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New Anti-knock Additives to Improve Gasoline Octane Number

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Abstract

Gasoline is a volatile mixture of flammable liquid hydrocarbons derived chiefly from crude petroleum, which is used principally as a fuel for internal-combustion engines. Gasoline is a blend of hydrocarbons with some contaminants, including sulfur, nitrogen, oxygen, and certain metals.

The octane number of gasoline increases continuously and linearly with antiknock additives percentages in gasoline. Hence, P (180-E.BP) is a fractionation cut of power former effective compound for increasing the value of the octane number of gasoline when added to unleaded gasoline in percentage of 5, 10, and 15 on volume basis. The engine performance improves as the percentages of P increase in the blend. Fuel additives are used to improve gasoline performance in vehicles and to reduce specific emissions.

Key word: Gasoline antiknock additives, Octane number enhancing, and TEL phase out.

Nomenclature Introduction

Cooperative Fuel Research.	**CFR**
Methylcyclopentadienyl Manganese Tricarbonyl.	**MMT**
Motor Octane Number.	**MON**
Methyl Tert-Butyl Ether	**MTBE**
Octane Number	**ON**
Power Formate cut (180C-E.Bp.).	**P**
Research Octane Number.	**RON**
Tetra Ethyl Lead.	**TEL**
Tetra Amyl Methyl Ether	**TAME**
Tetra methyl lead	**TML**

Introduction

The occurrence of knock in internal combustion engines strict limitations on their efficiency and fuel economy. Knock may be minimized by engine design and adjustment of operating conditions or by the use of high octane gasoline. The required levels of antiknock quality in motor gasoline are obtained by modification of refinery processing and the blending of gasoline as well as by the use of antiknock additives. By far the most widely used additives for control of knock have been the lead alkyls; particularly tetraethyl lead (TEL) and tetra methyl lead (TML) [1].The antiknock quality of the fuel can be enhanced by the addition of lead alkyls. The lead additives enhance the antiknock quality of gasoline, but on other hand, result in the formation and emission of toxic lead compounds.

Another disadvantage of using lead additives in their damaging effect on the active materials of the catalytic devices used to control emissions. For these reason, unleaded or reduced lead fuels are currently required in many countries around the world. A more recent practice is to enhance the antiknock property of the fuel by using certain high octane oxygen containing compounds called oxygenates. One of the commonly used oxygenates is ethyl alcohol or ethanol [2].

Gasoline additives are compounds introduced into gasoline after refining to improve automotive performance or correct deficiencies [3]. Use of additives began commercially in 1923, and in the following 90 years, many varieties were developed. An important use of additives is reducing engine knock, and for more than 70 years, organ metallic were the additives of choice [4]. Many articles exist detailing these additives and their history [5-11].

The phase out of lead from gasoline coupled with changes in economics of refinery operations has resulted in fuels which can be increasingly aggressive.

This stems from the need to maintain gasoline octane requirements which are necessary to meet goals of national automobile efficiency achieved largely through use of high engine compression ratios.

Gasoline now contains more aromatic compounds due to increased reliance on refinery hydro cracking and 0reforming operations. Many gasolines now also significantly contain oxygenated compounds to meet necessary octane requirements.

These oxygenates are principally composed of aliphatic ethers such as MTBE or TAME, but have also included various alcohols such as methanol and ethanol. These additives not only improve octane values, but also reduce net emissions of hydrocarbons and carbon monoxide [12].

Experimental work

The demand for gasoline as a motor fuel is one of the major factors which dictate the design and mode of operation of modern petroleum refinery. The gasoline product from a refinery is derived from several sources within the refinery including Al-Doura gasoline pool in Baghdad contains 45% Reformate, 25% Power Former, and 30% light Naphtha, the antiknock additives was prepared from power former fractionation by the following procedure:

(1) Power former was distilled by simple distillation unit, and the distill (180-E.Bp) was collected.

(2) Gasoline pool, and Power former cut “P” would be tested by IROX, and ASTM methods, results were shown in table (1).

(3) Power former cut “P” was added to gasoline pool (RON =84.5) at three ratios (5, 10, and 15vol %) with continuous stirring.

