oxidant flow rate on RON. The results of 2.1 ml/min oxygen flow rate are shown in table 5 and fig. 9. This flow rate is exhibited fluctuating in RON change between 20 min – 2 hr. Then, increase in RON change is produced reaching to the maximum RON change of 5.6 unit at 4 hr exposure time. At longer exposure time the RON value decreases.

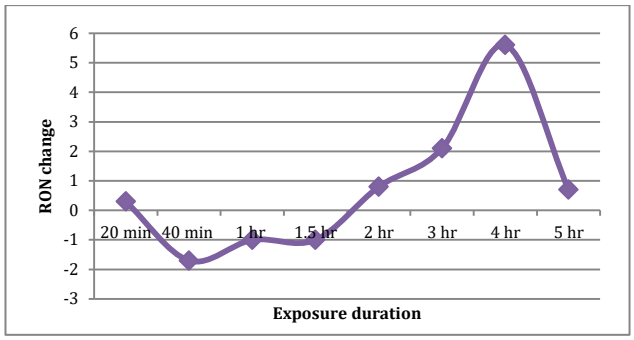


Fig.9 Results of naphtha exposed to UV rays with ZnO catalyst & (2.1 ml/min) O_2

Table 5 Results of naphtha exposed to UV rays with ZnO catalyst & (2.1 ml/min) O_2

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/m²) 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

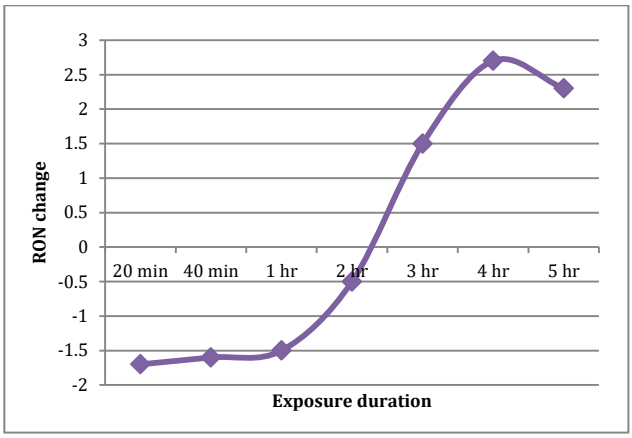


Fig.10 Results of naphtha exposed to UV rays with ZnO catalyst & (3.15 ml/min) O_2

Table 6 and fig.10 show the results of 3.15 ml/min oxygen flow rate. There is an increase in RON until 4 hr exposure time where the maximum change of 2.7 unit is reached. It is also noticed that at longer exposure time the RON value decreases.

Table 6 Results of naphtha exposed to UV rays with ZnO catalyst & (3.15 ml/min) O_2

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/m²) with ZnO catalyst & (3.15 ml/min) O_2.	20 min	0	25.5	26.4	51.2	49.5	- 1.7
	40 min	0	25.5	26.7	51.2	49.6	- 1.6
	1 hr	0	25.5	27	51.2	49.7	- 1.5
	2 hr	0	25.5	**27.8**	51.2	50.7	- 0.5
	3 hr	0	25.5	**28.6**	51.2	52.7	+ 1.5
	4 hr	0	25.5	**29**	51.2	53.9	+ 2.7
	5 hr	0	25.5	**29.5**	51.2	53.5	+ 2.3

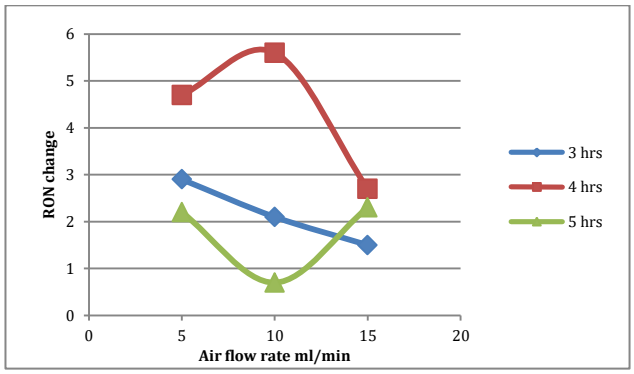


Fig.11 Effect of oxidant flow rate on the RON change

Fig. 11 shows the effect of oxidant flow rate on RON change for 3,4 and 5 hr exposure time. The figure shows that the optimum change in the RON is 5.6 at 4 hr with 2.1 ml/min oxidant flow rate.

