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Improvement of Antiknocking Characteristics of Iraqi Gasoline

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Abstract

Tetraethyl lead (TEL), which is a common additive to the Iraqi pool gasoline, is usually classified- among the most toxic selective additive even when it is added at low doses (~ 1.5-2.0 %v/v). The present work was devoted to prepare and investigate the effect of phenyl tert-butyl ether as an alternative selective additive to the Iraqi pool gasoline produced in Doura Refinary-Midland Refineries Co. Comparing with other additives-except TEL-, it was found that phenyl tert-butyl ether increased RON of Doura pool gasoline by (5.7 to 10%) at a dose of 5%v/v and it increased RON by (4.5 to 11.9%) at a dose of 8%v/v. Moreover, it appears to have no adverse human health effects which make the suggested additive promising for increasing the anti-knocking characteristic of Iraqi gasoline.

Keywords: Antiknock, Iraqi gasoline, additives, octane number.

الخلاصه

رابع اثيلات الرصاص , يستخدم حاليا في رفع العدد الاوكتاني لمنتوج الكازولين من مصافي النفط العراقيه, يعتبرمن اخطرالمضافات سمية وتاثيرا على البيئة الحياتية حتى عند اضافته بنسب حجمية قليلة (2- 1.5%) وخاصة في المدن المزدحمة بالسيارات. الدراسة الحالية تهدف الى تحضيرمادة مضافة- صديقة للبيئة- ولها كفائة عا لية نسبيا في رفع العدد الاوكتاني للكازولين العراقي. تم تحضير مادة- فنيل ترت بيوتايل ايثر- واجراء كافة التحليلات لتحديد المواصفات الفيزياوية. لتحديد كفائة المادة ، تم اضافتها بنسب حجمية مختلفة الى الكازولين الحوضي المنتج في مصفى الدورة ومقارنتها مع كفائة بعض المضافات المجربة على الكازولين الحوضي لمصفى الدورة. وجد ان العدد الاوكتاني للكازولين العراقي يزداد بنسبة (5.7 - 10%)

اكثر من المضافات الاخرى-عدا اثيلات الرصاص- عند اضافة 5% حجما. وعند اضافة 8% حجما تتحقق زيادة (4.5– 11.9%) اكثر من المضافات الاخرى- عدا رابع اثيلات الرصاص. ان المادة المحضرة تعتبر واعدة الاستخدام كون تاثيراتها البيئية قليلة جدا اضافة الى كفائتها العالية.

Introduction:

Since World War II, gasoline, as a main fuel for personal vehicles, becomes one of the most important resources in the world. In the early of 20th century, automotive engineers discovered that engines with no knock would operate smoother and more efficient. In 1916, Thomas Midgely a research scientist working for the Dayton Research Laboratories of Dayton Ohio, discovered that the addition of iodine to gasoline substantially reduced engine knocks. In a joint research work in 1917, Charles Kettering (inventor of electric self-starter) and Thomas Midgley blended ethyl alcohol (grain alcohol) with gasoline and concluded that alcohols mixed with gasoline could produce a suitable motor fuel. Manufacturing of tetra ethyl lead (TEL) began in 1923 with small operation in Dayton, Ohio that produced about 600L of TEL per day. One liter of TEL was enough to treat 1150 liter of gasoline [1]. Around the time of TEL production, William Mansfield Clark, a laboratory director in the United States Public Health Service (USPHS), warned of widespread use of TEL usage in gasoline. He stated that each liter of gasoline burned would emit 1 g of lead oxide that would build up to dangerous level along heavily traveled roads. Such a poor decision at that time did not allow a comprehensive understanding of the real dangers posed by TEL and lack of scientific research and evidence allowed the use of TEL for a few decades after its discovery. The use of leaded gasoline for highway vehicles was banned in the United States as of January 1, 1996 [2]. The comprehensive national Health and Nutrition Examination survey by the US Center for Disease Control and Prevention confirmed that the average blood lead levels in the United States decreased from 16 mg dl^{-1} to 3 mg dl^{-1} from 1976 to 1990 respectively. This is the period when the use

