

Improvement of Gasoline Octane Number Produced from Basrah Refinery Plant by new Additives

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Abstract:

Basrah Refinery Plant produces recently gasoline with low octane number reached to 75.5, 69.0 for leaded and unleaded gasoline respectively. These fuel causes severe damage to engines and also causes bad fuel combustion which increases air pollution due to the high percentage of [CO] and [CO₂] in the exhaust produced.

In this research it is tried to improve the gasoline octane number by new chemical additives [aromatic hydrocarbons, aliphatic and aromatic amines] with different percentages in gasoline.

This kinds of additives can also be used as antioxidants, antirust and anticorrosion which reduces the total amount of chemicals added to gasoline.

The better results obtained with aromatic amines as chemical additives which caused increasing in octane number up to [95.5, 88.0] for leaded and unleaded gasoline respectively.

The percentages of [CO] and [CO₂] gases formed after combustion are measured by orsat analysis based on dry analyses.

تحسين العدد الأوكتاني للكانزولين المنتج من مصفى البصرة بواسطة مضافات جديدة

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الخلاصة :

ينتج مصفى البصرة حالياً بترين السيارات ذو عدد اوكتاني واطئ يصل الى 78.5 بالنسبة الى البترين المضاف اليه رابع اليل الرصاص و 69.0 للكانزولين غير المضاف اليه رابع اليل الرصاص وهذا مما يؤدي الى زيادة الاحتراق داخل محرك السيارات مسبباً سرعة اندثار المحرك ومسبباً كذلك زيادة التلوث بغاز CO وغاز CO₂.

في هذا البحث حاولنا تحسين العدد الاوكتاني باضافة بعض المضافات الجديدة [هيدروكربونات اروماتية وواليفاتية وامينات اروماتية] بنسب اضافية مختلفة هذا النوع من المضافات يمكن ان يستخدم ايضاً كمضافات مضادة للاكسدة ومضادة للتآكل وهذا مما يؤدي الى تقليل مجموع المواد المضافة للكانزولين. اوضحت النتائج التي حصلنا عليها في البحث بان الامينات الاروماتية اعطت نتائج جيدة حيث تمت زيادة نسبة العدد الاوكتاني للبترين الى [95.5] بالنسبة للكانزولين المضاف له رابع اليلات الرصاص لـ [88.0] للكانزولين غير المضاف له رابع اليلات الرصاص تم قياس نسب غازات الاحتراق الناتجة بواسطة جهاز التحليل Orsat [CO₂,CO]

Introduction :

Octane number is almost used to measure the quality of produced gasoline [1]. A lot of work has been done to improve the octane number by several workers. Few of these used the tetra ethyl lead [TEL], but the disadvantages of this additives are the formation of solid products after combustion, which lead to deposit accumulation in the combustion chambers [2]. Also during the 1970s, the US identified motor vehicles as major source of urban air pollutions concomitant with this, was the recognition that lead poses significant health risk, lead emission from vehicles contributing to significant quantities of air borne lead in urban areas [3]. These issues lead to the international movement away from leaded gasoline.

Also the use of manganese additive MMT [Methyl cyclopentadienyl manganese tricarbonyl] is highly controversial. The automotive industry opposes the use of MMT and ferrocene as fuel additives because of perceived detrimental effects on the engine. Therefore MMT was prohibited from use in unleaded gasoline in 1977 because it was found to increase hydrocarbon emission [4].

In this study is tried to improve the octane number of gasoline by using aromatic hydrocarbons, aliphatic and aromatic amines with different percentages of two types of gasoline raw material product in Basrah Refinery plant. The first type is leaded gasoline [[50] vol% light naphtha + [50] vol% reformat + [0.03084] vol % TEL], has an octane number of 75.5. This fuel is sold in petrol station the other type of gasoline used is unleaded [[50] vol% light naphtha + [50] vol% reformat] with an octane number of 69.0

During the course of this work the gas composition after combustion its directly analyzed by orsat analysis dry bases.

The result show that the first feed stock has a research after octane number [99.1] addition of 50vol. % Para- xylene while the second type of stock the RON 95.9 with 50vol. % Para- xylene.

With aliphatic amines additives it's found that with 30vol. % of diethyl amines, RON become 96.6 for leaded gasoline and 88.7 for unleaded gasoline

While with aromatic amines additive it's found that RON was 94.2 with 6 vol. % aniline for leaded gasoline and 88.0 for unleaded gasoline with the same percentage of aniline.

Theoretical aspects :

Gasoline was produced by distillation of crude oil and thermal cracking of reduced crude, naphtha cracking and catalytic cracking ...etc.

