

***Chemical, Petroleum and Environmental Engineering***

**Determination of the Optimum formula for Composite Motor Gasoline  
Octane Number Blending Enhancer**

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**ABSTRACT**

To decrease the dependency of producing high octane number gasoline on the catalytic processes in petroleum refineries and to increase the gasoline pool, the effect of adding a suggested formula of composite blending octane number enhancer to motor gasoline composed of a mixture of oxygenated materials (ethanol and ether) and aromatic materials (toluene and xylene) was investigated by design of experiments made by Mini Tab 15 statistical software. The original gasoline before addition of the octane number blending enhancer has a value of (79) research octane number (RON). The design of experiments which study the optimum volumetric percentages of the four variables, ethanol, toluene, and ether and xylene materials leads to 30 experiments. The results obtained show that RON can reach a value of 103.1 (30.5% RON improvement) when a formula of composite octane number blending enhancer containing a volumetric percentage of 15, 25, 25 volumetric percent of ethanol, toluene and xylene respectively. The cost study in comparison with the price of high octane number gasoline sold in Iraq show that this formula has a high cost of 2050 Iraqi Dinar (IQD)/liter gasoline, while the formula of composite octane number blending enhancer containing 15% volumetric percentage of Ethanol only leading to gasoline of 89.6 RON (13.4 % ON improvement) gave minimum cost of 300 IQD / liter gasoline for the blend of octane number enhancer making the total price of the gasoline to be competitive with the high ON gasoline imported from outside Iraq. While the formula of 7.5, 12.5, 37.5 and 5% volumetric percentage of ethanol, toluene, xylene, and ether respectively have a maximum cost of 2525 IQD of produced gasoline of 101.3 RON (octane number improved by 28.23%).

**Keywords:** Octane number, motor gasoline, ethanol, design of experiment, Mini Tab software.

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## إيجاد التركيبة المثالية لمادة مزج مركبة معززة لرقم الأوكتان لبنزين السيارات

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### الخلاصة

لغرض توفير مقاطع مواد تستخدم في إنتاج بنزين سيارات مرتفع رقم الأوكتان وتقليل الاعتماد على المنتجات النفطية من المصافي النفطية ودون الحاجة الى استخدام وحدات التحسين في المصافي النفطية تم إنجاز هذا البحث باستخدام مواد مزج معززة مركبة لرقم الأوكتان في بنزين السيارات وزيادة كمية البنزين المنتج وتشمل المواد المستخدمة الأيثانول، التولوين، الزايلين والأثير ومن اجل ايجاد التركيبة المثلى لهذا المزيج المقترح الواجب اضافته لبنزين سيارات منخفض الأوكتان ومعرفة مقدار التحسين في رقم الأوكتان ومدى تأثير الخواص الأخرى تم عمل تصميم تجارب لهذه المتغيرات الاربعة بواسطة البرنامج الاحصائي Mini Tab 15.1 وأدى الى 30 تجربة ، حيث كانت المتغيرات للتركيبة المقترحة هي النسب الحجمية للمواد الاوكسجينية (الكحول والأثيرات) والمواد الأروماتية (التولوين والزايلين) وباعتبار هذا المزيج مادة معززة لرقم الأوكتان لبنزين السيارات منخفض الأوكتان. رقم الأوكتان للبنزين الاصلي قبل اضافة معزز رقم الأوكتان هو 79 بطريقة البحث. أن تصميم التجارب الخاص بدراسة تأثير المتغيرات الأربعة أعلاه أدى إلى (30) تجربة. أظهرت النتائج إنه يمكن الوصول الى رقم أوكتان مقداره (103.1) ( نسبة تحسين مقدارها 30.5%) عندما تكون خلطة المادة المضافة للمزيج المركب لمحسن رقم الأوكتان لبنزين السيارات تتكون من 25،25،15 و صفر% نسبة حجمية من الأيثانول ، التولوين، الزايلين والأثير على التوالي لكن دراسة الكلفة ومقارنتها مع سعر البنزين مرتفع الأوكتان المباع في العراق بينت أن هذه الخلطة تحمل كلفة عالية مقدارها (2050 دينار عراقي/لتر بنزين سيارات) وأقل كلفة كانت عند إضافة خلطة تتكون من 15% نسبة حجمية أيثانول فقط وأدت إلى الحصول على بنزين سيارات برقم أوكتان مقداره (89.6) مقاسة بطريقة البحث (نسبة زيادة لرقم الأوكتان عن البنزين المنخفض الأوكتان مقدارها 13.4%) بينما ومقدار الكلفة هو (300) دينار عراقي لكل لتر من البنزين يتم تحسينه بينما أعلى كلفة كانت بمقدار (2525) دينار عراقي /لتر عندما تحتوي الخلطة 7.5، 12.5، 5.37 و 5% نسبة حجمية من الأيثانول، التولوين، الزايلين والأثير على التوالي وكان رقم الأوكتان لبنزين السيارات الناتج مقداره 101.3 مقاس بطريقة البحث ( نسبة زيادة رقم الأوكتان للبنزين المنخفض الأوكتان مقدارها 28.23%).