(4) Blend mixture’s RON was measured using the CFR engine.

As shown in Table (1), the density of the power former cut is greater than that for normal gasoline. This suggests that the mixture’s density will increase.

This will raise serious issue on the suitability or functionality of carburetor with such fuel.

Further notice is the volatility (shown by the distillation curve) of the fuels. This clearly shows that the additive has lower volatility than that for the normal gasoline. This is expected since the power former boils at higher temperatures compared with gasoline. This causes the fuel to be hard in evaporation during winter season and suits the requirements for summer season, especially in Iraq where the temperature in summer exceeds 45 ^{o}C.

Further examination of the data reveals that the additive used has greater concentration of sulfur and water content. This is also not recommended due to its adverse environmental and engine operation impact and must be cured before been used as potential additive for gasoline.

If we add to that the higher Octane Number for the additive both as MON and RON, along with the calorific value, both will allow the use of higher compression ratio engines and greatly improve its performance.

Table(1): Gasoline pool, Power former, and Power Former cut (P) properties

properties items	Test methods	Gasoline Pool	Power Former	Power former cut (180-E.BP)
Sp.gr.	IROX test	0.715	0.757	0.889
RVP bar	ASTM D323	0.6	0.37	0.09
Distillation temp. ^{o}C	ASTM D86			
IBP		36	40	180
10%		54	58	182
20%		64	77	184
30%		72	95	187
40%		82	117	189
50%		92	135	193
60%		102	152	196
70%		115	168	203
80%		129	186	208
90%		148	198	215
EBP		187	219	222
T.D.ml		98.5	98.5	99
Max.S.content ppm	ASTM D4294	43.8	34.80	57.8
Water content ppm	ASTM D4928	131.95	42.00	191.5
Existent Gum mgm/100ml	ASTM D381	1.2	Nill	0.0
Calorific value kcal/kgm		11326	11197	10740.3
MON	IROX test	80	84.80	182.1
RON	IROX test	84.5	89.30	192.3
vol%				
Aromatics	IROX test	24.25	39.23	76.3
Olefins	IROX test	0	0.00	0
Paraffins & Naphthenes	IROX test	75.75	60.77	23.7

Result and Discussion

This study as the title suggest, describes the effect of the additives on the fuel properties. The results of this study are shown in figures (1 through 5). Some sort of liner regression was utilized to help compare between the experimental and empirical data.

The empirical equation accepted for the calculation of the RON of a mixture is given below [13]:

$$\text{RON of blend} = \sum_{i=1}^{n} X_i\,(\text{RON})_i \quad \text{...} \quad \textbf{(1)}$$

Where:

X_i = concentration of component I in blends.

$(\text{RON})_i$ = octane number of component I in blends.

Using the following initial data for the pure mixture as follows: RON of Power former = 89.3; RON of Power former cut (P) = 192.3; RON = 84.5, the RON of the mixture was calculated and compared with the experimental data. The results are shown in figures (1 through 3).