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. The aromatic compounds have high RON values in comparison with the other hydrocarbons groups as shown in fig. 12, (Albahri, T. A. *et al* (2002)). Therefore, the GCMS analysis indicates the changes in aromatic group in addition to the iso-paraffin (Isooctane) may be the cause of changes in the RON values.

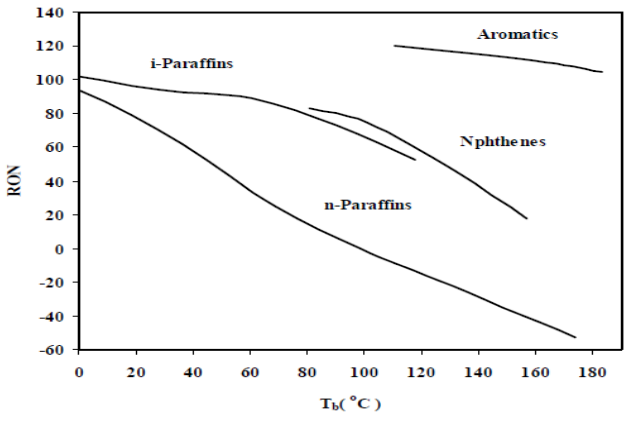


Fig. 12 Research Octane Number of Pure Hydrocarbons from Different Families (Albahri, T. A. *et al* (2002))

A GCMS tests is performed on a sample of naphtha before and after three hours exposure of UV rays and the result is shown in figs. 13,14 and tables 7, 8. The RON change of this sample is 2.1 unit increase with the mentioned conditions in table (5).

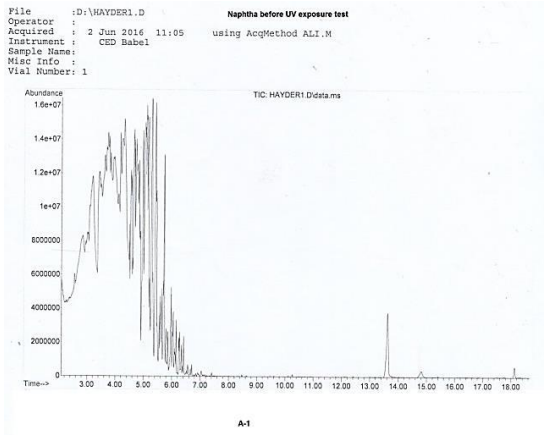


Fig.13 GCMS curve of sample before UV exposure

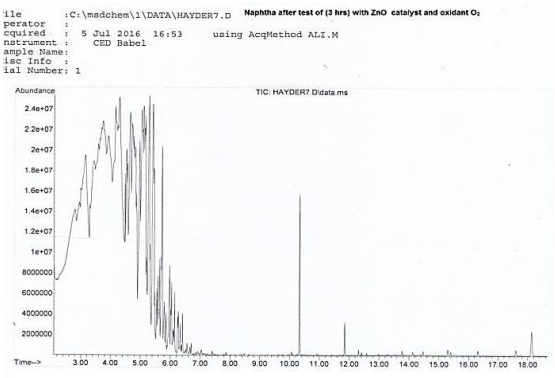


Fig. 14 GCMS curve of RON increasing sample after UV exposure

Table 7 Area percent report of sample before exposure

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%

Table 8 Area percent report of RON increasing sample after exposure

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	2507574390	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 9 and fig. 15 show the percentage change in the main effective six compounds which are Isooctane, Benzene, P-xylene, O-xylene, M-xylene and Toluene. The results show that there are increases in the percentages of Isooctane, Benzene, P-xylene, O-xylene and M-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 six compounds. specially, after taking into account the high RON values of these effective compounds.

Table 9 The changes in percentage 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
5	O-xylene	4.154	2.508	6.657
6	M-xylene	4.154	2.508	6.657

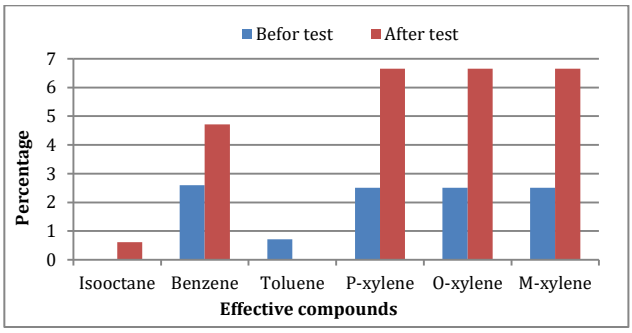


Fig.15 The changes in percentage of the effective compounds according to the GCMS tests

FTIR Test

This test is required to know the functional groups of bonds that are created or eliminated due to UV rays exposure. This test is carried out on the same sample mentioned in the GCMS test. Figs 16 and 17 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}), $C \equiv C$ bond from (alkynes) functional group and at frequency of (1350.86 cm^{-1}), $C - H$ bond from (alkanes) functional group are existed before UV exposure, but they are eliminated after the exposure.