**الكلمات الرئيسية:** رقم الأوكتان ، بنزين السيارات ، الأيثانول ، تصميم التجارب ، برنامج ميني تاب.

## 1. INTRODUCTION

Gasoline is normally produced by petroleum refineries. The petroleum fractions can be easily separated by distillation processes to give (gasoline, different distillate fuels, and residual products). Normally naphtha is the product which can be used to make the gasoline cut, but it suffers from its low octane number 78 research octane number (RON) and 75 motor octane number (MON), where the difference between RON and MON is the conditions at which the test in the octane number machine is different, in the MON method, more severe conditions of rpm and temperature are used and will represent the actual work of engine on the road. Chemical changes are done in petroleum refineries to increase the octane number of the cuts used in making gasoline, these processes include catalytic reforming, alkylation, and isomerization. But the use of blending agent to increase the octane number is sometimes used to produce the gasoline. The blending agent is a material not belonging to petroleum such as ethanol, ether, and aromatics such as toluene, **NREL, 2000.**

Octane number enhancer addition will increase the capacity of petroleum refineries for producing high RON gasoline and prevent the necessity to transport raw materials and building new units with a high cost. Petroleum refineries can refine crude oil and supply gasoline with 20% of the products from crude oil while the demand in Iraq is about 50% from the products of refining crude oil, **NREL, 2000, and Marathon Petroleum Company, 2015.**

Gasoline is used as the main fuel for internal ignition engines over 100 years ago. But another fuel such as alcohol and gasoline-alcohol blend was also used later and ethanol was used in a blend with gasoline with 10 percent volume and about 13 billion gallons of ethanol used in



2010. Ethanol blend with gasoline fuel makes the pollutant emissions less and it is used as an environment friend fuel. In this work, a mixture of octane number enhancers were blended and resulted in a composite gasoline octane number enhancer by using toluene, xylene, and ether in addition to ethanol and its emission is tested to compare it with the normal gasoline without the octane number enhancer addition, **NREL and Yanowitz, et al., 2011 and Pikunas, et al., 2003.**

Gasoline with different octane number grades can be produced by the method of blending nonpetroleum materials with the base gasoline of low octane number produced in petroleum refineries **Albahri, 2018.**

Ethanol can be used as motor gasoline octane number enhancer, it is blended up to 10% with gasoline and it is an oxygenated enhancer. It was used in many states of the United States since 1993, **U.S Energy Information Administration, 2011.**

In 2007, ethanol was used in motor fuel with an amount of 6.48 billion gallons.

Gasoline is produced with high octane number in order to prevent pre-ignition of fuels which causes knocking in internal combustion engines and the power is lost and makes mechanical problems in parts of the engine. Normally high-grade octane number motor gasoline can be produced by using different cuts produced in refineries such as catalytic reformat, alkylate, isomerizate ...etc. But because Iraq now suffers from a deficiency of the alkylate, isomerizate and catalytic reformat which give cuts for blending gasoline of high octane number. Many times, researchers work on finding octane number enhancers and cuts which can be used in the reformulation of low-grade octane number gasoline. Normally in the past, tetraethyl lead (TEL) was the best shooting octane number enhancer used in motor gasoline but because of the environmental regulation nowadays and the health problems caused from the TEL in gasoline, it was prevented totally from any more use, **Hamadi, 2010.**

Octane number (ON) is a number representing resistance of gasoline to early burning in internal combustion engines (ICE), and it is measured by comparing the combustion of the fuel sample in a standard engine cylinder with a standard mixture composed of isooctane which has a value of ON=100 and n-heptane whose ON= 0, **Perdih, et al., 2006.**

The catalytic reforming unit in petroleum refineries is one of the important processes by which reforming of hydrocarbons materials which have low octane number (naphtha) to high octane number gasoline without changing the range of boiling points, **Saihod, et al., 2014.** Gasoline is a mixture of hydrocarbons boiling below (180-200 °C) and contains three types of hydrocarbons, which are paraffin (including both the branched and cycloparaffins), aromatics and olefins, **Heinemann and Speight, 2006.**

Gasoline classified according to octane number as; Normal motor gasoline having 85 RON, Regular 91 gasoline, having 91 RON, Premium gasoline with 95 RON and Super 98 gasoline having 98 RON, **Dormer, 1998.**

## 2. EXPERIMENTAL WORK:

### 2.1 Materials:

- Motor Gasoline produced in Al-Doura Refinery, having specifications as shown in **Table 2.**
- Toluene (Romil –SA Company), laboratory reagent of > 99.5% assay.
- Technical Ethyl alcohol 99%.
- Xylene laboratory reagent. (Chinese made) of > 95% assay.
- Diethyl ether (Laboratory reagent).

**Note:** The RON and MON for the above materials before blend is as shown in **Table 1.**

### 2.2 Equipment:

The equipment used in this work consisting of:



- a. Laboratory volumetric flasks of different capacities.
- b. Glass graduated cylinders (50,100 and 250 ml).
- c. Laboratory beakers of different capacities.
- d. Octane number measuring machine in Doura refinery (manufactured in the USA by Waukesha Company).
- e. Engine cycle analyzer (ECA100) with one cylinder internal combustion gasoline engine type TD211 manufactured by TecQuipment Ltd company, UK and digital tachometer (Photo type) model DT-2234a+ manufactured by Rinchco company (China).
- f. Distillation test apparatus according to ASTM D86
- g. Specific gravity hydrometers.
- h. Glass funnel.

### 2.3 Procedure:

- 1- Design of experiments (DOE) was made using Minitab 15 software, studying four variables used in the formulation of composite octane number blending enhancer which is the volumetric percent of ethyl alcohol, toluene, xylene, and ethyl ether.
- 2- DOE leads to 30 experiments, **Table 3** shows the conditions of the volumetric percent for the variables in each experiment.
- 3- Samples for the experimental conditions fixed in the table of DOE were prepared using laboratory volumetric flasks, beakers and graduated cylinders.
- 4- Physical properties tests including distillation, SG were done in the petroleum technology laboratory belong to Institute of Technology Baghdad, while the RON tests were done in Al-Dora Refinery, Quality Control and Researches Laboratory.
- 5- Emission comparison was made by Engine cycle analyzer (ECA100) with one cylinder internal combustion gasoline engine type TD211 and controlling the speed of the engine by using digital tachometer (Photo type) model DT-2234a+ to improve the environment-friendly enhancer used in this study.

