Determination of the Octane Number of Olifenic Hydrocarbons Present in Gasoline

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Abstract:

The study involved calculation of octane numbers (ON) of olifens having different molecular formula, carbon number 5 to 9, and boiling points in the range of (40-186 ^{o} C) which are present in the gasoline and determining the factors affecting them. Multiple linear regression analysis method is used for this purpose. The suggested parameters in the experimental section are relied on the geometry and structure of the olifens. The results indicate that the double bond length and charge on both sides of the double bond, and the charge of the carbon attached to the double bond as a substituent showed a great effect on the octane number. This gives us a certain conclusion about the oxidation ability when the charge on the double bond is slightly high to start oxidation and radical formation and finally molecular cleavage and energy evolution to continue the engine work. Other parameters are also effective such as the position of the double bond in central and terminal location.

Introduction:

Gasoline can vary widely in composition, even those with the same octane numbers. The overall components are quite different not only in their physical make-up, but also in the molecular structure of the constituents [1,2].

Gasoline is defined as any hydrocarbon blend that could burn without introducing any knocking or little knocking in the engine. The main components present in gasoline are paraffin (P), iso-paraffin (I), olefin (O), naphthenic (N) and aromatic (A) hydrocarbons (PIONA)[3]. Gasoline was never been analyzed, for individual components, yet around 1500 compounds were isolated just for academic interest. They are of two main types; natural and industrial gasoline. The latter includes; reformate, cooker, polymeric, cracked and hydro cracked gasoline [3,4,5].

Gasoline has a very high volatility and boiling temperature. The characteristics of the produced gasoline in all its types and form, which is used as fuel, make the refiner to choose a certain cut and a certain relevant process to match the regulation and to fulfill the octane number requirements [6,7]. Recently [8] blending various components with a boiling range within the gasoline scale, accepted volatility and low hetroatom content produces gasoline. The processes used mainly in the production of gasoline are; alkylation, isomerization, reforming and finally destructive distillation. The knowledge, which is obtained by Mark [9] during the course of the study of the hydrocarbon type present in the gasoline is very essential to fit in construction and design of internal combustion engine. Group of researchers [10] studied 30 types of gasoline having a boiling range of 38-200 ^{o}C. They found that light gasoline constitutes 70-80%, while medium boiling is %15 and about 5% heavy. The study revealed that gasoline is mainly isoparaffinic, naphthenic, olefinic and aromatic nature. Normal paraffins have slightly low octane numbers and their octane numbers decrease with increasing molecular weight [10]. Iso-paraffins have higher octane numbers if they compared to the same molecular weight of n-paraffins. On the other hand, olefinic hydrocarbons that present in cracked gasoline and some times in cooked gasoline have a high octane number value compared to the paraffin analog. Keeping in mind that olefin is thermally unstable and may be polymerized in the presence of light to high molecular weight gum and colored compounds. Naphthenic hydrocarbons of five and six member rings carrying small substituents have slightly high octane numbers even if they present in small amounts. Aromatic hydrocarbons present in small quantities and contribute largely to octane number but they cause carbon deposition [5,11].

Octane numbers can be very confusing due to several different terminology used in discussion. The octane quality of a gasoline is its ability to resist detonation, a form of abnormal combustion. Detonation occurs when the air-fuel mixture reaches a temperature and/or pressure at which it can be no longer kept from self-igniting. Two types of abnormal combustion are common; the first is detonation as previously mentioned and the other is pre-ignition [3].

Minimum motor octane numbers (MMON) for pooled gasoline are also beginning to be set to ensure good fuel performance. These octane values are higher than those of past years and have forced the refiners to review, in the short-term means by which octane number can be improved from existing capacity since the fluid catalytic cracking (FCC) reforming, alkylation and isomerisation of the feed stock to produce gasoline, contributes the highest percentage of the gasoline pool in most refineries. This research work was aimed to investigate the effect of the chemical structure and other physical properties on the octane number of pure olefinic hydrocarbons and no such work has been found in the literature before.