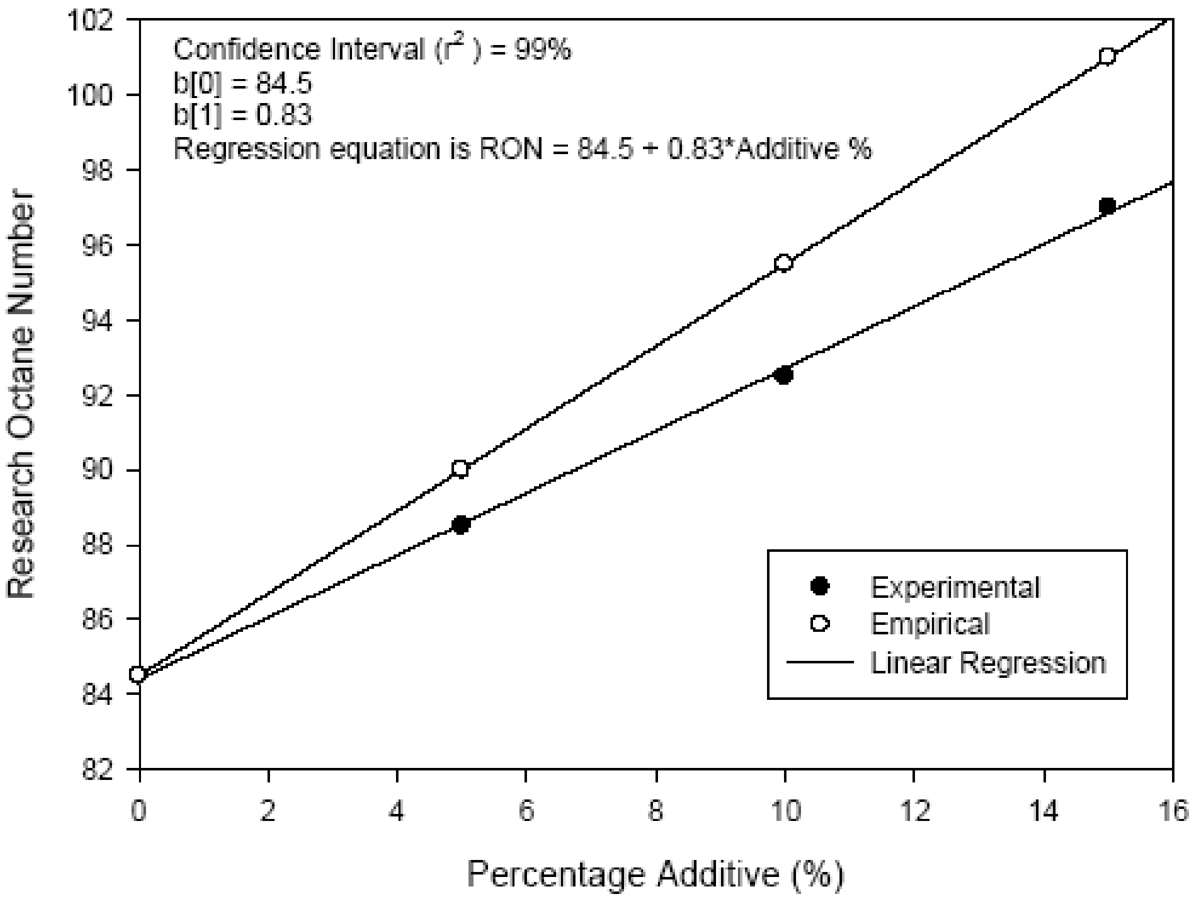

Fig (1): Variation of RON with additive percentage experimentally and predicted.

This figure shows that the research octane number increases as the additive percentage is increased. The rate of increase for the experimental data is shown by the linear regression equation to be 0.83 within the range studied. Further noticed is the wide difference between the values obtained experimentally and using empirical equation.

The amount of improvement in RON is shown in figure (2). This figure shows continuous and linear improvement with the addition of additives. With the difference in values shown for both experimental and empirical data.