of leaded gasoline fell from its peak to near zero in the United States [2]. Widespread use of oxygenates in gasoline dates to 1979, when methyl tert-butyl ether (MTBE) was added to gasoline to substitute TEL and to increase the octane rating of the fuel. As part of the Clean Air Act Amendments of 1990, and through an intensive negotiation between the USEPA, state officials, oil and automobile industry representatives, gasoline retailers, oxygenate suppliers, environmental organizations, and consumer groups, the federal government introduce the reformulated gasoline (RFG) program in two phases into United States most polluted cities. Both phases of the program require that RFG contain 2% by weight oxygen. This program was aimed at reducing the level of highly toxic aromatics (such as benzene, toluene, ethyl benzene and xylenes) from gasoline and increasing the oxygen content of gasoline by adding larger quantities of oxygenates. Addition of oxygen to gasoline had a two-fold objective, to enhance the octane rating of internal combustion engines and to reduce air pollution (summer time smog, winter time carbon monoxide, and year-round air toxics) with provision of more complete fuel combustion in the engines [3]. 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 [4]. Octane rating or octane number is a standard measure of the performance of a motor or aviation fuel. The higher the octane number, the more compression the fuel can withstand before detonating. In broad terms, fuels with a higher octane rating are used in high-compression engines that generally have higher performance. The most common type of octane rating worldwide is the Research Octane Number (RON). RON is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane. There is another type of octane rating called Motor Octane Number (MON), or the aviation lean octane rating, which is a better measure of how the fuel behaves when under load, as it is determined at 900 rpm engine speed, instead of

the 600 rpm for RON [5]. Figure (1) depicts RON of families of pure hydrocarbons as function of their boiling points. Three of the more common oxygenated fuel additives that have been used with unleaded gasoline are methanol, ethanol, and methyl tertiary-butyl ether (MTBE). Methanol is obtained from petroleum (from methane or by reacting carbon monoxide and water); ethanol is obtained from corn by fermentation; and MTBE is made synthetically from petroleum feed stocks. The choice of which of the compounds commonly used in oxygenated fuels to use is dependent on region, cost of production, and availability of raw materials, table (1) shows properties of some gasoline active additives. The Table depicts the dependency of RON on $\%O_2$ of the active additive.

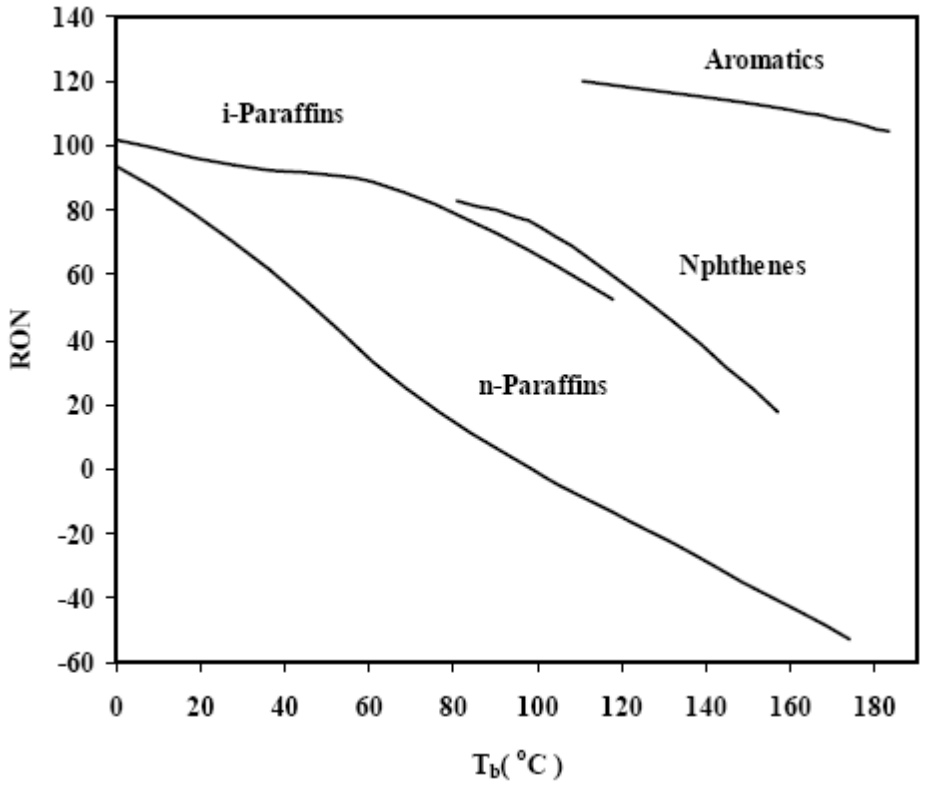

Fig. (1) Research Octane Number of pure hydrocarbons from different families [6,7]

Table (1) Properties of some Active Additives [8].