### 2.4 Test Methods:

**RON Test:** This test is done according to ASTM D2699 in the quality control and research laboratories in Al-Doura Refinery in Baghdad which belongs to the General State of the Middle Refineries. The machine is manufactured by Waukesha Company.

**Distillation:** is done in Al-Doura Refinery and in the Laboratory in the Chemical Industries Department according to ASTM D86.

**Reid Vapor Pressure:** is done in the Laboratory in the Chemical Industries Department according to ASTM D323.

**Specific Gravity:** is done in the Laboratory in the Chemical Industries Department according to ASTM D4082.

**Emission Test:** is done by burning the gasoline in one cylinder internal engine and using engine cycle analyzer mentioned above which is available in the Machinery and Equipment Department in the Baghdad Institute of Technology.

## 3. RESULTS AND DISCUSSION:

**Table 4** shows the results of the octane number, distillation, specific gravity and Reid vapor pressure laboratory tests for the experiments belong to the table of DOE.

Results of this work confirm that the materials suggested to be blended with the gasoline of low octane number is effective to increase the octane number and will also increase the quantity of the gasoline produced in the Iraqi petroleum refineries without the need of building of new refineries and making reformed gasoline by reforming units, alkylation and isomerization processes.



RON reached high numbers such as 103 or 101, but the cost of the composite blends for the above RON is high and it is not competitive with the prices of high octane number gasoline imported from outside Iraq, but the formula of a blend using 15% volumetric percent ethanol only (Experiment No. 13) which leads to gasoline having 89.6 RON (13% RON improvement) and its cost is competitive compared with the imported gasoline.

The addition of ethanol to low RON in gasoline will result also in less emissions than gasoline and yield higher RON and this is agreement with all the studies done on this subject. The addition of ethanol will increase the gasoline pool without the need of building new refineries and will give a new economic chance to operate many workers for producing ethyl alcohol and will save the foreign currency from losing from Iraq.

**Table 5** shows the cost estimation for the composite blend ON enhancer, the prices for the materials used in the blend are shown in **Table 6**.

**Table 7** and **8** show the results for the comparison of emissions from regular gasoline of low octane number and with the improved gasoline added to it 15 % vol ethanol. The results confirm that the original gasoline with low octane number has higher CO and HC (hydrocarbons) emissions rate because it has low octane number which result to un-efficient combustion, while the gasoline which was improved with 15% ethanol as octane number enhancer results in complete combustion and efficient work of engine as showed in its lower CO and HC emissions and higher CO<sub>2</sub> emissions and leads to higher NO<sub>x</sub> emissions which confirm that the temperature and pressure are higher in the cylinder when using improved octane number gasoline because of its complete combustion and less misfiring occurs in the engine. This shows that ethanol will be environment friend additive and fuel.

**Equations 1-9** show the regression equations which relates RON with the vol% of the different combinations of the four variables studied for the blend enhancer (ethanol, Ether, toluene, and xylene vol %) which were found from the statistical Mini Tab 15.1 Software.

$$\text{Octane Number} = 85.2 + 0.426\text{Ethanol}\% + 0.247\text{Toluene}\% + 0.238\text{Xylene}\% + 0.351\text{Ether}\% \quad (1)$$

$$\text{Octane Number} = 92.87 + 0.2073 \text{ Toluene}\% + 0.001062 \text{ Toluene}\%^2 \quad (2)$$

$$\text{Octane Number} = 93.09 + 0.3574 \text{ Ethanol}\% + 0.00199 \text{ Ethanol}\%^2 \quad (3)$$

$$\text{Octane Number} = 88.2 + 0.387 \text{ Ethanol}\% + 0.247 \text{ Toluene}\% + 0.351 \text{ Ethers}\% \quad (4)$$

$$\text{Octane Number} = 94.3 + 0.295 \text{ Ethers}\% \quad (5)$$

$$\text{Octane Number} = 90.1 + 0.387\text{Ethanol}\% + 0.234\text{Toluene}\% \quad (6)$$

$$\text{Octane Number} = 93.3 + 0.213 \text{ Xylene}\% \quad (7)$$

$$\text{Octane Number} = 90.0 + 0.426 \text{ Ethanol}\% + 0.238 \text{ Xylene}\% \quad (8)$$

$$\text{Octane Number} = 90.9 + 0.247 \text{ Toluene}\% + 0.351 \text{ Ethers} \quad (9)$$

**Fig. 1** shows the RON of the different experiments of the table of DOE of this work, it confirms that the addition of the suggested materials in any blend raises the RON to a range of 80-103, the maximum RON is with experiment No. 27 and the lowest RON is with experiment No. 30.

**Fig. 2** illustrates the minimum cost for the blend is in experiment No. 13 and the maximum cost occurs with experiments 7 and 30. The blend of experiment 13 which contain only 15 ethanol vol % (experiment 13) has reasonable cost (700-750 IQD) and it is competitive with the cost of high RON gasoline imported from outside Iraq. The blend from experiment 13 yields RON of 89.6 (around 90).

**Fig. 3** and **4** show that the relationship between the volumetric percentage of additives used in this work and the resulted RON is linear and RON increase with the increase of additive material added (ethanol, toluene, ether, and Xylene), this is because those additives have high RON.