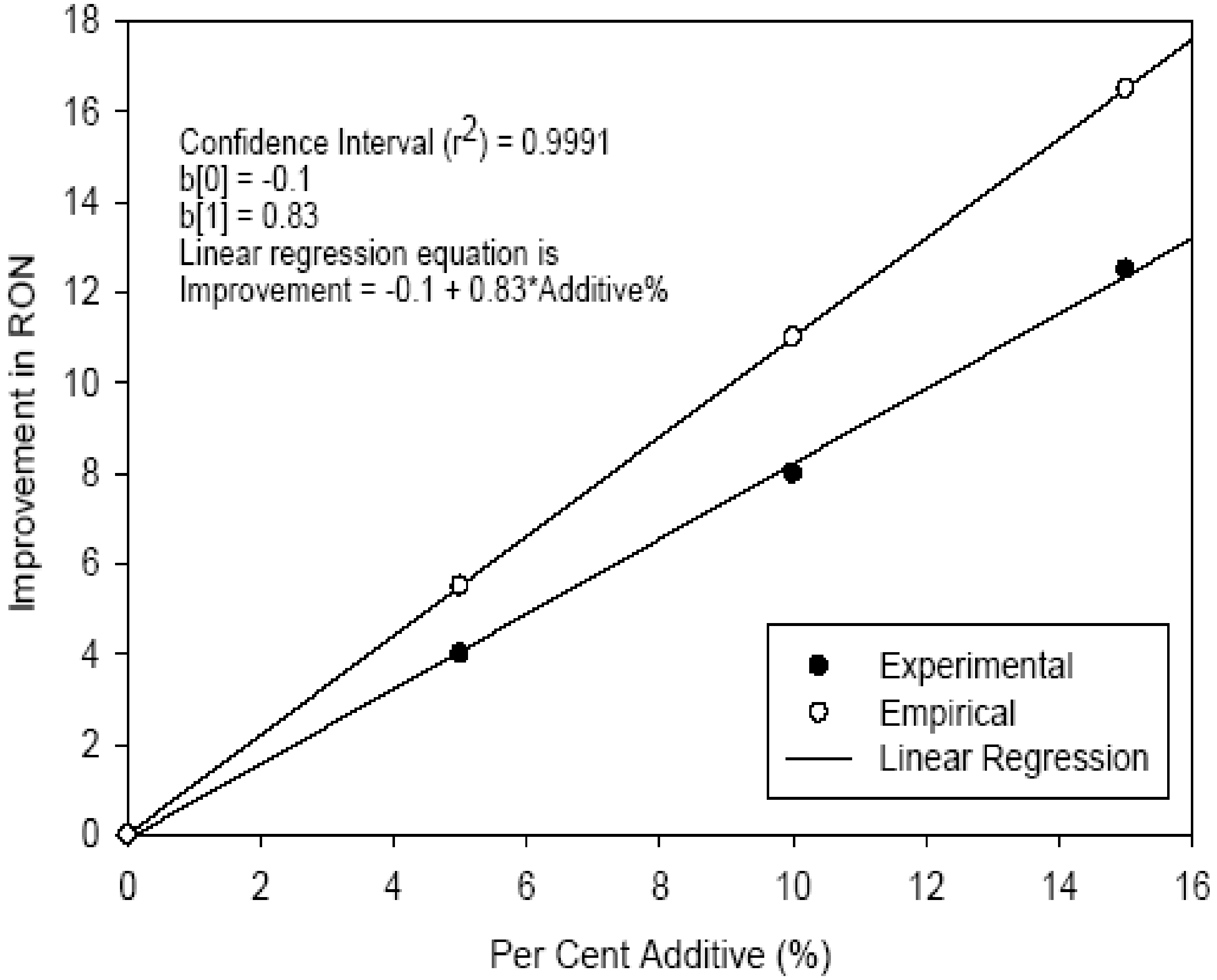

Fig (2): RON improvement with additive percentage experimentally and predicted.

Figure (3) shows linear regression analysis of the difference between both the experimental and empirical data. The figure suggests continuous difference of linear form. This implies that the empirical formula must be refined to care for this difference within this range of study.