	Sp. Gr(kg/L)	$\%O_2$(wt)	RON	MON
Methanol	0.796	49.9	130	100
Ethanol	0.794	34.7	115	100
IPA	0.789	26.6	117	100
TBA	0.791	21.6	100	90
MTBE	0.744	18.2	110	100
ETBE	0.770	15.7	112	100
TAME	0.770	15.7	105	100

Toxicity or "hazard" of gasoline of interest to those reading a toxicity profile varies tremendously with the exact gasoline in question. Table (2) shows the exposure limits of some active additives. It indicates that the most hazardous materials are Benzene and TEL. The object of this study is to provide a method of preparing a selective additive, which is an environmental friendly additive, and blending with gasoline pool produced in Al Doura Refinery to enhancing the octane number. Other objects will be apparent to that who skilled-in-the-arts.

Theoretical Aspects

MON Correlation

Once clear RON is known, clear MON can be estimated from the following correlation derived from the correlation proposed by [9] for olefin free fuels.

MON 22.5, 0.83 RON 20.0 SG…… (1)

Blended Values

The blended value of an active additive is calculated by adding it to the RON of the gasoline which is to be treated, the change in RON is calculated by dividing the volume% of additive added. The Blending Value is a measure of affectivity of an additive [10].

BV = [BASE RON] + [Δ RON/vol% added] …… (2)

Table (2) exposures limits guidelines

	Governing Body	Exposure Limits		
ALKYLATE	Sunoco	TWA	100	ppm
BENZENE	ACGIH	STEL	2.5	ppm
BENZENE	OSHA	STEL	5	ppm
BENZENE	ACGIH	TWA	0.5	ppm
BENZENE	OSHA	TWA	1	ppm
BUTANE	ACGIH	TWA	1000	ppm
ETHYL ALCOHOL	ACGIH	TWA	1000	ppm
ETHYL ALCOHOL	OSHA	TWA	1000	ppm
ISOPENTANE	Sunoco	STEL	750	ppm
ISOPENTANE	ACGIH	TWA	600	ppm
ISOPENTANE	Sunoco	TWA	600	ppm
N-HEXANE	ACGIH	TWA	50	ppm
N-HEXANE	OSHA	TWA	500	ppm
TOLUENE	NIOSH	STEL	150	ppm
TOLUENE	ACGIH	TWA	20	ppm
TOLUENE	OSHA	TWA	200	ppm
ETHYLBENZENE	ACGIH	STEL	125	ppm
ETHYLBENZENE	ACGIH	TWA	100	ppm
xylenes	OSHA	TWA	100	ppm
TETRAETHYL LEAD	ACGIH	TWA	0.1	mg/m^3
TETRAETHYL LEAD	OSHA	TWA	0.075	mg/m^3
MTBE	ACGIH	TWA	50	ppm

Octane Number Sensitivity

Fuels with lower sensitivity are desirable. Because the two test methods use different test conditions, especially the intake mixture temperatures and engine speeds, fuel that is sensitive to changes in operating conditions will have a larger difference between the two rating methods. Modern fuels typically have sensitivities around 10. Equation 3 was used to estimate octane number sensitivity [11].

RON - MON = Sensitivity..... (3)

Iraqi Pool Gasoline

Gasoline Pool Production in Al Doura Refinery

Two units operated in Al Doura Refinery to improve octane number of gasoline, one is called Reformer unit, the feed for this unit is a mixture of 30%LSRN and 70% HSRN, and the product is Reformate. The other unit is Power Former, feed is HSRN and the product is Power Formate. Gasoline production in Al Doura Refinery included many streams such as :

•LSRN (RON =69.2).

•Reformate (RON= 90.5) (from Reforming a mixture of 30%LSRN and 70%HSRN).

•Power Formate (RON=89.3) (from Reforming HSRN).

All feeds and products of Reformer and Power Former units were tested by ASTM standards and IROX analyzer. Table (3) shows Octane number of petroleum cuts, pool, and leaded gasoline of Al Doura Refinery by ZX-101C (Zeltex, Inc., Hagerstown, MD) measurements.

Table (3) Octane numbers of petroleum cuts, pool, leaded gasoline produced by Al Doura Refinery measured by ZX-101C [12].