**Fig. 5-9** show the contours of the RON with different materials added and from those contours the exact composition of the composite octane number blend enhancer for the required RON of the gasoline can be deduced for any value of Octane number required.

#### 4. CONCLUSIONS

The following results are obtained from this research:

1. Low octane number gasoline produced in refineries and distributed to gasoline stations can be improved by adding octane number enhancer depending on the octane number required and the cost that the user can pay for it.
2. Ethanol can be used easily with the volumetric percent of 15% as octane number enhancer to low octane number regular gasoline to raise its octane number and making it as premium unleaded gasoline.
3. Octane number composite enhancer can be used for special engines even for aircraft to get excellent gasoline of more than 100 RON.
4. The benefit of this composite octane number is that it can be purchased from the drivers and added to the gasoline when each filling from the gasoline station made and anywhere, (5 Liter container can be enough for a trip of about 500 km). Also, this idea will remove the pressure on refineries to produce high octane number when there is no ability to build expensive units in petroleum refineries and when the capacity of the refining is under the capacity of demand to gasoline or when there are no refineries in damaged governorates like Mosul or Anbar...etc.
5. The suggested composite octane number enhancer will supply gasoline with greenhouse gases and without using prohibited environment tetra ethyl led additives.
6. The cost was estimated on personal market and with small quantities, when the government apply the idea for this work, the cost can be reduced very much because of importing the materials from the original manufacturing companies with lower prices and for ethanol, it can be produced in Iraq with lower prices because Iraq is rich dates palm which is the raw material for fermentation to produce ethanol and will also give a chance for many work opportunities to unworked youth people.
7. In this work, new composite octane number enhancers were approved in addition to the previous researches of using only ethanol to gasoline.
8. Ethanol will be very effective in the engine of the cars at higher speed and it was shown by its emission results in table

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**Table 1.** RON & MON for the materials used in the blend of the composite enhancer.

Serial	Material	Research octane number(RON)	Motor Octane Number(MON)
1	Toluene	124	112
2	Xylene	120	103
3	Ethanol	108.6	89.7
4	Ethyl Ether	110.5	-

**Table 2.** Specification of base gasoline produced in Doura refinery (low ON) used before addition of blending agent.

Serial	Property	Value
1	Specific Gravity @15.6 °C	0.7012
2	API @15.6oC	70.3
3	Research Octane Number	79
4	Reid Vapor Pressure (R.V.P) psi	13
5	Distillation	
	Initial Boiling Point °C	32
	10%	41
	20%	47
	30%	53
	40%	60
	50%	68
	60%	78
	70%	109
	80%	138
	90%	178
	Total Distillate	99.5ml
	Residue	0.5ml
	Losses	1.0ml
	Distillate at 100 °C	75ml
	Distillate at 145 °C	92 ml

**Table 3.** Design of experiments (DOE) of this study by statistical software Mini Tab 15.

No. Of Experiment	Ethanol Vol%	Toluene Vol %	Xylene Vol%	Ether vol%
1	7.5	12.5	12.5	5.0
2	7.5	12.5	12.5	5.0
3	7.5	12.5	12.5	15.0
4	7.5	12.5	12.5	5.0
5	7.5	12.5	12.5	5.0
6	7.5	12.5	12.5	5.0
7	7.5	12.5	37.5	5.0
8	7.5	37.5	12.5	5.0
9	22.5	12.5	12.5	5.0
10	7.5	12.5	12.5	5.0
11	15	0.0	25.0	10.0
12	0.0	0.0	25.0	0.0
13	15	0.0	0.0	0.0
14	0.0	0.0	25.0	10.0
15	15	25.0	0.0	0.0
16	0.0	0.0	0.0	0.0
17	15	0.0	25.0	0.0
18	15	25.0	25.0	10.0
19	7.5	12.5	12.5	5.0
20	15	0.0	0.0	10.0
21	0.0	25.0	25.0	0.0
22	7.5	12.5	12.5	5.0
23	0.0	25.0	0.0	10.0
24	7.5	12.5	12.5	5.0
25	0.0	25.0	25.0	10.0
26	15	25.0	0.0	10.0
27	15	25.0	25.0	0.0
28	0.0	25.0	0.0	0.0
29	7.5	12.5	12.5	5.0
30	0.0	0.0	0.0	10.0





**Table 4.** Results of tests on samples of DOE.

Test	Experiment No.																
	1	21	23	7	12	3	8	9	15	13	20	30	25	26	27	28	11
SG @15.6°C	0.748	0.774	0.79	0.791	0.736	0.76	0.786	0.761	0.75	0.709	0.716	0.7	0.783	0.76	0.79	0.74	0.752
RVP psi	1.62	1.47	2.35	1.029	1.47	2.94	2.646	2.94	1.47	2.94	2.646	2.94	1.176	1.176	1.16	1.18	1.176
Distillation																	
IBP °C	48	38	40	45	42	49	47	40	43	42	41	38	40	46	48	42	41
10%	59	69	54	69	62	59	64	61	56	50	51	48	62	60	65	56	55
20%	64	64	59	70	74	66	70	67	62	55	56	52	69	66		68	62
30%	69	94	64	74	84	70	72	71	69	60	62	58	72	70	70	81	68
40%	70	102	65	98	108	76	90	75	73	65	66	62	100	74	74	92	71
50%	107	104	102	118		77		76	73	69	70	66		76	79		75
Rec. @ 100 °C	48	-	-	42	40	55	42	66	55	67	71	72	41	67	43	47	56
RON	95.6	98.5	93.5	101.3	90.6	100.2	102.3	101.6	97.2	89.6	96	85.7	101.8	101	103.1	90.3	103