Experimental:

a-Choice of the olefinic hydrocarbons:

Olefinic hydrocarbons present in gasoline of a certain quality are of many types and include mainly hydrocarbons that have carbon number of five to nine. These compounds have according to the available knowledge high octane numbers but on the other hand have certain instability toward storage and heat.

b-Choice of parameters:

The parameters present in this work depend mainly on our previous study [6] for the octane number and the effect of certain type of these parameters is recognized. Theoretical values of the suggested parameters depend mainly on the data obtained from quantum mechanical calculations employing the software supplied by Cambridge University under the scientific name Chem. Office version 1999.

The suggested parameters (Table (1)) are: charge on the two carbon atoms of the double bond, length of the double bond, position of the double bond on the chemical structure of the olefinic molecule, total steric energy of the whole molecular structure determined from the non bonded interactions, the heat of formation (ΔH_f) of the olefinic molecule depending on the bond energy of the system, dipole moment, molecular weight, and the total carbon atoms of the molecule. Afterward the regression analysis gave unsatisfied result which lead to suggest and add another two parameters. These are; charge of the substituent on the (C=C) double bond, also the degree of substitution on the system.

Table(1): Parameters suggested to calculate the octane numbers of olefinic hydrocarbons

Compound	ON	Charge on carbon atoms of $C^1=C^2$ C^1	C^2	Length of C=C A^o	Position of C=C	Total energy Kcal/mole	$-\Delta H_f$ Kcal/mole	Dipolar interaction	No. of C-atoms	Degree of sub.	Charge of subtituent on C=C
1-Pentene	77	-0.191	0.052	1.340	1	2.15	6.75	0	5	0	0
1-Hexene	76	-0.192	0.052	1.340	1	2.80	13.60	0	6	0	0
2-Hexene	81	-.054	-.045	1.342	2	2.02	16.66	0.0765	6	0	0
1-Octene	29	-0.192	0.53	1.341	1	5.97	25.18	0	8	0	0
2-Octene	56	-0.054	-0.044	1.342	2	6.54	28.28	0.0766	8	0	0
3-Octene	72	-0.054	-0.060	1.342	3	4.48	29.14	0.0764	8	0	0
2-Me-2-Butene	85	0.071	-0.120	1.345	2	1.74	10.03	0.1798	5	1	-0.141
2-Me-1-Hexene	91	-0.272	0.161	1.343	1	3.16	20.63	0	5	1	-0.138
2-Me-2-Pentene	97	0.072	-0.127	1.345	2	3.09	16.73	0.1825	6	1	-0.141
3-Me-2-Pentene	98	-0.126	0.067	1.346	2	3.65	15.68	0.1803	6	1	-0.143
4-Me-2-Pentene	99	-0.061	-0.050	1.342	2	3.09	13.56	0.0763	6	1	0
2,3,4-tri Me-1- Pentene	86	-0.287	0.165	1.342	1	6.51	20.28	0	8	3	-0.135

Me, CH_3 ; ON, octane number

Results and Discussion:

The parameters related to the geometrical structure of olefin under study are given in Table (1). The results of the regression analysis are listed in Table (2) and a comparison between the observed octane numbers and those calculated from the regression analysis are shown in Table (3).

Table (2): Results of regression analysis of the suggested parameters.

