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تطوير طريقة جديدة لحساب العدد الاوكتاني بالاستناد الى طرق ميكانيك الكم

همام طه سلطان صالح **زيد شهاب احمد مصطفى**

مديرية تربية نينوى، العراق

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ملخص البحث:

استخدم في هذه الدراسة طريقة من طرق ميكانيك الكم (طريقة الحسابات الاساسية DFT) في حساب بعض الخصائص الفيزيائية التي تؤثر على العدد الاوكتاني (ON) ثم تم ربط هذه المتغيرات المحسوبة نظرياً مع بعضها البعض كمتغيرات مستقلة ومع قيم العدد الاوكتاني لمشتقات الكازولين والمحسوبة عملياً كمتغير معتمد. ان افضل نتيجة تم الحصول عليه من خلال هذه العلاقات كانت (Total Energy, HOMO , LUMO, Torsion) والذي كان معامل الارتباط قريب من الواحد الصحيح وقيمه الانحراف المعياري القريب من الصفر. من خلال نتائج العلاقات تم اقتراح علاقة رياضية من خلالها تم نظرياً حساب العدد الاوكتاني لمشتقات الكازولين وكان هنالك تقارب بين القيم العملية مع القيم المحسوبة نظرياً مما يدل على نجاح الطريقة الحسابية المطورة.

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Developing a New Method for Calculating the Octane Number Based on Quantum Mechanics Methods

Homam T. S. AL-Sayd Toohi **Zaid S.Ahmed**
Directorate of Education in Nineveh, Iraq.

Abstract

In this study, one of the quantum mechanics methods, the ab-initio method DFT, was used in calculating the number of the physical variables that affect the octane number (ON). Then, these theoretically calculated variables were linked with each other as independent variables and with the octane number values of gasoline derivatives, which were calculated in practice as a dependent variable. The best result obtained through these relationships was (Total Energy, HOMO, LUMO, and Torsion), where the correlation coefficient was close to the right one and the value of the standard deviation is little. Through the results of the relations, a mathematical relationship was proposed through which the ON of gasoline derivatives was theoretically calculated, there was a convergence between the practical values with the theoretically calculated values, which indicated the success of the developed mathematical method.

Introduction:

Gasoline fuel is a mixture of different types of hydrocarbons such as paraffins, olefins, naphthenes and aromatics, and they differ according to the source of the crude oil and according to the refining processes[1,2].

The octane number is the approved characteristic for the evaluation of gasoline, which represents the volume percentage of iso-octane (C8H18) in a mixture with ordinary n-heptane (C_7H_{16}) at the same intensity of crackle [3,4].

The octane number of any mixture of hydrocarbons is determined by comparing its combustion characteristics in a standard engine with the combustion characteristics of models with different ratios of iso-octane and normal heptane. There are several methods for calculating the octane number of petroleum fuels [5-7].

Computational chemistry has been recently used in estimating many important variables that support laboratory work in many cases, as well as reducing effort, time and costs. The chemistry of theoretical calculations includes many mathematical methods, which are classified into two main categories: molecular mechanics and quantum mechanics [8,9].

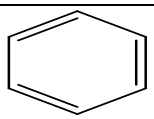
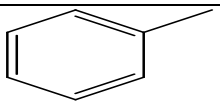
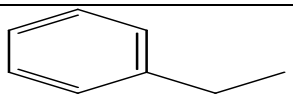
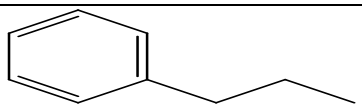
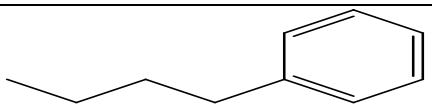
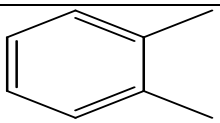
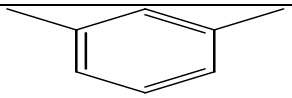
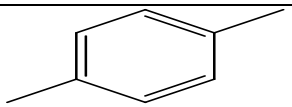
Calculations method:

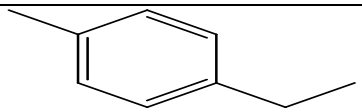
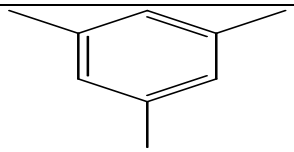
Physical variables calculated theoretically and based on the program (Chem.office), which are linked statistically and finding their values theoretically and using the statistical program (SPSS). Some of the calculated variables are related to the energy of the molecule …. Others relate to their steric shapes, such as Mulliken charge, (Total energy), which is equal to the sum of a number of variables such as stretching and bending energy..etc. Other energies such as HOMO orbital LUMO, Hardness (η), Electronic Chemical Potential (μ) and Global Electrophilicity Index (W) (source) were also calculated [10].

Results and discussion:

In this study, some physical variables were theoretically calculated using the same steps followed in a previous study [11], but using the DFT method (ab intion), using Chem .Office Program (version 12, 2010 of Cambridge software, USA).