**Table 5.** Results for cost estimation and ON improvement percent for all the gasoline samples prepared.

Experiment No.																	
11	28	27	26	25	30	20	13	15	9	8	3	12	7	23	21	1	Additive
15	0	15	15	0	0	15	15	15	22.5	7.5	7.5	0	7.5	0	0	7.5	Ethanol
0	25	25	25	25	0	0	0	25	12.5	37.5	12.5	0	12.5	25	25	12.5	Toluene
25	0	25	0	25	0	0	0	0	12.5	12.5	12.5	25	37.5	0	25	12.5	Xylene
10	5	0	10	10	10	10	0	0	5	5	15	0	5	10	0	5	Ethers
103	90.3	103.1	101	101.8	85.7	96	89.6	97.2	101.6	102.3	100.2	90.6	101.3	93.5	98.5	95.6	RON
30.37	14.30	30.50	27.84	28.86	8.48	21.51	13.41	23.03	28.6	29.49	26.83	14.68	28.22	18.35	24.68	21.01	% Reform
2050	750	2050	1300	2250	500	800	300	800	1575	1775	1775	1250	2525	1000	1750	1275	Cost Est. for the blend added per liter Gasoline Iraqi Dinar



Table 6. Cost for the materials used in the composite blend ON enhancer.

Serial	Material	Price IQD/Lt.
1	Ethanol	2000
2	Toluene	2000
3	Xylene	5000
4	Diethyl ether	5000

Table 7. Emission results for Normal gasoline.

N rpm	Torque	CO	CO <sub>2</sub>	HC	O <sub>2</sub>	NO <sub>x</sub>
1300	3	5.4	3.7	624	22	20
1400	4.5	3.61	6	471	22	124
1500	5.5	3.5	6.7	418	22	220
1600	6.1	4.05	6.8	428	22	161

Table 8. Emission results for modified gasoline with ON enhancer composed of 15% vol ethanol.

N rpm	Torque	CO	CO <sub>2</sub>	HC	O <sub>2</sub>	NO <sub>x</sub>
1300	3	3.9	3.9	494	22	30
1400	4.5	1.4	6.3	334	22	293
1500	5.5	3.3	5.3	366	22	141
1600	6.1	0.833	7.7	384	22	490

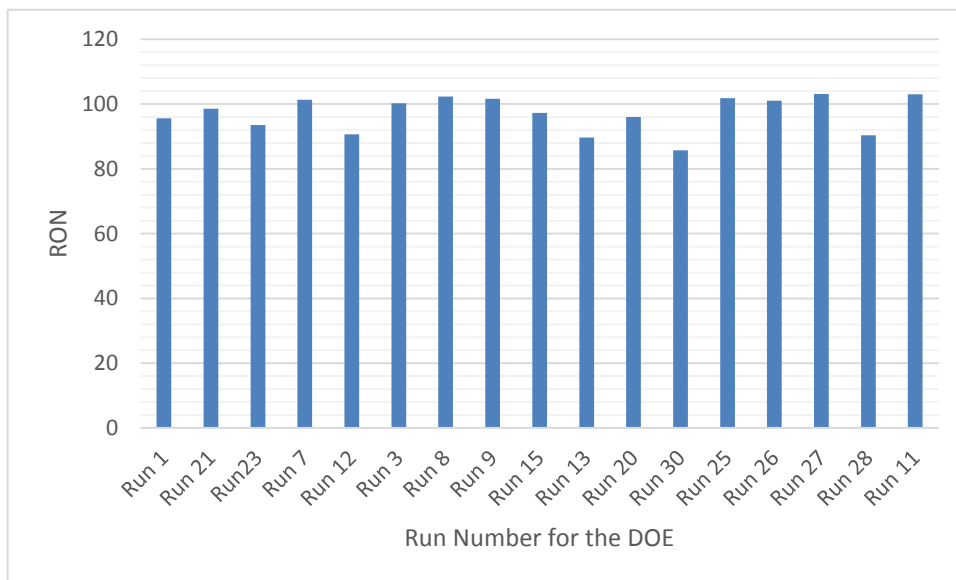


Figure 1. Results of research octane number for different runs Of DOE.

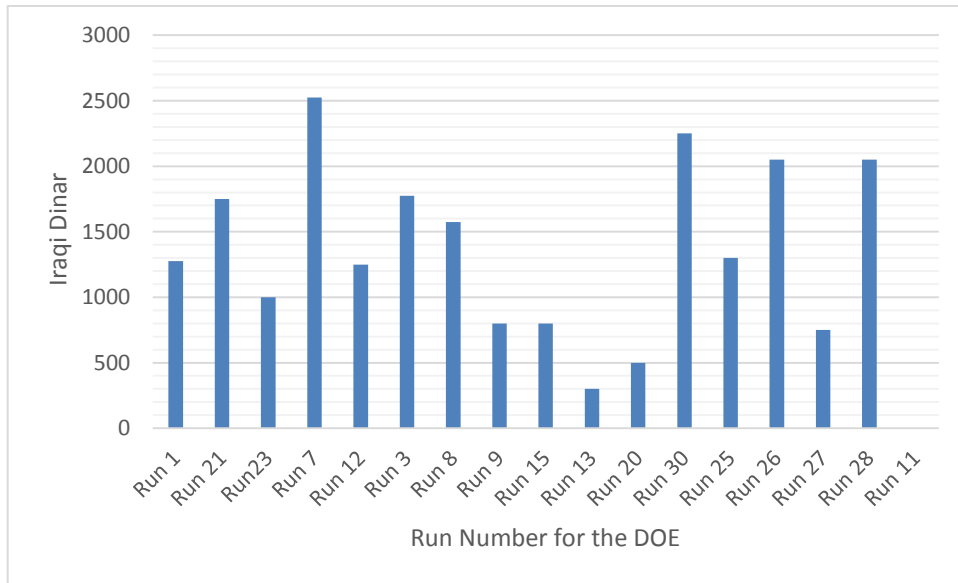


Figure 2. Cost of the blend for different runs of DOE.