Parameter	Coefficient of Parameter
Charge on C^1 of ($C^1=C^2$)	-1709.542
Charge on C^2 of ($C^1=C^2$)	-1602.314
Length of the (C=C) bond	-3126.960
Position of the (C=C) bond	-7.455
Total energy of molecule	13.145
Heat of formation	-28.767
Dipole-Dipole interaction	280.791
Number of carbon atoms	208.489
Degree of substitution	73.491
Charge on substituent on (C=C)	68.680
Constant = 4851.193 Corrélation coefficient = 1 Standard deviation = 0.0105	

Table (3): Observed and calculated octane number of the olefinic hydrocarbons under study

Compound	Observed octane number	Calculated Octane number
1-Pentene	77	77.00
1-Hexene	76	75.99
2-Hexene	81	81.07
1-Octene	29	29.00
2-Octene	56	56.00
3-Octene	72	72.00
2-Me-2-Butene	85	84.99
2-Me-1-Hexene	91	91.00
2-Me-2-Pentene	97	97.00
3-Me-2-Pentene	98	98.00
4-Me-2-Pentene	99	99.00
2,3,4-Tri-Me-1- Pentene	86	86.00

The results in Table (2) indicate that the most effective factor that affects the octane number of the olefinic hydrocarbons is the charge at the double bond of the olefin. The charge on the unsaturated center include the electron density at both side of the (C=C) bond, which is designed as C^1 and C^2.The amount of charge has direct relationship to the cleavage of the π - bond in the system which lead to the formation of free radicals which is the starting point of the oxidation, burning and energy formation. The location of the double bond on the hydrocarbon system and the presence of the substituent may affect the ability of the double bond to rapture when it is rich in electrons and the π electrons expand over the whole system which may lead to difficult oxidized hydrocarbon due to the geometrical change around the

bond, i.e. the length of the double bond has the greatest effect on the octane number value due to stability or instability of the double bond in central or terminal olefins. In general our expectation of the value of the octane number may be greatly influenced by the charge content of the two sides of the double bond, its length and substituent position.

The heat of formation for the olefinic system shows some fluctuated value which may indicate the connection of the effect of a parameter with other variables in the system suggested or required to be developed. However, the ΔH_f showed slight effect on the octane number. On the other hand, the total number of carbon atoms may also affect the octane number positively due to the large number of radicals formed and oxidized to produce energetic species that may lead to good octane number numerical values.

Finally we may conclude that the octane numbers of olefins are greatly influenced by;

a- Size and geometry of olefin,
b- Charge on both sides of the double bond,
c- Unsymmetrical properties of the molecule,
d- The overall energy and heat of formation, which may lead to enhanced oxidation.

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تقدير العدد الاوكتاني للهيدروكاربونات الاوليفينية الموجودة في الكازولين

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الملخص:

تضمنت هذه الدراسة حساب العدد ألا وكتاني والعوامل المؤثرة عليه لعدد من الاوليفينات التي تختلف في صيغها الجزيئية والتي تمتلك عدد كاربوني (٥ آلي ٩) ذرات فضلا عن أنها ذات درجات غليان تتراوح في المدى (٤٠-١٦٠)م والمتوقع وجودها في الكازولين. وقد استخدمت طريقة التحليل الانحداري الخطي متعدد المتغيرات لهذا الغرض. تعتمد العوامل (أو المتغيرات) المقترحة في هذه الدراسة على التركيب الكيميائي والأبعاد الهندسية للاولفينات المدروسة.

أظهرت النتائج ان لطول الاصرة المزدوجة والشحنة على طرفي الاصرة، فضلا عن الشحنة على ذرات كاربون المعوضات المرتبطة بالاصرة المزدوجة، تأثيرا كبيرا على العدد الاوكتاني. هذه النتيجة يمكن ان تعطي اشارة الى قابلية حدوث عملية الاكسدة، اذ انه عندما تكون الشحنة عالية نوعا ما على الاصرة المزدوجة فان ذلك يساعد على بدأ عملية الاكسدة وتكوين الجذور الحرة والذي يقود في النهاية الى كسر الجزيئة لاعطاء الطاقة اللازمة لاستمرار عمل المحرك. اشارت الدراسة ايضا الى ان هناك عوامل اخرى تؤثر على قيمة العدد الاوكتاني كموقع الاصرة المزدوجة (طرفية او مركزية) في التركيب الجزيئي للمركبات المدروسة.