Components	RON	MON
Light Naphtha	69.0	60.5
Heavy Naphtha	57.0	51.8
Reformate	90.0	85.5
Power Formate	88.6	84.3
Pool	80.0	76.0
Leaded Gasoline	82.3	78.3

Table (4) shows the properties of Al- Doura pool gasoline as recorded by Lab-Tests.

Table (4) Summarized Lab-Tests of AL-Doura Refinery pool gasoline [13].

Properties	Test methods	Al-Doura pool
Sp. Gr. (kg/L)	IROX	0.715
RVP (bar)	ASTM D323	0.6
Water content (ppm)	ASTM D4928	131.95
Sulfur content (ppm)	ASTM D4294	43.8
MON	ASTM D2700	80
RON	ASTM D2699	84.5
Aromatics	IROX	24.25
Olefins	IROX	0
Paraffins & Naphthenes	IROX	75.75

RON of blended gasoline is shown in table (5). As expected none of the alcohols achieve the target specification. Isopropanol at 10% is the best at approaching RON ≈90. However, for Isopropanol at 10%, the RVP value is well over the 60 kPa target and even exceeds 60 kPa at 5%. At 10% Isopropanol l, oxygen is well over the 2.7% limit but the heating value of the fuel is only marginally less than the base stock. Using alcohols, sensitivity declines slightly and none of the alcohols achieve the 85 MON target.

Table (5) RON of pool gasoline of Al-Doura Refinery after blended with selective additives [12].

Vol.% / Selective additive	0.0	0.5	1.0	1.5	2.0	2.9	5.7	8.3	10.7
TEL	83.0	88.0	91.5	94	-------	-------	-------	-------	-------
Isopropanol	83.0	------	------	------	------	85.0	86.5	88.0	90.5
Methanol	83.0		------	------	------	84.0	85.0	85.8	87.5
Isopropyl Ether	83.0	------	------	------	------	83.5	84.2	84.5	85.6
Xylene	83.0	------	------	------	------	86.3	88.7	90.0	91.0

Materials and Methods

In present work, materials used to prepare selective additive (i.e., phenyl-t-butyl ether) are shown in table (6).

Table (6). Chemical materials for preparation of the selective additive.

Item	Material	Chemical Structure	state	Purity	Supplier
1	Nitrogen	N_2	gas	99%min.	Al-Mansour Factory/Baghdad
2	Magnesium metal turnings	Mg	solid	98%min.	Sigma Chemical Co.
3	bromobenzene	C_6H_5Br	liquid	98.5%min.	Pvt. Ltd/India
4	Enhydrous Ether	$C_4H_{10}O$	liquid	98%	Advanced Scientific & Chemical Inc.
5	Magnesium Sulfate	$MgSO_4$	crystalline solid	98%min.	Fluka
6	Hydrochloric acid	HCl	liquid	37%	Sigma Chemical Co.

* Preparation of the selective additives

As it is known to that skilled in-the-art, the octane number of gasoline may be increased by the addition of various aliphatic ethers which have no environmental impact. The phenyl-t-butyl ether which may be used an octane appreciator of the process of this study may not readily available; therefore, it is prepared as here under.

Experimental set-up-

Figure (2) represents a schematic diagram of the experimental apparatus that used to prepare phenyl-t-butyl ether.

A three-necked, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a 500-ml of what. Pressure-equalized dropping funnel is arranged for conducting a reaction in an atmosphere of nitrogen by fitting into the top of the condenser a T-tube attached to a low-pressure supply of nitrogen and to a mercury bubbler.

Method of Preparation-

The detail of the preparation method of phenyl *t*-butyl ether (PTBE) is found elsewhere [14].The flask is dried by warming it with a soft flame as a slow stream of nitrogen is passed through the system. In the cooled flask a solution of phenylmagnesiumbromide is prepared from 13 g. (0.53 g. atoms) of magnesium turnings, 79 g. (0.5 moles, 53.6 ml.) of bromobenzene, and 200 ml. of anhydrous ether. After the preparation of phenylmagnesium bromide is complete, the ethereal solution is cooled in an ice bath and 200 ml. of anhydrous ether is added. A solution of 58.3 g. (0.3 mole, 56 ml.) of *t*-butyl perbenzoate in 120 ml. of anhydrous ether is added, dropwise, with stirring over a 30-minute period, and the stirring is continued for an additional 5 minutes. The reaction mixture is poured carefully into a cold solution of 40 ml. of concentrated hydrochloric acid in 1:1 of water. The ethereal layer is separated, and the aqueous layer is extracted twice with 150-ml. portions of ether. The combined organic layers are extracted with three 25-ml. portions of 2*M*sodium hydroxide solution, washed with water until the washings are neutral, and then dried over anhydrous magnesium sulfate. The dried solution is concentrated and the product distilled under reduced pressure, B.P. 58–60°C/8.6mm. The yield of phenyl *t*-butyl ether is 34–36 g. (76–81%).

