# Improvement of Gasoline Octane Number by Using Organic Compounds

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## Abstract:

The toxic lead additives to gasoline are no longer used in many countries around the world. Many other countries are now phasing out the lead in gasoline. Although the lead fuel is still in use in Iraq, several plans are considered to phase out the lead. The use of organic compounds to replace the lead additives in gasoline is considered now as an option in Iraqi refineries.

The main objective of this project was preparation of premium gasoline, by blending of gasoline with Alternative additives (alcohol, aromatic) to enhancing octane number of Al-Doura gasoline pool. Improved gasoline was tested by ASTM standard method which includes octane number measuring by CFR engine analyzer.

Gasoline pool RON (80) was used and selective components were added to the gasoline pool (1-3%) to improving it octane, such as ethanol, methanol,isopropanol,isobutanol, benzene, nitrobenzene, Aniline, and nitro aniline. Octane number of blends was measured by CFR engine. Mixture of alternative additives was prepared and adding in 1-3%vol to the gasoline pool.

It was found that the additives show significant improvement of octane number of gasoline but the important increasing of RON was shown on use mixture of alcohols and aniline.

**Key words: gasoline, octane number, antiknock additive, CFR analyzer**

## Introduction:

Internal combustion engines produce moderately high pollution levels, due to incomplete combustion of carbonaceous fuel, leading to carbon monoxide and some soot along with oxides of nitrogen , sulfur and some unburnt hydrocarbons, depending on the operating conditions and the fuel/air ratio[1].

Gasoline is a complex mixture of hydrocarbons that normally boils below 355°F (180°C) or at the most, below 390°F (200°C). The hydrocarbon constituents in this range are those that have 4 to 12 carbon atoms in their molecular structure. These hydrocarbons fall into three categories such as paraffins, olefins and aromatics [2]. Automotive gasoline has been classified into two grades, premium and regular on the basis of octane number. Gasoline with higher octane number has numerous benefits including reduced exhaust emissions [3] and engine noise, improved cold starting and engine durability. The key indication of performance property of gasoline under various engine conditions is its octane number (ON) which included : Research Octane Number (RON) and

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Motor Octane Number (MON).Finished gasoline must meet certain octane number specifications[4,5] .
Octane Number is defined as the volume percentage of iso octane in blend of normal heptane and iso octane , which produces the same knock intensity as the test fuel under standard test conditions in an ASTM internal combustion engine[5].

In the last 80 years ,the petrochemical methods for the production of fuels improved continuously to meet the demand both on the simultaneously growing amounts and the constantly increasing knock resistance of gasoline. Different additives were applied to achieve the required specifications of the highly knock resisting super grade gasolines used today . Selective components were used as antiknock agent to improve octane number of unleaded gasoline divided to many groups: metallic, alcohols, aromatics ,and others[6].
Historically ,lead has been an important source of increasing octane number. Because of the harmfulness of tetra ethyl lead ,its use has been forbidden in almost all countries[7] .
The addition of oxygenates to gasoline offers many advantages, among which: more complete combustion and reduction of carbon monoxide emission ,being a renewable energy source ,increased octane number ,and increased volatility. There are also disadvantages in adding oxygenates to gasoline among which includes: corrosion, lower energy content, increased cost, and increased volatility[8].

Alcohols are higher octane number than typical gasoline. They are more effective in low octane gasoline than in high octane gasoline. The behaviour of alcohols in mixed component as octane improvers of gasoline was not known and the literature of this subject is few [9].
Thus ,the main objective of this research was to study the effect of the addition of aromatic and alcoholic compounds (each of them alone and together ) to the gasoline fuel that produced in Al-Doura Refinery by measuring octane number by CFR engine.

## Materials and Methods:

**Table (1)Nomenclature**

| Symbol | Descrption |
|---|---|
| ASTM | American Socety for Testing Material |
| RON | Research Octane Number |
| MON | Motor Octane Number |
| Sp.gr | Specific Gravity |
| RVP | Reid Vapor Pressure |
| Temp | Temperature |
| I.B.P | Initial Boiling Point |
| AKI | Antiknock Index |
| CFR | Cooperative Fuel Research |
| E.B.P | Ending Boiling Point |

**Materials**
1- Gasoline
Gasoline were used and obtained from Al-Doura refinery which have properties and test methods are clearly defined in the table (2).

**Table (2)Specification and Test Method of Al -Doura Commercial Gasoline**

| Properties Items | Test Methods | A-Doura Commercial Gasoline |
|---|---|---|
| Sp.gr. | IROX test | 0.856 |
| RVP bar | ASTM D323 | 6.5 |
| Distillation | ASTM D86 | |
| Temp C° I.B.P. | | 40 |
| %10 | 43 | 62 |
| %20 | 52 | 67 |
| %30 | 58 | 75 |
| %40 | 63 | 85 |
| %50 | 68 | 98 |
| %60 | 74 | 114 |
| %70 | 80 | 129 |
| %80 | 86 | 143 |
| %90 | 97 | 167 |
| E.B.P | 115 | 219 |
| Max.Soot content ppm | ASTM D4294 | 648.6 |
| Water content ppm | ASTM D4928 | 133.09 |
| Existent gum mgm/100ml | ASTM D381 | 3.4 |
| Calorific value kcal/kgm1 | 11488 | 11253 |
| MON | ASTM D2700 | 80 |
| RON | ASTM D2699 | 84 |
| Aromatics vol% | IROX test | 60.91 |
| Olefins vol% | IROX test | 0 |
| Naphthenes vol% | IROX test | 2.35 |
| Paraffins vol% | IROX test | 36.74 |

2- Absolute methanol, absolute ethanol ,isopropanol ,isobutanol ,benzene, nitrobenzene, aniline, and m-nitroaniline of 99.95% purity were of analytical reagent grade and were obtained from SIGMA COMPANY.