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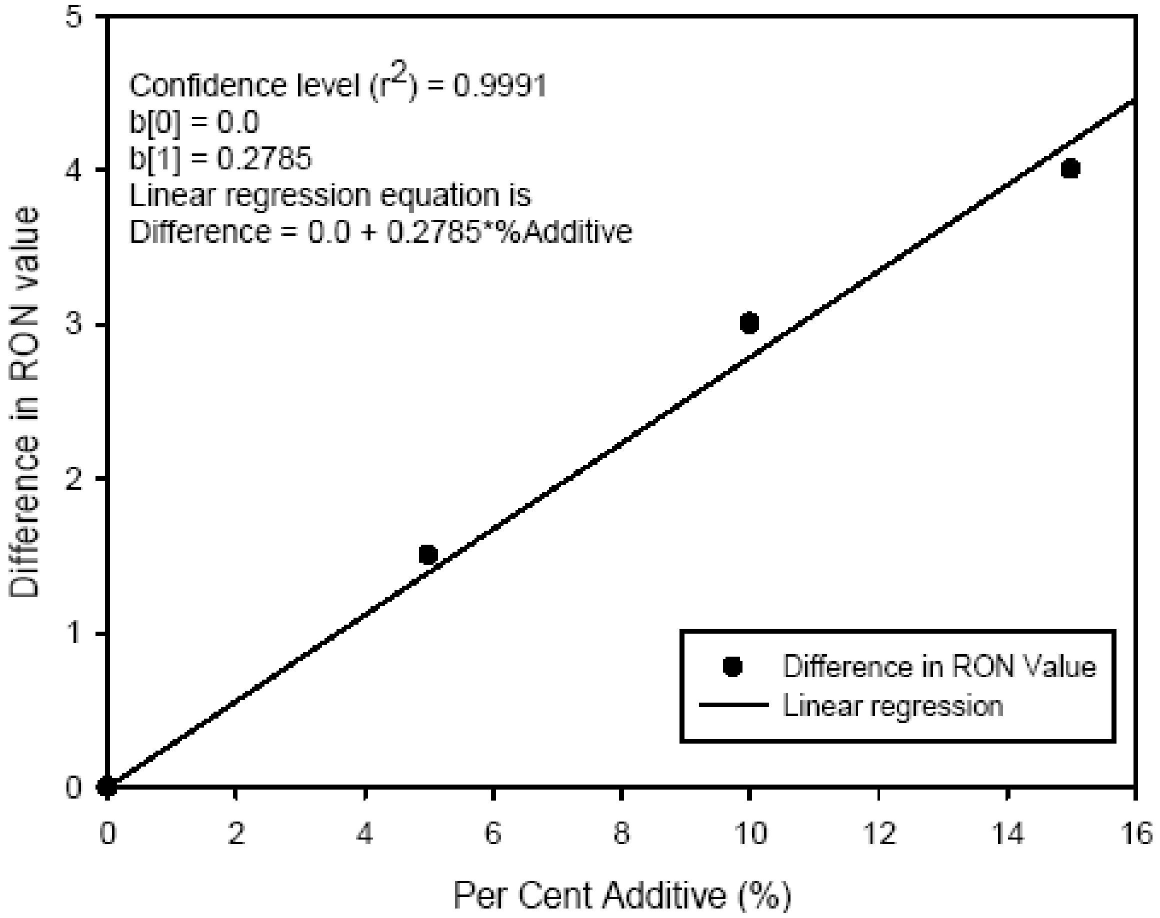

Fig (3): Error analysis between the experimental and predicted value of RON.

Table (2) shows the major constituents of the mixture that has significant effect on

the ON. As noticed, the percentage of aromatics increases with the increase in additives. This is the key factor for the change in the fuel properties. Further, since the

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aromatics are a by-product of the crude oil processing; it is advantageous to use it as

an additive to improve the properties of the fuel

Table (2): composition of blends gasoline with (P) in different ratios.

Vol.% Power former cut (P)	Aromatics Vol.%	Olefins Vol.%	Saturates Vol.%
5	**26.9**	**0.0**	**73.1**
10	**29.6**	**0.0**	**70.4**
15	**32.25**	**0.0**	**67.7**

The specific gravity of the fuel mixture was measured experimentally and the results are shown in Figure (4). As expected, due to the higher concentration of the

aromatics and heavier components of the fuel, the specific gravity of the fuel increase.

This implies that such fuel needs special attention since higher density fuels become

difficult to atomize. Hence, it must be used with specific fuel feeding systems like

injectors.

Now, the caloric value of the mixture was determined from the following empirical equation [14].

Caloric value = 12400-2100(sp.gr)^2……………………………………………(2)