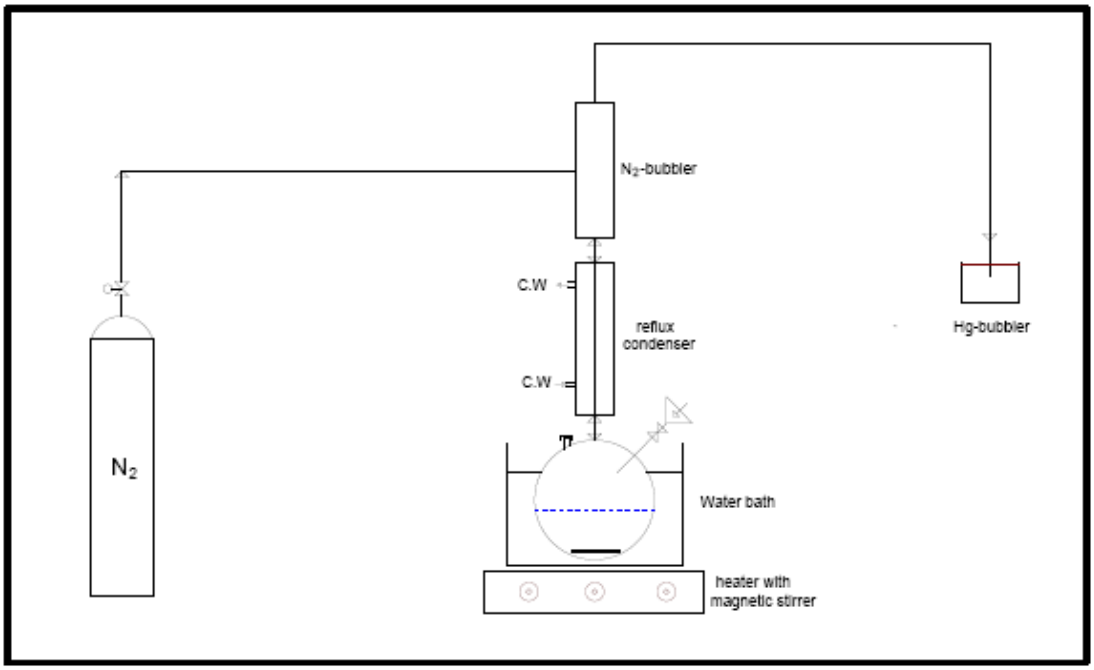

Fig. (2) Experimental setup.

Results and discussion

The prepared additive was analyzed using standard methods. Table (7) presents the physical properties measured by advanced laboratory instruments.

Table (7) Analysis of phenyl t-butyl etherused in the present work.

Property	
Boiling point (^{0}C)[1]	183.6
Density (g/cc)[2]	0.92(at 25 ^{0}C)
Refractine index[3]	1.481
(C,H,O)[4]	79.2%, 9.4%, 10.55%
(RON)[5]	117

1- Measured using melting point and boiling point instrument type M-565 from Buchi.

2- Measured using DDM 2910 densitometer from Rudolph Research Analytical.

3- Measured by Abbe refractometer type 2WAJ from Optika SRL.

4- Measured by elmental analyzer type 2400 series II from Perkin Elmer.

5- Measured by octane meter type: SX-200 from Shatox.

To identify the functional groups in the prepared additive, an analysis was carried out using FTIR- Type TENSOR 27 from BRUKER. Figure (3) illustrates such identification-before distillation step. The plot depicts several absorptions in the fingerprint region. The most prominent band is C-H stretch 1300-1000 cm^{-1}phenyl alkyl ethers which gives two strong bands at about 1158.20 to 1233.68cm^{-1}[15].