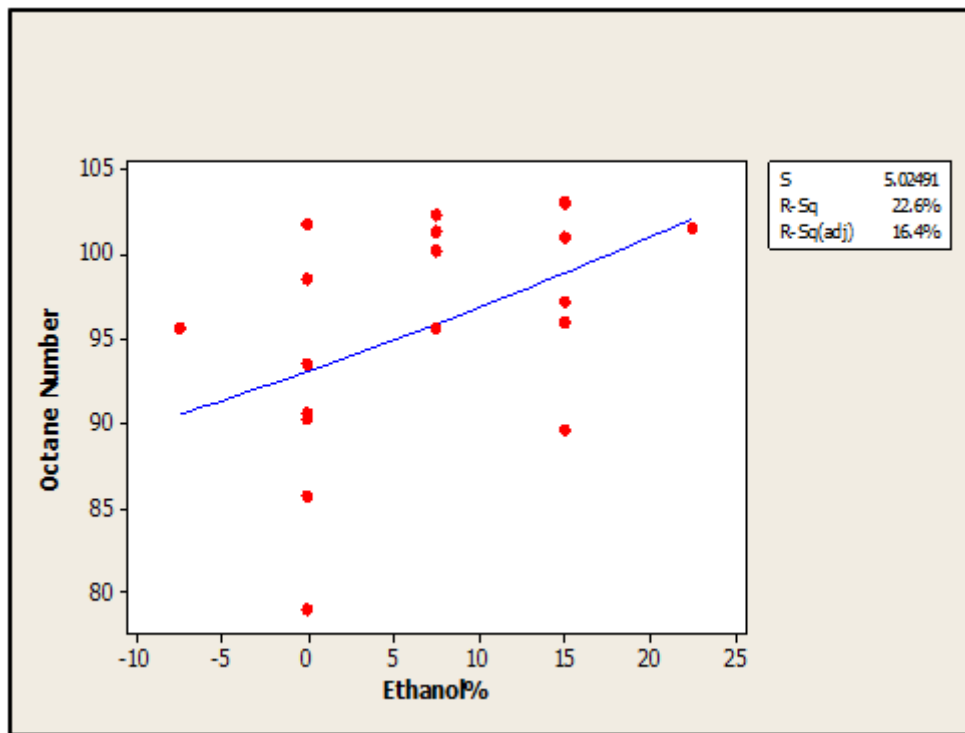


Figure 3. Fitted line plot for octane number with ethanol.

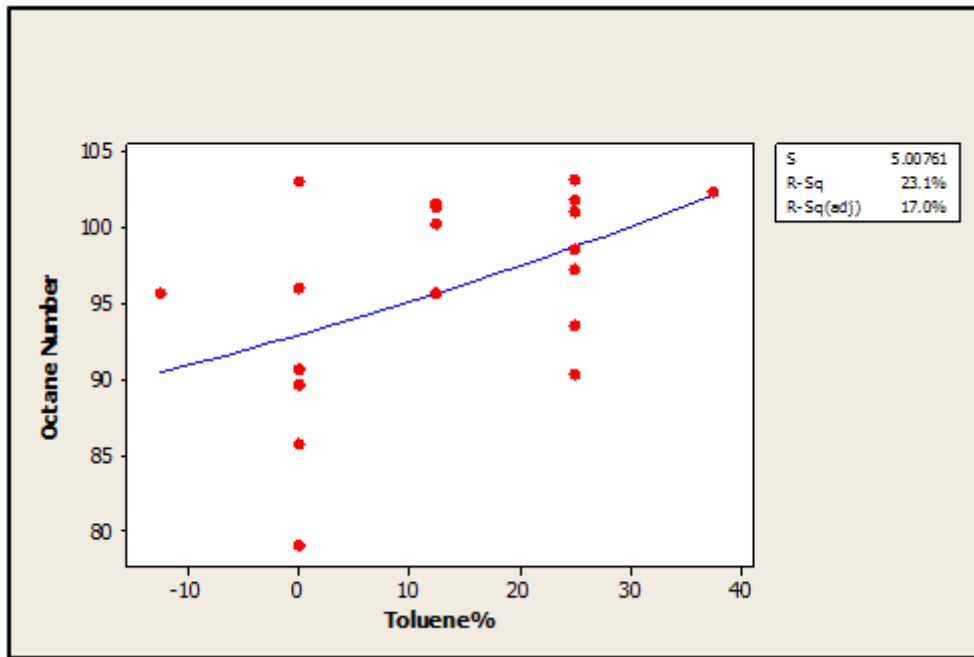


Figure 4. Fitted line plot for octane number with toluene.