There are number of tests applied on gasoline product before marketing which are unable us to evaluate the efficiency of the produced gasoline such as ; octane number , specific gravity at 15.6° C, API gravity at 15.6° C , color, red vapor pressure , lead [pb] content, corrosion [copper strip], existent gum, sulphur content, distillation [initial] , recovery at 100° C , recovery at 145° C , final boiling point and aniline point .

The most important characteristic of gasoline is the octane number, which is a measure of how resistant to premature detonation which causes knocking .

The octane number of a particular gasoline sample is determined by blending n-heptane , which has zero octane's, and iso- octane, which has 100 octane, in the correct proportion to produce the same knock intensity ; as the sample being run in the test engine . The percent of iso-octane in the blend is then as signal as the octane number of the test simple .

There are two common methods of octane number measurements, Research Octane Number [RON] ; is indication of the fuels anti- knock performance at lower engine speed [600rpm] and typical acceleration condition , Motor Octane Number [MON]; reflects the anti-knock performance of fuel under high engine speed [900] and higher load condition [5] .

The Experimental Work :

The leaded gasoline which contains [50 volume percent of light naphtha 50 volume percent of reformat gasoline + variant volume percent of tetra ethyl lead], also the only unleaded gasoline which contain [50volume percent of lights naphtha + 50 volume percent of reformat gasoline] have been studied . The comparison was made between the above two types of gasoline by the addition of different additives instead of tetra ethyl lead in order to improve the octane number , which are :

- 1- Aromatic hydrocarbons [Benzene Toluene , Pare- xylen]

- 2- Aliphatic amine hydrocarbons [Di-ethyl amine, Di-propyl amine]
- 3- Aromatic amine hydrocarbons [Aniline, ortho toluidene].

A comparison was made between these additives and their effect on leaded and unleaded gasoline.

Different volume percent of these additives were mixed with the gasoline and the improvement of octane number of each additive for each volume percent been checked by using [ASTM CFR FUEL RESEARCH ENGINE], fig. [1].

This engine used to study Research Octane Number [RON] by following international procedure [D2699-03.9 STANDARD TEST METHOD for RESEARCH OCTANE NUMBER OF SPARK-IGNITION ENGINE FUEL].

The results of this machine called [RON], [RON] have been checked three times for every percent of additions and then the mean average of these three reading have been taken.

The study also included the checking another gasoline properties such as the vapor pressure, specific gravity, the binary boiling point and the temperature at which received 5%, 10%, 30%, 50%, 70%, 90% and 95% of gasoline and final boiling point, and we checked also the amount of gasoline residue.

To analyze the exhaust gas emission we took samples from the improved gasoline by the new additives with different volume percent and burned by on engine, after that, samples from the output flue gas have been analyzed by using [ORSAT; PROT ECH FIUX 200-4, INFRARED 4 GAS ANALYSED] fig. [2]; Which gave us the volume percent of CO [carbon monoxide] and CO₂ [carbon dioxide] gases.

Results and Discussion:

All experimental results of research octane number, specific gravity, red vapor pressure, distillation [initial boiling point]; recovery at [5,10,30,50,70,90,95] °C, end boiling point moreover the volume percentage of CO and CO₂ after combustion, were carried out for leaded and unleaded gasoline. The above test have been used with different types and concentration of additives Tab. [13-20].

Experiments of leaded gasoline with aromatic hydrocarbon additives such as [benzene, toluene, and para-xylene] showed increasing in research octane number from 75.8 to 91.0 with 50% vol. benzene and to 92.2 with 60% vol.

toluene and to 99.1 with 50% vol. para-xylene as shown in fig. [3] and table [1].

The above experiments were repeated with unleaded gasoline and the results showed increasing in [RON] from 69.0 to 87.5 with 50% vol. benzene and to 88.7 with 50% vol. toluene and to 95.9 with 50% vol. para-xylene as showed in fig. [4] and table [2].

It have been concluded from the above results that the para-xylene was the best aromatic hydrocarbons as additive for leaded and unleaded gasoline.

Aliphatic amines such as [diethyl amine and di propyl amine] as another additives have been tried to improve the [RON] of the leaded and unleaded gasoline in well. [RON] increased from 75.5 to 96.6 with 30% vol. diethyl amine and the 89.1 with 30% vol. dipropyl amine as in the fig. [5] and table [3] with leaded gasoline, and in case of unleaded gasoline [RON] increased from 69.0 to 88.7 with 30% vol. diethyl amine and to 80.4 with 30% vol. dipropyl amine as in fig. [6] and table [4].

Aromatic amine such as [Aniline, Ortho-toluidine] as another additive have been used to improve the [RON] of leaded and unleaded gasoline. [RON] increased from 75.9 to 94.7 with 6% vol. aniline and to 91.2 with 5% vol. ortho-toluidene as in fig. [7] and tab. [5], with leaded gasoline. [RON] increased from 69.0 to 88.0 with 6% vol. aniline and to 83.4 with 5% vol. ortho-toluidene, with unleaded gasoline as in fig. [8] and tab. [6].