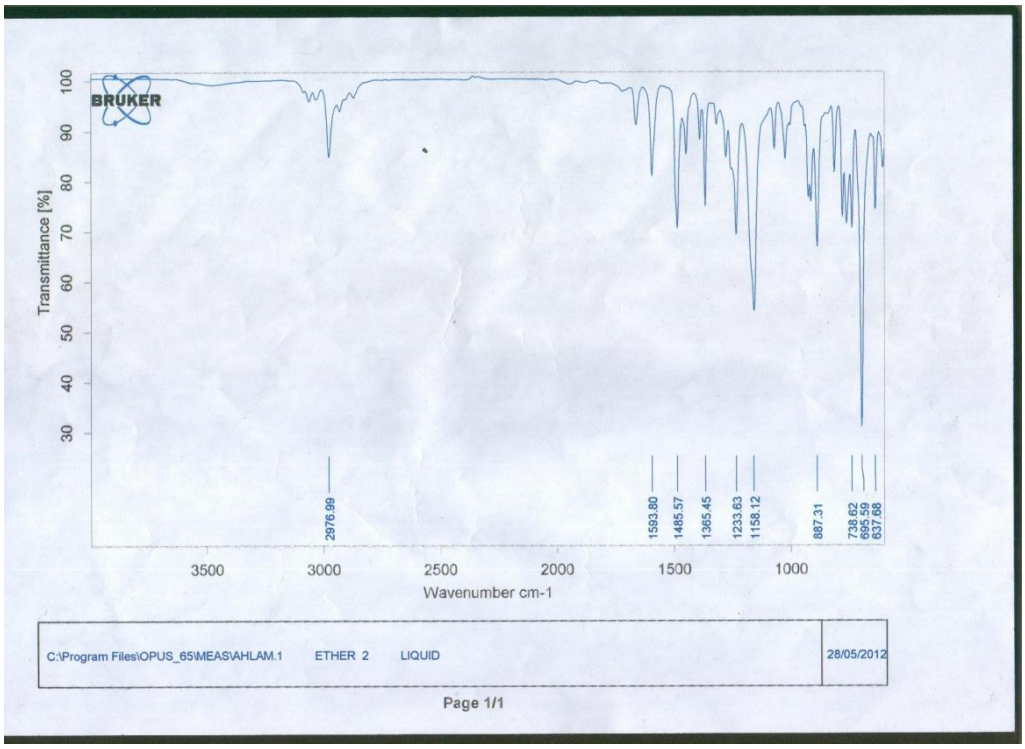

Fig. (3) Idetification of functional groups in phenyl t-butyl ether.

In present work, the selective component was added to Al-Doura pool gasoline at different vol% as follows:

1- RON and other related properties of pool gasoline were measured using octane meter type: SX-200 from Shatoxthen pool gasoline was added to five glass containers of 250 ml each.

2-The selective additive was added in different concentrations to each container with shaking by using pipette.

3-The blended mixture was evaluated by measuring the required properties.

Table (8) shows RON of pool gasoline of Al-Doura Refinery after blended with different concentrations of phenyl *t*-butyl ether additive.

Table (8) RON of pool gasoline of Al-Doura Refinery after blended with different concentrations of phenyl *t*-butyl ether additive.

Vol% / item	0	2	5	8	10
phenyl *t*-butyl ether	83.0	86.4	93.1	94.3	95.2

Table (9) depicts the additive affectivity (BV) of some selective additive volumes blended with pool gasoline of AL-Doura Refinery.

Table (9) Comparison of additive affectivity (BV) of some selective additives blended with pool gasoline with that of present work.

Vol.% / Selective additive	0.5	1.0	1.5	2	2.9	5.7	10.7	References
TEL	1083.0	933.0	816.3	-------	--------	-------	--------	[12])
Xylene	--------	--------	--------	--------	193.0	125.1	113.8	[12]
PTBE				253	--------	267	200.75	Present work

Figure (4) illustrates the variation of gasoline RON against %vol added of some selective additives. As can be seen, phenyl t-butyl ether (PTBE) could be considered as a superior octane appreciator. Moreover, it has no environmental impact which makes it a candidate additive.

Figure (5) plots the variation of additive affectivity against %vol addition of some selective additives. Figure (5) shows an interesting image which represents the magnitude of the regression slope of each additive verses proportional of its ability to increase the octane number of that additive.