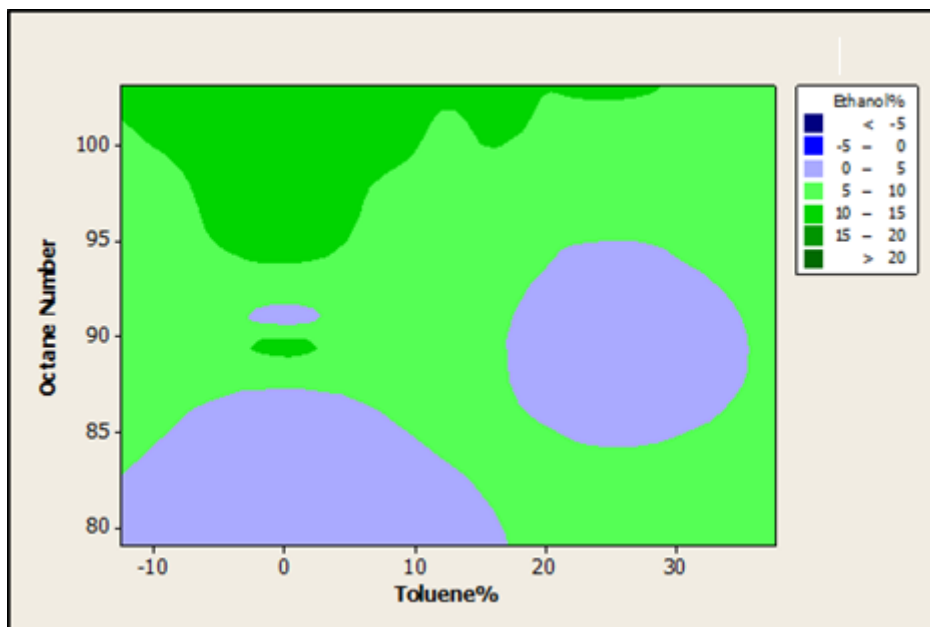


Figure 5. Contour plot of ethanol vs octane number, toluene%.

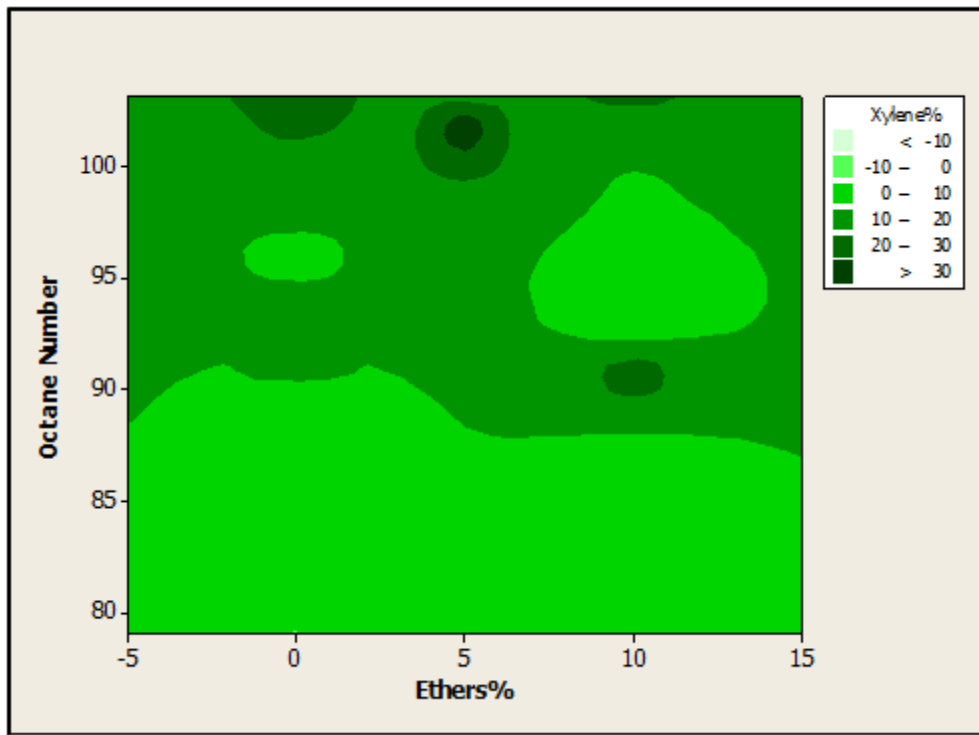


Figure 6. Contour plot of xylene vs octane number, ethers%.

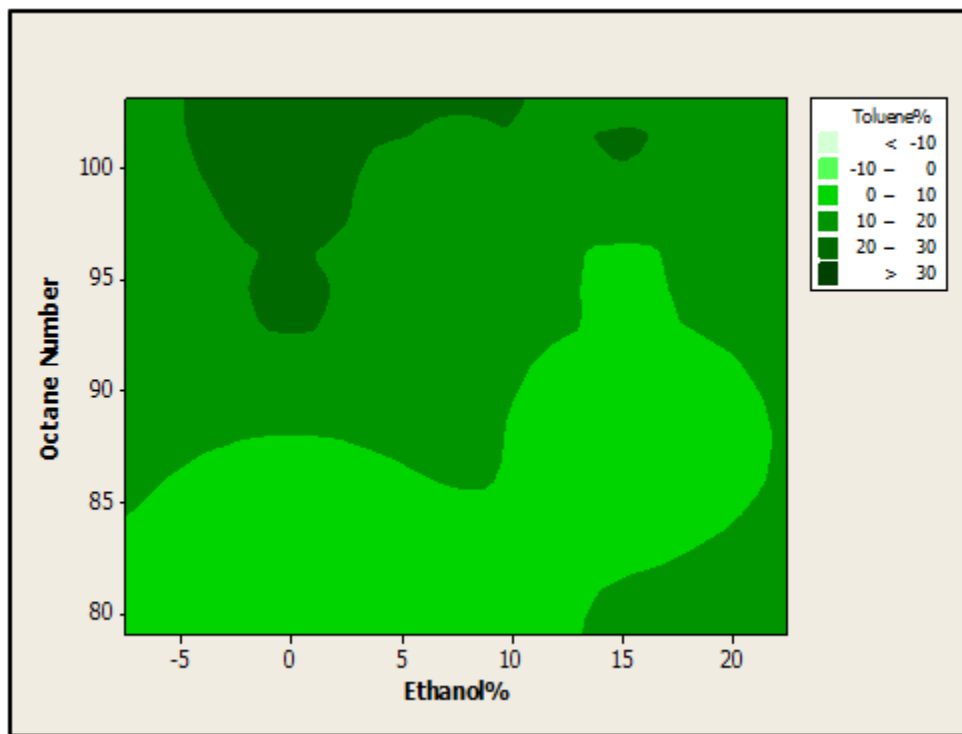


Figure 7. Contour plot of toluene vs octane number, ethanol%.