From the above results we showed that [RON] increases rapidly with increasing the volume percentage of the additives for both leaded and unleaded gasoline, also the aromatic amine [Aniline] was the best additive in comparison with the other additives that due to the chemical structure of aniline which is more active than the other additives and for the volume percentage of the aniline was little compared with other volume percentage of additives.

After combustion of improved leaded and unleaded gasoline, the concentration of carbon monoxide gas [CO] decrease when the [RON] increases while the concentration of carbon dioxide gas [CO₂] increase, therefore the ratio of CO/CO₂ decrease that due to the approximately complete combustion of the fuel as in fig. [9-14] tab. [7-12].

The ratio of CO/CO₂ decrease with increase of the volume percentage of additives due to the same reason mentioned above as in fig. [9-14] and table [7-12].

Conclusions

1. The gasoline which produced in Basrah Refinery plant with low octane number [76.5 for leaded gasoline and 69.0 for unleaded gasoline was improved by using different additives.
2. The best additive which used is Aniline improved [RON] for leaded gasoline up to [94.2] and [88.0] for unleaded gasoline.
3. Using of improved gasoline decreases the environmental pollution toxicity by decreasing Co gas emission.

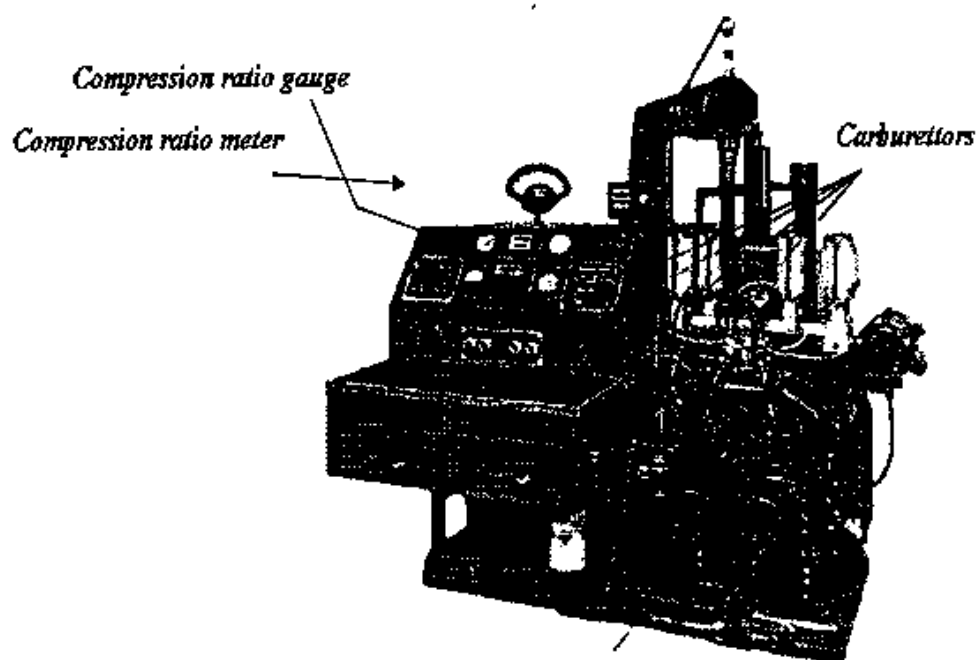
Recommendations:

1. Improving the gasoline by using other types of additives.
2. Improving other petroleum products.
3. Improving other properties of gasoline.
4. Study the effect of improving gasoline in [MON].
5. Study the effect of new additives for improving octane number, as anticorrosion and antirust additives.

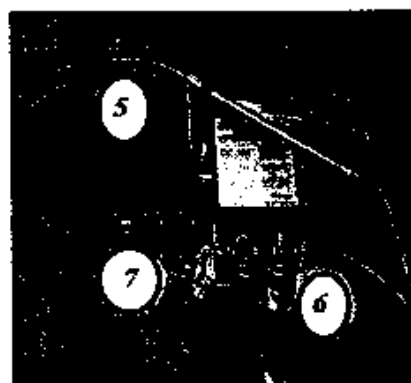
Reference:

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2. . Lovell W. G. "Gibson H. J. , and Jones B. A., " Combustion Chamber Deposits in Auto mobile Engines ". pp. 553-577, 1955.
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"Figure (1) ASTM CFR FUEL RESEARCH ENGINE"



**Figure (2):
ORSAT, PROTECH FLUX 2000-4, INFRARED 4 GAS ANALYSER**

1-CO % VOL.