## Experimental procedure

### 1- First Stage

All selective components are added to the Al- Doura gasoline at different vol% as follow:

1- 300ml of gasoline was prepared at refrigerator temp. in glass container had fitting cover.

2- Octane number of gasoline was measured by CFR engine.

3-(1.5-6) ml of each component included (methanol ,ethanol, isopropanol, isobutanol, benzene ,nitrobenzene, aniline) were taken by using pipette to blend with 300 ml of gasoline in glass container with shaking , and wieght amount of m-nitroanilline and dissolved in solvent ,next add to gasoline container.

4- Octane number of these blend were measured by CFR engine.

5-Repeat the 3 and 4 with another selective component.

### 2-Second Stage

Additives prepared from selective components which used at different vol% by blending components which appeared activity to enhancement octane preparation of pool like alcohols and aromatics in different vol%. All prepared additives were tested by added to prepare pool and measured octane number of the blends as follows:

1- 300 ml preparation gasoline must be prepared for measuring octane number by CFR engine.

2- (3-9)ml of prepared additives were taken by using pipette to blend with 300 ml of gasoline in glass container with shaking.

3-Octane number of blended gasoline is measured by CFR engine.

### Analysis Method

Cooperative Fuel Research Engines (CFR) (D2699, D2700) was used to determine the octane number as follows:

1- The Research octane number RON of a spark-ignition engine fuel is determined using a standard test engine and operating conditions to compare its knock characteristic with those of PRF blends of known RON. Compression ratio and fuel-air ratio are adjusted to produce standard AKI for the sample fuel, as measured by a specific electronic detonation meter instrument system. A standard AKI. guide table relates CFR engine to RON level for this specific method. The fuel-air ratio

for the sample fuel and each of the primary reference fuel blends is adjusted to maximize AKI for each fuel.

2- The fuel-air ratio for maximum AKI. may be obtained:

a-By making incremental step changes in mixture strength, observing the equilibrium AKI value for each step, and then selecting the condition that maximizes the reading .

b-By picking the maximum AKI as the mixture strength is changed from either rich-to-lean or lean-to-rich at a constant rate (ASTM D2699 1989).

## Results and Discussions

To find the optimum dosage of chemical components that enhance the octane number of the gasoline produced in Al-Doura Refinery, chemical components were used as in the different stages.

**1- First Stage**

It was been investigated that the effectiveness of different components in Al-Doura refinery gasoline. The following were used as the octane-increasing components in the studies:

1- Alcohols. 2- Aromatics Compounds. Selective components are added to the Al-Doura gasoline pool in various 0.5-3vol% and octane number is measured by CFR engine, as follows:

**Alcohol components:** Alcohols were used as antiknock agent to enhance octane value of unleaded gasoline. Alcohol components added to Al-Doura gasoline in various vol%, octane number was measured by CFR engine, and the results are listed in table(3).

**Table (3)Octane Number of Al-Doura Refinery Unleaded Gasoline with Alcohol Components in Different vol%**

| Alcohol Components | Vol% | | | | |
|---|---|---|---|---|---|
| | 0 | 0.5 | 1 | 1.5 | 2 |
| Methanol | 80 | 82 | 82.5 | 83 | 83.5 |
| Ethanol | 80 | 80.5 | 81.1 | 81.6 | 82 |
| Isopropanol | 80 | 82.4 | 83.2 | 83.7 | 84 |
| Isobutanol | 80 | 81.5 | 82 | 82.5 | 83.5 |

Methanol, ethanol, isopropanol,and isobutanol in the amount of 0.5-2 vol% are used as octane booster. They are attractive because of their low cost in comparison to other components. On addition of 2 vol% alcohol components, the octane number of gasoline increased by 2-4 points. Isopropanol can thus be recommended as an octane booster for production of high octane unleaded gasoline. The oxygen ratio content in alcohol was an influence factor on RON of blended gasoline with alcohol components.

**Aromatics Components:** Selected aromatics components added to Al-Doura pool in various vol%, octane number was measured by CFR engine. From the result appears in table (4) it can be concluded that benzene and nitrobenzene had same effect for increasing octane value of blended Al-Doura refinery unleaded gasoline at the 2 vol%, while aromatic amine (aniline) in concentration at 2 vol% increasing the octane number by 7.5 points.