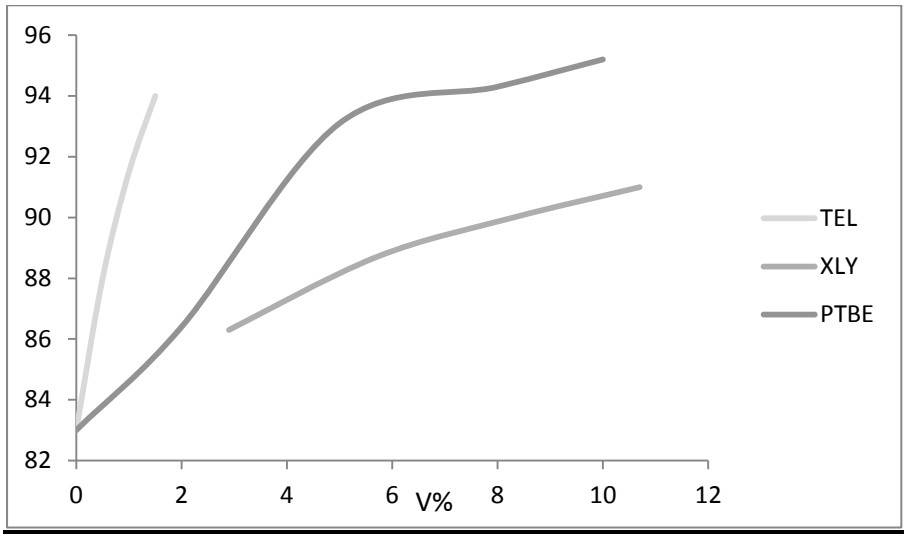

Fig. (4) Variation of RON of pool gasoline blended with different vol% of selective additives.

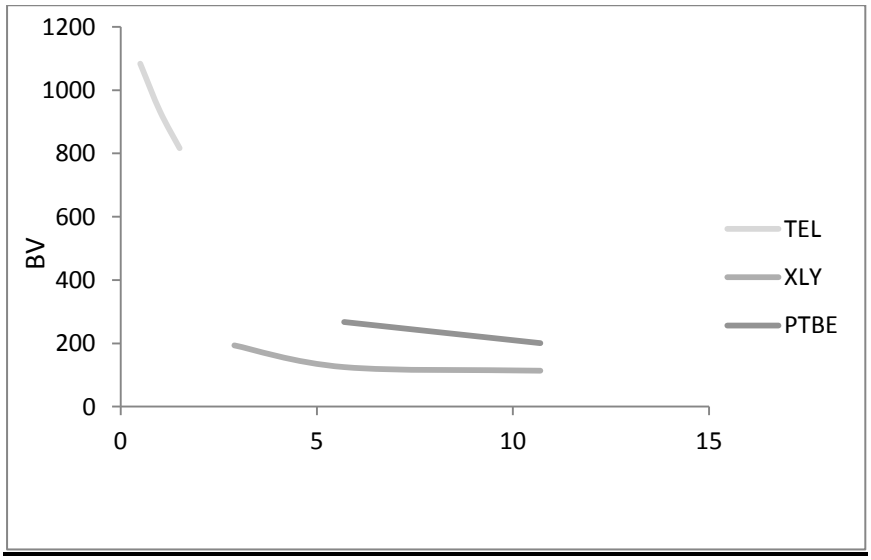

Fig. (5) Variation of additive affectivity against different vol% of selective additive.

Conclusion:

The present work is devoted to prepare and examine a novel fuel additive as an alternative to the most toxic additive that used to improve antiknock characteristics of gasoline produced in Iraqi Refineries.

From the results of the present study, one may conclude the following:

- The prepared material (i. e., phenyl t-butyl ether) increases RON of gasoline pool from 4.5 to 11.9% which is more than does any other oxygenators literary scanned in the present work- except TEL-.
- It appears that this additive has no effects to human health which makes it a candidate additive.

Nomenclature:

ACGIH American Conference of Governmental Industrial Hygienists.

BV Blended value.

HSRN Heavy straight-run naphtha.

LSRN Light straight-run naphtha.

MON Motor Octane Number.

NIOSH National Institute of Occupational Safety and Health

OSHA U.S. Occupational Safety & Health Administration.

RON Research Octane Number

RVP Reid vapor pressure (kPa)

SG Specific gravity of the fuel at 15.5 ^{o}C.

STEL Short-Term Exposure Limit (generally 15 minutes).

Sunoco Sun Company Inc. (American petroleum and petrochemical manufacturer).

TWA Time Weighted Average (8 hr.).

USPHS United States Public Health Service.

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