2-HC PPM VOL.

3-CO₂ % VOL.

4-O₂ % VOL.

5-Power.

6-Sincere.

7- Exhaust gas filters.

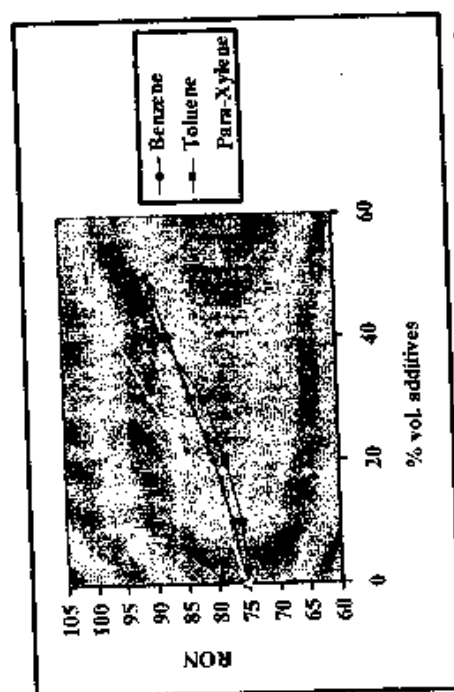


Figure (3). The relation between research octane numbers (RON) of aromatic compounds as additive to leaded gasoline and percentage of this additive.

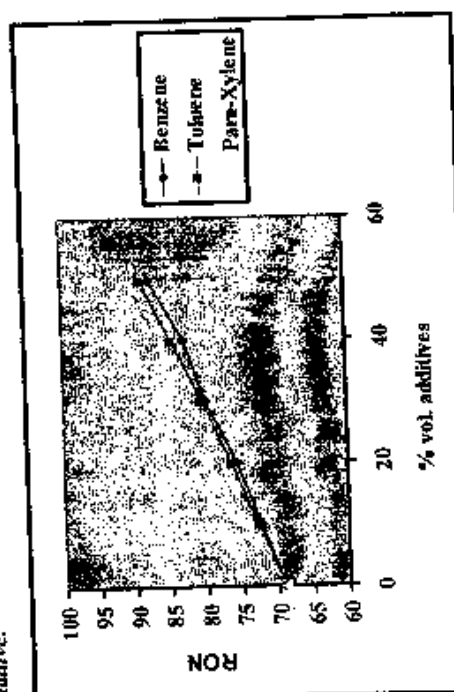


Figure (4). The relation between research octane numbers (RON) of aromatic compounds as additive to unleaded gasoline and percentage of this additive.

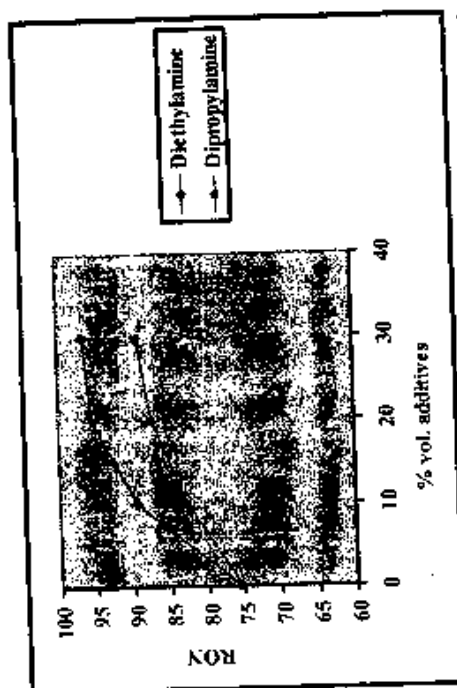


Figure (5). The relation between research octane numbers (RON) of aliphatic amine compounds as additives to leaded gasoline and percentage of these additives.

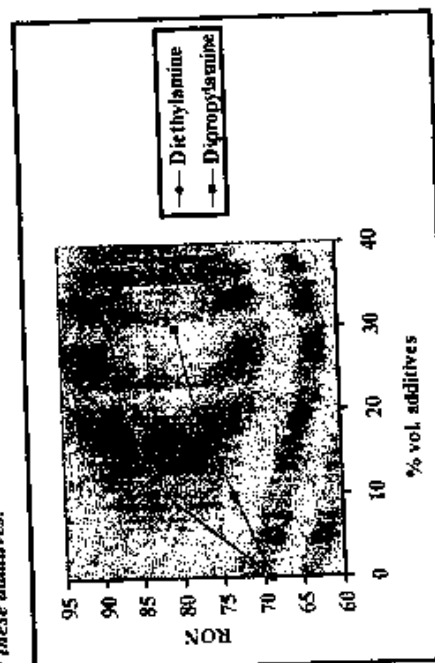


Figure (6). The relation between research octane numbers of aliphatic amine compounds as additives to unleaded gasoline and percentage of these additives.