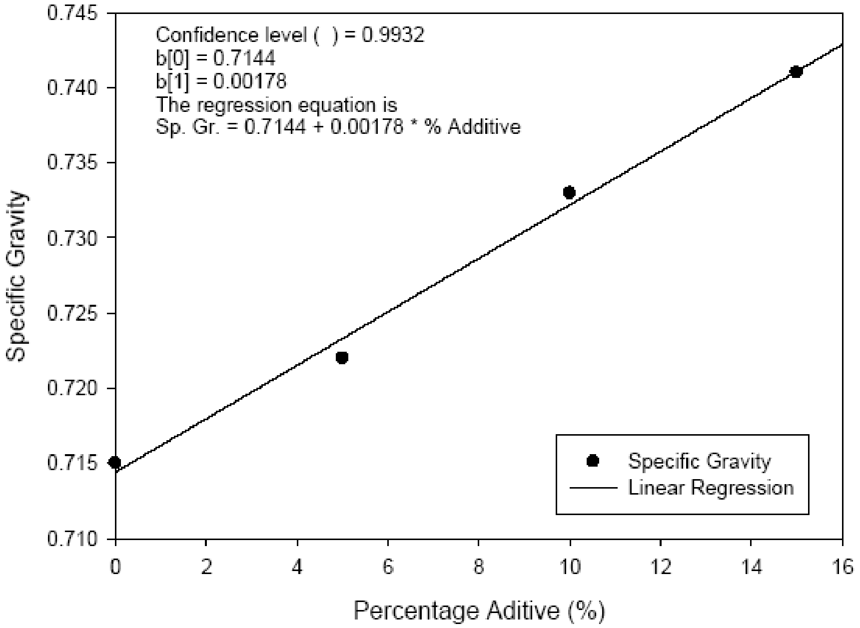

Fig (4)**:** Variation of the specific gravity with additive percentage.

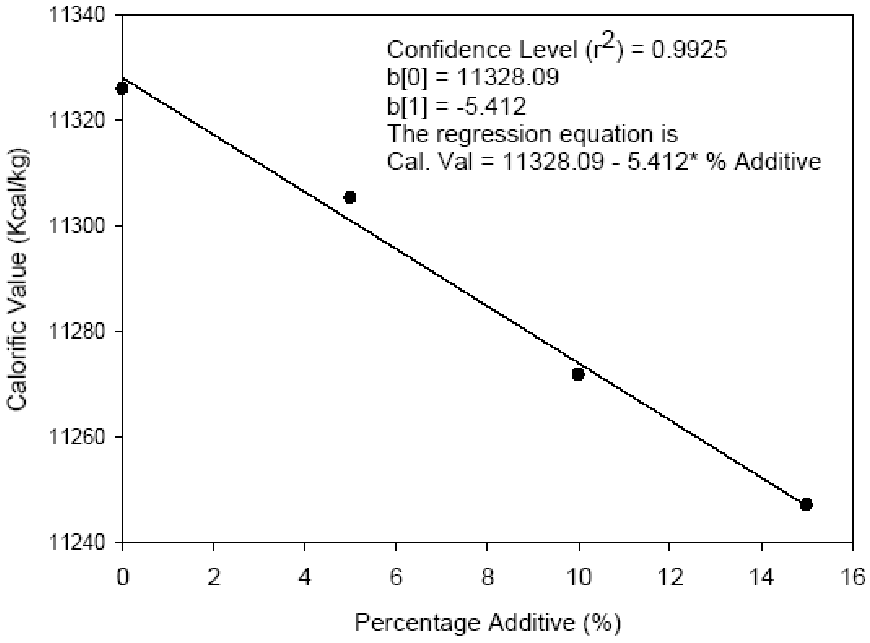

Fig (5): Variation of the calorific value with additive percentage.

As shown in the figure above, one of the major drawbacks of adding the new additive is that it reduces the energy content of the fuel. Using simple linear regression analysis, the calorific value decreases by about 0.7% maximum with 15%

additives. This can be considered as significant loss in the fuel calorific value.

Conclusion

(1) A new additive to improve the ON of the regular fuel used in Iraq was tested and has proved to be competent to TEL.

(2) The new additive significantly improved the fuel ON (within the range of additives used).

(3) The new additive prepared from the petroleum products by fractionation contains (76.3%) aromatics, zero olefins, and (23.7%) saturates.

(4) The new additive used has little impact on the calorific value of the fuel. Hence there is little chance that the engine power will be affected.

(5) The new additive tested increased the specific gravity (hence the density) of the fuel. This will mean that the new fuel will be little dense and hard to atomize using simple carburetor, perhaps fuel injectors will be preferred.

(6) More work is needed to test the additive under real engine test conditions to check its effect on the engine performance and emission characteristics.

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