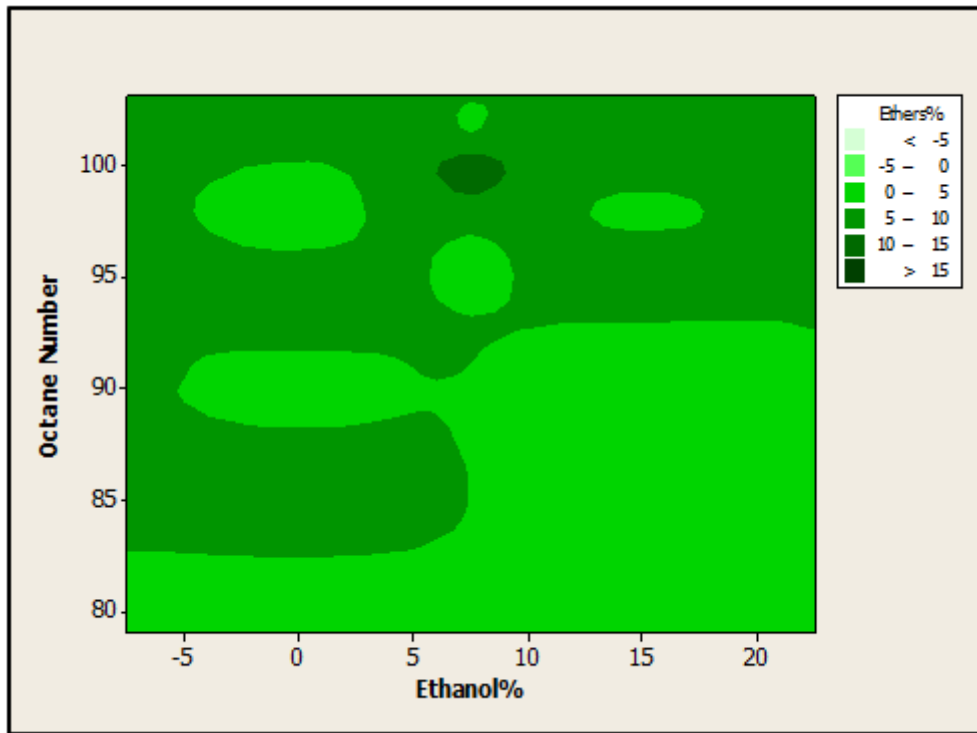


Figure 8. Contour plot of ether vs octane number, ethanol%.

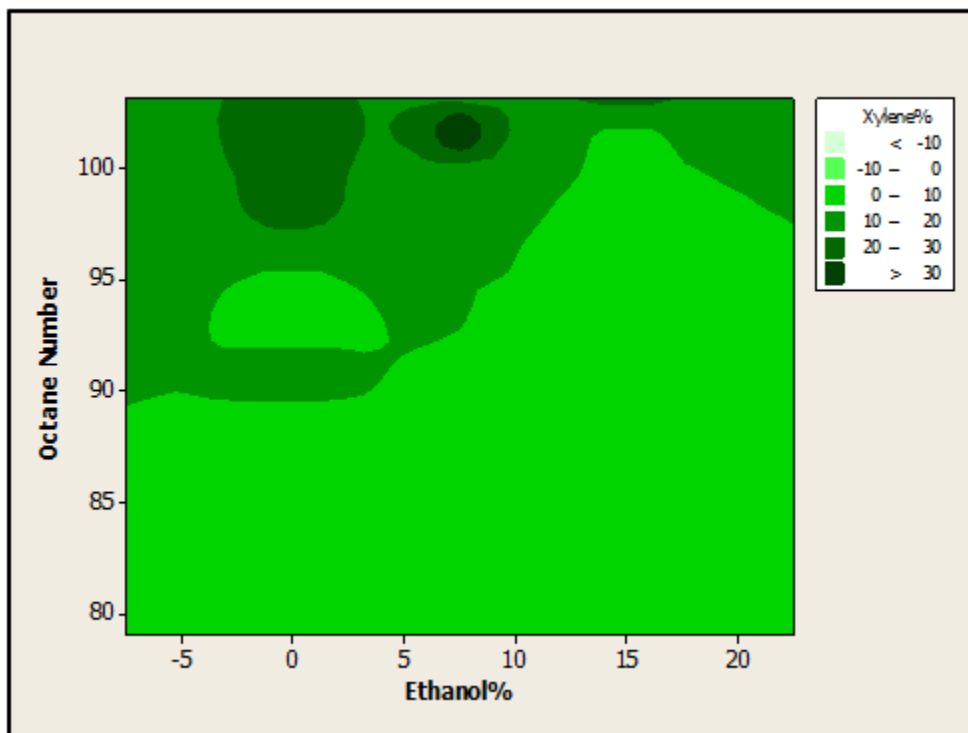


Figure 9. Contour plot of xylene vs octane number, ethanol%.