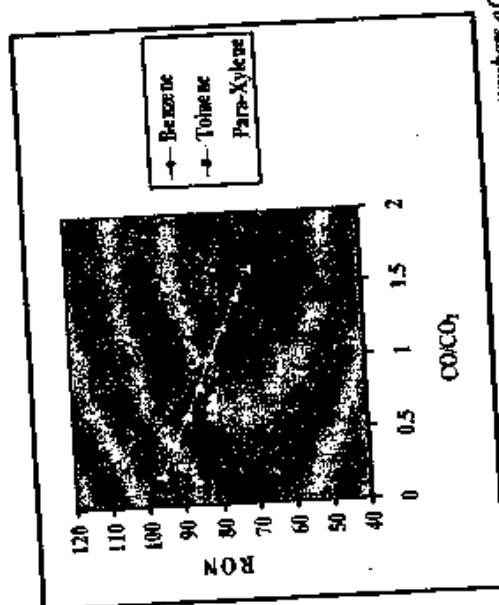


Figure (9). The relation between research octane numbers of aromatic compounds as additive to leaded gasoline and ratio of CO/CO₂.

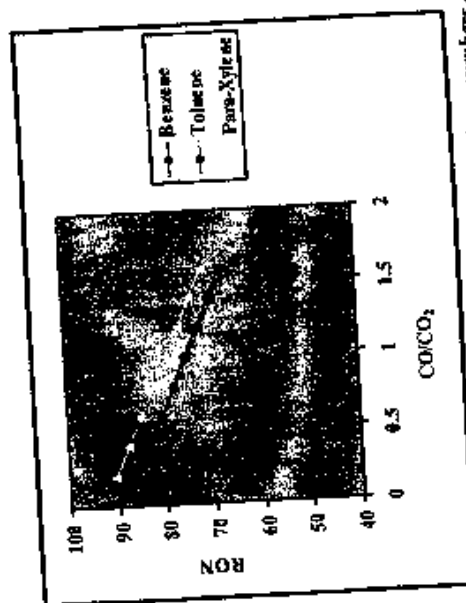


Figure (10). The relation between research octane numbers of aromatic compounds as additive to unleaded gasoline and ratio of CO/CO₂.

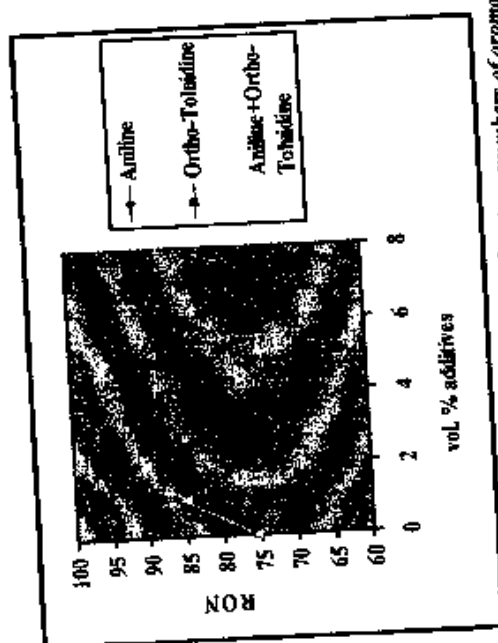


Figure (7). The relation between research octane numbers of aromatic amine compounds as additives to leaded gasoline and percentage of these additives.

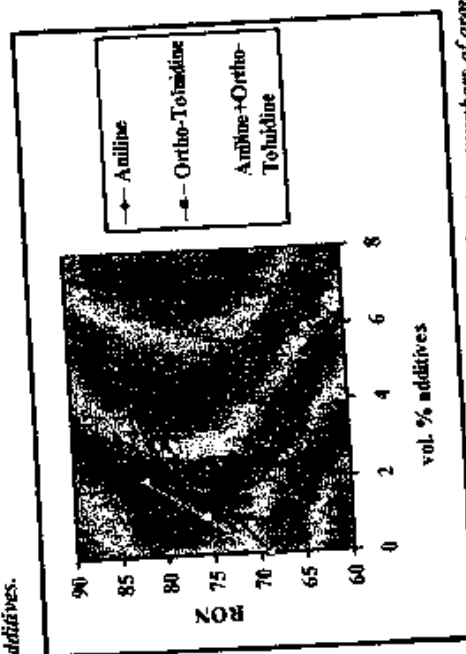


Figure (8). The relation between research octane numbers of aromatic amine compounds as additives to unleaded gasoline and percentage of these additives.