**Table (4) Octane Number of Al-Doura Refinery Unleaded Gasoline with Aromatic Components**

| Aromatic Components | vol% | | | | |
|---|---|---|---|---|---|
| | 0 | 0.5 | 1 | 1.5 | 2 |
| Benzene | 80 | 80.6 | 81.2 | 82.1 | 83 |
| Nitrobenzene | 80 | 81.1 | 81.7 | 82.3 | 83 |
| Aniline | 80 | 82 | 84.2 | 86.1 | 87.5 |
| Nitroaniline | 80 | 81 | 81.2 | 81.2 | 81.2 |

For nitro compounds the proposed mechanism of ignition is free radical

,the nitro group cleave at space and time in the stratified injection spray such that the corresponding free radicals together with free radicals of fuel are sufficient to promote quicker ignition, the nitro group must cleave neither too early nor too late. In addition ,the aromatic ring should be free of groups that tend to stabilize the radical formed by the cleavage of the nitro group and thus aromatic rings are undesirable because of their ability to stabilize free radicals and delay the ignition[10]. As a result nitro aromatic compounds don't shown significant increasing octane number of gasoline.

**2- Second stage**

Optimum result may be obtained by using a mixture of alcohols. RON 84.2 was obtained from blending prepared unleaded gasoline with 2% vol preparation of components mixture which contain mixed alcohols and appear in table (5).

**Table (5) Octane Number of Al-Doura Refinery Unleaded Gasoline with Preparation Alcohols Mixture**

| Vol % | RON | Increasing RON |
|---|---|---|
| 0 | 80 | 0 |
| 0.5 | 81.6 | 1.6 |
| 1 | 82.2 | 2.2 |
| 1.5 | 82.7 | 2.7 |
| 2 | 84.2 | 4.2 |

Optimum result may be obtained by using a mixture of additives so as to ameliorate the deficiencies of each the additives. RON 89.3 was obtained from blending prepared unleaded gasoline with (1.5%mixed alcohols and 1.5 %aniline) components mixture; blended RON was measured by CFR engine. The results of blended RON for blending prepared component mixtures which contain (alcohols and aromatics) appear in table (6).These component mixture have the greatest effect in gasoline than use each component alone.

**Table (6) Octane Number of Al-Doura Refinery Unleaded Gasoline with Preparation Component Mixture (mixed alcohols &aniline)**

| Vol % | RON | Increasing RON |
|---|---|---|
| 0 | 80 | 0 |
| 1 | 84.4 | 4.4 |
| 2 | 87.8 | 7.8 |
| 3 | 89.3 | 9.3 |

## Conclusions:

Based on the previously discussed analyses, the following conclusions may be drawn:

- The experimental results of this project for RON measuring method showed fast, accuracy, and reliable analysis of gasoline.
- All selective chemical components act positively to improved octane number of Al- Doura gasoline.
- The Octane Booster of this project was Aniline, which was recorded the largest RON.
- Mixture of component was prepared from active selective components; include alcohol and aromatic compounds.
- The best preparation component mixture is better act with high octane gasoline than use each component alone.

**Recommendations**

There is still a need to generate data and experience by running tests and analyzing the environmental effects of blending gasoline. Thus the need to apply the precautionary principle to any gasoline blending component, and insist on a thorough evaluation of implications of such a decision. We must be much more certain of the toxicity, persistence and bioaccumulation of gasoline blending components, since it is given that these

chemicals will be used in large amounts throughout the world.

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# تحسين العدد الاوكتاني للكازولين باستخدام مركبات عضوية مختلفة

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**الخلاصة:**
لقد تم الاستغناء عن استعمال مركبات الرصاص السامة كمضافات رئيسية إلى الكازولينِ في العديد مِنْ بلدانِ العالمِ غير إن هنالك بعض الدول مازالت لحد ألان تستعمله والعراق من بين هذه الدول. ،إلا انه وضعت خطط عديدة للاستغناء عن استخدامه واستعمال المركّباتِ العضوية كبدائل للإضافاتِ الرئيسيةِ في الكازولينِ في المصافي العراقيةِ.
ويهدف البحث الحالي إلى دراسةِ تأثيرِ المركّباتِ العضويةِ الأكثر شيوعا على تَحسين العددِ الأوكتانيِ للكازولينِ في مصفى الدورة وكذلك فيَ تحضيرَ الكازولينِ بمَزْجه مع بَعْض المضافات الإنتقائيةِ) الكحولات، المركبات الاروماتية (وقياس العدد الأوكتاني للكازولينَ بطريقة محلل المحركِ القياسية .
لقد تم استخدام الكازولين ذو العدد الاوكتاني 80 كأساس وتمت إضافة االكحولات مثل الميثانول والايثانول والايسوبروبانول والايسوبيوتانول والمركبات الاروماتية مثل البنزين والنتروبنزين والانيلين والنتروانيلين بنسب تتراوح من( 0.5-2)% وتم استخدام مزيج من المضافات) الكحولات والانيلين( بنسب1-3%)وقياس العدد الاوكتاني للبنزين المحسن.
وقد وجد ان استخدام المضافات عملت على رفع العدد الاوكتاني بنسبة لاباس بها ولكن الزيادة الواضحة كانت باستخدام 3% من مزيج الكحولات والانيلين.