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

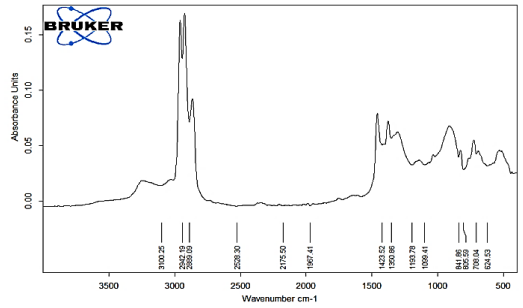


Fig.16 FTIR curve of RON increasing sample before UV exposure

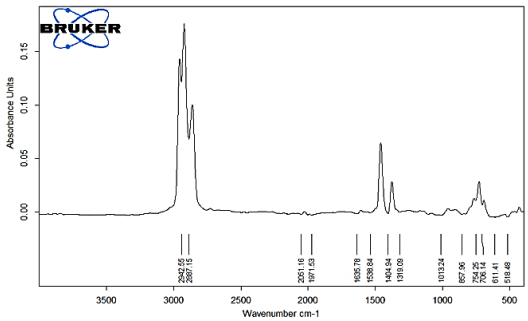


Fig.17 FTIR curve of RON increasing sample after UV exposure

Comparison

The results of this work are compared with the results of reference (Ali H. Ali Rashed*, et. al*., 2013)**,** as shown in fig. 18.

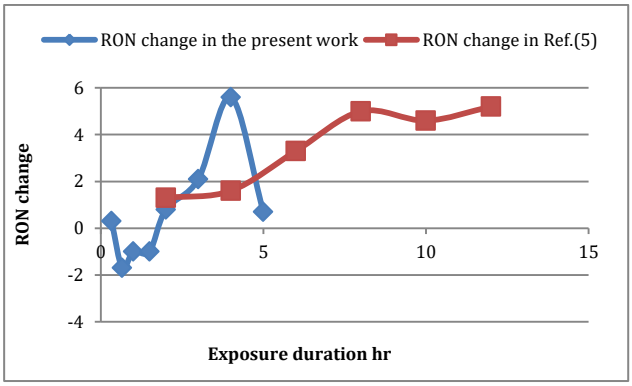


Fig.18 Comparison between the results of this work and those which obtained in Ref (Ali H. Ali Rashed*, et. al*., 2013)

The aim of both researches is improving the fuel Octane number by using UV rays. The results of Ref. (Ali H. Ali Rashed*, et. al*., 2013)exhibited gradual increase in the RON between (2 hr) to (12 hr) of UV exposure with maximum rise of RON about (5) at (8 hr), after 12 hr the RON will be stable approximately. In the present work, there is a sudden increase in the RON between (3 hrs) to (4 hrs) obtaining the maximum rise of RON about (5.6) at (4 hr) followed by severe drop between (4 hrs) to (5 hrs). These differences between the present work results and those of Ref. (Ali H. Ali Rashed*, et. al*., 2013)are attributed to:

1. The work of Ref. (Ali H. Ali Rashed*, et. al*., 2013) is carried out on pool of (30% light naphtha + 70% Reformate), but this work is carried out on naphtha.
2. The used system in the work of Ref (Ali H. Ali Rashed*, et. al*., 2013) is continuous, but in the present work batch system is used.
3. O_2 feeding is used in the present work, while no oxidant is used in the work of Ref (Ali H. Ali Rashed*, et. al*., 2013).

Conclusions

Based on the results and their discussions, the following conclusions can be drawn:

1. ZnO catalyst is more active in the photo-catalysis process than TiO_2 catalyst.
2. The best percent of air feeding is (10 ml/min for each 500 ml of naphtha) or (2.1 ml/min Oxygen for each 500 ml of naphtha).
3. To improve the Octane number of the hydrocarbon fuel, the photo-catalysis process requires a

capturer to react with electrons in conduction band of catalyst. An oxidizer (air) is used as a capturer in this work.

4. The maximum RON improvement of naphtha fuel obtained in this work is 5.6 units under the following conditions :
   a. No cooling.
   b. ZnO catalyst.
   c. Exposure under atmospheric pressure.
   d. 2.1 ml/min oxygen flow rate.
   e. Four hours UV exposure duration for each (500 ml) of naphtha.

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