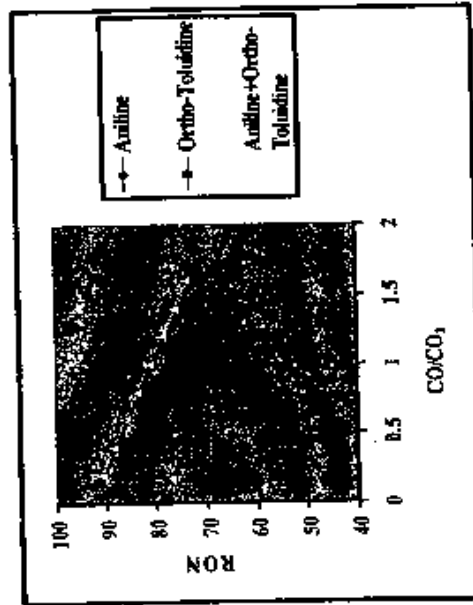


Figure (11). The relation between research octane numbers of aliphatic amine compounds as additive to unleaded gasoline and ratio of CO/CO₂.

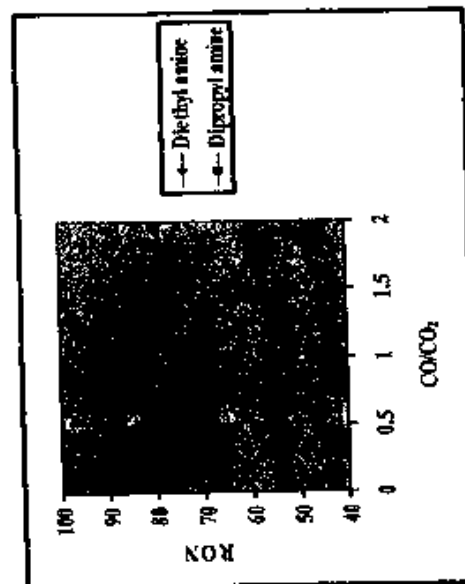


Figure (12). The relation between research octane numbers of aliphatic amine compounds as additive to unleaded gasoline and ratio of CO/CO₂.

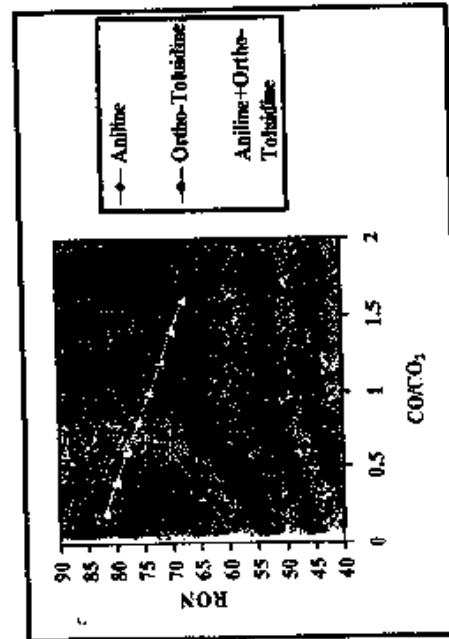


Figure (14). The relation between research octane numbers of aromatic amine compounds as additive to unleaded gasoline and ratio of CO/CO₂.

Table no. (1):**Research octane numbers of leaded gasoline with using aromatic hydrocarbon compounds as enhancers:**

Leaded gasoline	Leaded gasoline	Leaded gasoline	Leaded gasoline
0	75.5	75.5	75.5
1	-	75.9	75.6
10	77.6	76.0	79.0
20	80.2	78.4	85.0
30	84.0	81.8	90.5
40	87.3	88.4	96.1
50	91.0	92.2	99.1

Table no. (2):**Research octane numbers of unleaded gasoline with using aromatic hydrocarbon compounds as enhancers:**

Unleaded gasoline	Unleaded gasoline	Unleaded gasoline	Unleaded gasoline
0	69.0	69.0	69.0
1	-	69.8	70.5
10	72.3	72.8	74.5
20	75.5	76.4	79.6
30	79.8	80.3	86.2
40	82.8	84.7	90.8
50	87.5	88.7	95.9

Table no. (3):
Research octane numbers of leaded gasoline with using aliphatic amine compounds as enhancers:

0	75.5	75.3
1	77.1	-
3	81.1	-
5	-	-
10	89.3	82.6
20	95.4	87.2
30	96.6	89.1
40	-	89.7
50	-	89.7

Table no. (4):
Research octane number of unleaded gasoline with using aliphatic amine compounds as enhancers:

0	69.0	69.0
1	69.4	-
3	72.1	-
5	-	-
10	82.1	73.6
20	87.4	78.1
30	88.7	80.4
40	-	81.2
50	-	81.2