Table 1: Names and compositions of gasoline derivatives studied in this research.

Comp. No.	Name	Structure
١	Benzene	
٢	Toluene	
٣	Ethylbenzene	
٤	Propyl benzene	
٥	Butyl benzene	
٦	o-xylene	
٧	m-xylene	
٨	p-xylene	

٩	p-ethyl toluene	
10	Mesitylene	

The physical constants were calculated using the DFT basic calculation methods. The choice of these methods was based on the fact that they are the most common and most widely used in this field of studies and their preference for obtaining accurate results.

Table (2): The theoretically calculated physical variables for the compounds by DFT method.

Comp. No.	Stretch	Bend	Stretch-Bend	Torsion	Non-1,4 VDW	1,4 VDW	Potential Energy Kcal/mol	Total Energy Kcal/mol
1	٠,٠٦٧٦	٠,٠٠٠٠	٠,٠٠٠٠	-5.5800	-0.3627	3.2337	-288471.4999	-144841.9564
2	٠,١٤٦٠	٠,١٣٣٦	-0.0036	-6.3000	-0.5828	3.7671	-337324.3171	-169361.5476
3	٠,٢٦٦١	٠,٩٢٥٨	٠,٠٤٠٣	-6.4353	-0.3294	4.6367	-386152.0441	-193878.5947
4	٠,٣٤٦٦	١,٠٧٢٥	٠,٠٦٢١	-6.4346	-0.5684	5.3382	-434988.8358	-218396.7294
5	٠,٤٣٢٠	١,١٠٦٨	٠,٠٨٢٢	-6.4313	-0.7496	6.0104	-483832.4846	-242915.1308
6	٠,٤١٧٣	١,٥٩٢٧	-0.0019	-7.1200	0.1584	4.4027	-386149.2811	-193878.7538
7	٠,١٩٧٢	٠,٢٧١٤	-0.0058	-7.0200	-0.8261	4.3188	-386160.7824	-193881.0464

8	٠,٢٠٨٧	٠,٢٨٢٩	-0.0050	-7.0200	-0.8283	4.2876	-386165.8958	-193881.0328
9	٠,٣٠٠٦	١,٠٢٨٥	0.0365	-7.1556	-0.5444	5.1896	-434986.8719	-218399.3143
10	٠,٢٥٩١	٠,٤٢٢٣	-0.0077	-7.7400	-1.0589	4.8430	-434997.1059	-218400.6074

Table (3): The theoretically calculated values of energy functions for the studied compounds according to the DFT method.

Comp. No.	LUMO (ev)	HOMO (ev)	LUMO- HOMO	ɳ (ev)	μ (ev)	W (ev)
1	0.0085	-0.2483	0.2568	0.1284	-0.1199	0.0560
2	0.0091	-0.2451	0.2542	0.1271	-0.1180	0.0548
3	0.0099	-0.2438	0.2537	0.1269	-0.1170	0.0539
4	0.0102	-0.2436	0.2538	0.1269	-0.1167	0.0537
5	0.0104	-0.2433	0.2537	0.1269	-0.1165	0.0535
6	0.0098	-0.2354	0.2452	0.1226	-0.1128	0.0519
7	0.0098	-0.2361	0.2459	0.1230	-0.1132	0.0521
8	0.0096	-0.2422	0.2518	0.1259	-0.1163	0.0537
9	0.0139	-0.2408	0.2547	0.1274	-0.1135	0.0505
10	0.0125	-0.2282	0.2407	0.1204	-0.1079	0.0483

All variables which are expected to affect the calculation of the ON. Of the gasoline derivatives were calculated then the statistical analysis by using SPSS program was achieved in order to find the best of these variables.

The best linear relationship through which the best result and the best equation of calculating values of ON. Theoretically to compare these values with values collected practically[12].

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.970[a]	.940	.893	7.140

a. Predictors: (Constant), Torsion, TE, LUMO, HOMO

ANOVA[b]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	4014.008	4	1003.502	19.685	.003[a]
	Residual	254.892	5	50.978		
	Total	4268.900	9			

a. Predictors: (Constant), TOR, TE, LUMO, HOMO

b. Dependent Variable: ON

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	298.958	299.745		.997	.364
	HOMO	1205.129	997.810	.322	1.208	.281
	LUMO	-1092.339	2254.722	-.081	-.484	.649
	TE	0.0001	.000	.511	3.526	.017
	TOR	-30.986	11.066	-.860	-2.800	.038

a. Dependent Variable: ON

Table (4): theoretical and practical octane number values of gasoline derivatives of the studied compounds.

Comp. No.	ON. Calculated	ON. Observed
1	101	99
2	122	120
3	129	124
4	133	127
5	94	98
6	144	140
7	139	145
8	137	146
9	127	132
10	168	171

When observing the results in Table (4), we find that there is a convergence of some theoretically calculated octane number values with the practically calculated values, and this relationship indicates the accuracy of the calculation used in this research. The DFT method (ab ition) was closer to practical values than the AM1 method (semi-empirical) of calculations used in a previous study [(11)].

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