Table no. (5):
Research octane numbers of leaded gasoline with using aromatic amine compounds as enhancers:

0	75.5	75.5	75.5
1	-	80.3	84.8
2	-	-	90.3
3	87.2	88.8	-
5	90.9	91.2	-
6	94.2	-	-

Table no. (6):
Research octane number of unleaded gasoline with using aromatic amine compounds as enhancers:

0	69.0	69.0	69.0
1	-	72.6	75.9
2	-	-	82.3
3	81.6	79.9	-
5	85.6	83.4	-
6	88.0	-	-

Table no. (7):
Exhaust gas analysis of (leaded gasoline + aromatic compounds as enhancers):

%vol. additives	Benzene			Toluene			Para-xylene		
	RON	%Vol. CO ₂	%Vol. CO	%Vol. CO ₂	%Vol. CO	%Vol. CO	%Vol. CO ₂	%Vol. CO	%Vol. CO ₂
0	75.5	3.60	2.45	1.469	75.5	3.60	1.469	75.5	3.06
10	77.6	3.57	2.85	1.2526	76.0	3.437	1.1294	79.0	3.4925
20	80.2	3.55	3.317	1.07	78.4	3.983	1.0127	85.0	3.46
30	84.0	3.05	3.4	0.897	81.8	3.208	0.692	90.5	3.387
40	87.3	2.49	4.6	0.54	88.4	1.530	0.266	96.1	2.934
50	91.0	2.39	6.2	0.385	92.2	1.303	0.2046	99.1	2.473
									6.5
									0.38

Table no. (8):
Exhaust gas analysis of (unleaded gasoline + aromatic compounds as enhancers):

%vol. additives	Benzene			Toluene			Para-xylene		
	RON	%Vol. CO ₂	%Vol. CO	%Vol. CO ₂	%Vol. CO	%Vol. CO	%Vol. CO ₂	%Vol. CO	%Vol. CO ₂
0	69.0	4.75	3.10	1.532	69.0	4.75	1.532	69.0	1.532
10	72.3	3.945	3.12	1.264	72.8	3.783	1.081	74.5	3.8875
20	75.5	3.712	4.25	0.8734	76.4	3.377	0.723	79.6	3.825
30	79.8	3.321	5.65	0.587	80.3	3.2467	0.553	86.2	3.627
40	82.8	2.41	6.325	0.381	84.7	1.637	0.2714	90.8	3.6225
50	87.5	1.195	6.6	0.181	88.7	1.32	0.215	95.9	2.583
									6.067
									0.4257

Table no. (9):

Exhaust gas analysis of (leaded gasoline + aliphatic amines compounds as enhancers):

%vol additives	Diethyl amine			Dipropyl amine		
	RON	% Vol. CO	% Vol. CO ₂	RON	% Vol. CO	% Vol. CO ₂
0	75.5	3.60	2.45	75.5	3.60	2.45
10	89.3	3.40	5.703	82.6	1.92	5.25
20	95.4	2.78	5.90	87.2	1.67	5.97
30	96.6	2.44	6.27	89.1	1.52	6.01
						0.2529

Table no. (10):

Exhaust gas analysis of (unleaded gasoline + aliphatic amines compounds as enhancers):

%vol additives	Diethyl amine			Dipropyl amine		
	RON	% Vol. CO	% Vol. CO ₂	RON	% Vol. CO	% Vol. CO ₂
0	69.0	4.75	3.10	69.0	4.75	3.10
10	82.1	3.9	5.796	73.6	4.5	4.47
20	87.4	2.95	5.97	78.1	3.4	4.5
30	88.7	2.94	6.3	80.4	1.813	6.2
						0.2924

Table no. (11): Exhaust gas analysis of (leaded gasoline + aromatic amines compounds as enhancers):

%vol additives	Aniline			Orthotoluidine			Aniline + orthotoluidine		
	CO	HC	NOx	CO	HC	NOx	CO	HC	NOx
0	75.5	3.60	2.45	1.469	75.5	3.60	1.469	75.5	3.60
1	-	-	-	-	80.3	3.59	0.71089	84.8	2.33
2	-	-	-	-	-	-	-	90.3	1.67
3	87.2	1.62	4.5	0.36	88.8	2.413	0.402167	-	-
5	90.9	1.523	5.63	0.271	91.2	1.758	0.2768	-	-

Table no. (12): Exhaust gas analysis of (unleaded gasoline + aromatic amines compounds as enhancers):

%vol additives	Aniline			Orthotoluidine			Aniline + orthotoluidine		
	CO	HC	NOx	CO	HC	NOx	CO	HC	NOx
0	69.0	4.75	3.10	1.532	69.0	4.75	1.532	69.0	4.75
1	-	-	-	-	72.6	4.157	0.9237	75.9	2.56
2	-	-	-	-	-	-	-	82.3	1.66
3	81.6	2.36	4.5	0.524	79.9	3.53	0.61178	-	-
5	85.6	1.62	5.6	0.2892	83.4	2.373	0.3827	-	-

Table no. (13): Specification of (leaded gasoline + aromatic compounds as enhancers):

Sample	10% benzene	40% toluene	50% Para-xylene	Leaded gasoline
Specific gravity at 15.6°C	0.7138	0.7621	0.7631	0.7156
R.V.P. at 37.8°C at (psi)	9.6	6.2	6.5	
Distillation: 1 B P °C	37	44	41	32
5% °C	48	55	51	44
10% °C	53	66	60	51
30% °C	68	85	90	67
50% °C	87	100	110	89
70% °C	99	110	130	113
90% °C	147	130	140	147
95% °C	157	155	148	159
E. P. °C	158	171	161	178
T. D. Vol %	97	98	98	98
Resd	3	2	2	2

Table no. (14):

Specification of (unleaded gasoline + aromatic compounds as enhancers):

Sample	10% benzene	40% toluene	50% Para-xylene	Unleaded gasoline
Specific gravity at 15.6°C	0.770	0.7646	0.7502	0.7006
R.V.P. at 37.8°C at (psi)	10.0	6.2	6.5	7.6
Distillation: 1 B P °C	34	38	39	40
5% °C	45	45	50	47
10% °C	61	55	57	51
30% °C	68	75	70	58
50% °C	78	95	88	65
70% °C	90	110	130	85
90% °C	135	122	141	130
95% °C	155	138	151	145
E. P. °C	160	158	162	162
T. D. Vol %	98	97	98	98
Resd	2	3	2	2

Specification of amines compound:

A- Specification of aliphatic amines compounds:

Table no. (15):

Specification of (leaded gasoline + aliphatic amines compounds as enhancers):

sample	10% Diethyl amine	20% Dipropyl amine	Leaded gasoline
Specific gravity at 15.6°C	0.7143	0.7217	0.7156
R.V.P. at 37.8°C at (psi)	12.2	7.1	
Distillation: 1 B P °C	31	37	32
5% °C	40	47	44
10% °C	50	58	51
30% °C	65	83	67
50% °C	85	100	89
70% °C	110	110	113
90% °C	150	140	147
95% °C	161	150	159
E. P. °C	170	167	178
T. D. Vol %	98	97	98
Resd	2	3	2

Table no. (16):

Specification of (unleaded gasoline + aliphatic amines compounds as enhancers):

sample	10% Diethyl amine	20% Dipropyl amine	Unleaded gasoline
Specific gravity at 15.6°C	0.7200	0.7257	0.7006
R.V.P. at 37.8°C at (psi)	12.2	8.0	7.6
Distillation: 1 B P °C	35	37	40
5% °C	45	47	47
10% °C	51	58	51
30% °C	63	71	58
50% °C	80	80	65
70% °C	105	90	85
90% °C	149	132	130
95% °C	165	157	145
E. P. °C	173	171	162
T. D. Vol %	98	98	98
Resd	2	2	2

B - Specification of aromatic amines compounds:**Table no. (17): Specification of (leaded gasoline + aromatic amines compounds as enhancers)**

sample	5% aniline	3% Ortho toluidine	1% aniline + 1% Ortho toluidine	leaded gasoline
Specific gravity at 15.6°C	0.7317	0.7252	0.7231	0.7156
R.V.P. at 37.8°C at (psi)	8.8	8	11.2	
Distillation: 1 B P °C	35	35	34	32
5% °C	42	47	48	44
10% °C	50	55	55	51
30% °C	75	75	73	67
50% °C	100	96	98	89
70% °C	125	122	125	113
90% °C	155	155	145	147
95% °C	170	171	165	159
E. P. °C		182	173	178
T. D. Vol %		99	98	98
Resd		1	2	2

Table no. (18): Specification of (unleaded gasoline + aromatic amines compounds as enhancers)

sample	5% aniline	3% Ortho toluidine	1% aniline + 1% Ortho toluidine	Unleaded gasoline
Specific gravity at 15.6°C	0.7427	0.7381	0.7351	0.7006
R.V.P. at 37.8°C at (psi)	8.4	9.6	10.0	7.6
Distillation: 1 B P °C	38	35	36	40
5% °C	50	44	45	47
10% °C	58	54	55	51
30% °C	72	71	71	58
50% °C	90	92	95	65
70% °C	127	120	120	85
90% °C	158	155	151	130
95% °C	170	170	161	145
E. P. °C	178	180	175	162
T. D. Vol %	98	97	98	98
Resd	2	3	2	2