

Artículo de investigación

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Chemical approach “structure-conformation” of regular gasoline in the ecuadorian fuel market

Enfoque químico “estructura-conformación” de la gasolina regular en el mercado de combustibles ecuatoriano



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Abstract: A source of chemical energy storage is fossil fuels that in Ecuador are represented by two derivatives: regular gasoline -EcoPlus- (89 octanes), premium -EcoPremium- (96 octanes), and diesel. This shows that the market is not only focused on automobiles but also on agricultural and industrial machinery. There is currently a remission of the sale price to the public as there are subsidies from the Ecuadorian government. Regular 89-octane gasoline is the most widely used for the abovementioned purposes and for implementing and adapting new proposals in modifying 4-stroke engines. This gasoline mixture's composition and octane isomers were analyzed for physicochemical properties related to its liquid state and intermolecular interactions concerning variables such as boiling points and volatility. With the three-dimensional conformation obtained, it was possible to correlate the variables, as mentioned earlier, with the stabilized structures in the gasoline mixtures.

Keywords: Conformation, gasoline, intermolecular interactions, octane, physicochemical properties.

Resumen: Una fuente de almacenamiento de energía química son los combustibles fósiles que en el Ecuador están representados por dos derivados: gasolina regular -EcoPlus- (89 octanos), premium -EcoPremium- (96 octanos) y diésel. Mostrando un mercado no sólo enfocado a los automóviles sino también a la maquinaria agrícola e industrial. Actualmente existe una condonación del precio de venta al público ya que existen subsidios del gobierno ecuatoriano. La gasolina regular de 89 octanos es la más utilizada para los fines antes mencionados y para implementar y adaptar nuevas propuestas en la modificación de motores de 4 tiempos. Se analizó la composición de esta mezcla de gasolina y los isómeros de octanaje para determinar propiedades fisicoquímicas relacionadas con su estado líquido e interacciones intermoleculares relacionadas con variables como puntos de ebullición y volatilidad. Con la conformación tridimensional obtenida fue posible correlacionar las variables, como se mencionó anteriormente, con las estructuras estabilizadas en las mezclas de gasolina.

Palabras Clave: Conformación, gasolina, interacciones intermoleculares, octanaje, propiedades fisicoquímicas.

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I. Introduction

In Ecuador, the history of Petroleum can be divided into two parts: on the one hand, the subject of exploration and exploitation of which there are data since 1909 according to the Central Bank of Ecuador in 1911. The first oil, named Ancón 1, was discovered in Santa Elena. With this event, the exploitation of oil, asphalt, and natural gas deposits in Ecuador began, while exports started in 1973 (Pablo Mateo & García, 2014).

The INEN 935 Standard states that regular gasoline has a composition of at least 87 Research Octane Number (RON), 50% distillation in the range of 77-121 °C, maximum vapor pressure 60 kPa, sulfur content 0.065%, oxygen 2.7% corresponds to mass fraction expressed as a percentage. In contrast, the range of aromatic compounds is a maximum of 35%, benzene 2%, and olefins 25%, which corresponds to the fraction of its volume expressed as a percentage (Servicio Ecuatoriano de Normalización INEN – Ecuador, 2024b).

The composition of gasoline depends on the crude oil of its origin, the obtaining processes, the regulations of each country, and local climatic characteristics. Gasoline derivatives usually contain approximately 15% linear alkanes (n-alkanes) of between 4 and 8 carbons, between 25% and 40% branched alkanes (isoparaffins), 10% naphthenes (cycloalkanes), less than 25% aromatic hydrocarbons and 10% olefins (alkenes); being those grouped as BTEX: benzene, toluene, ethylbenzene, and xylenes, the most

dangerous for health and the environment. Gasoline has a calorific value of 43 950 kJ/kg, a density of 740-765 kg/m³, an autoignition temperature of 257 °C, a kinematic viscosity of 0.5-0.6 mm²/s and a stoichiometric ratio 14.2-15.1 A/F (Muda et al., 2023).

Gasoline is obtained by fractional distillation of petroleum. The most volatile elements of crude oil, such as methane, ethane, propane, butane, and isobutane, are the components of light naphtha (Abdellatief et al., 2023).

The NTE INEN 2 341:2003 standard states that the octane number measures gasoline's quality and anti-knock capacity to prevent detonations and explosions in internal combustion engines. To produce the maximum amount of valuable energy, it is expressed in the volume of iso-octane in a mixture with n-heptane with the same anti-knock characteristics of gasoline tested in a single-cylinder engine (Servicio Ecuatoriano de Normalización INEN – Ecuador, 2024a).

Ecuadorian gasoline production from January to September 2020 was 7 458 319 barrels, as detailed by Petroecuador. However, it is surpassed by the new EcoPaís gasoline, a mixture of regular gasoline plus (maximum of 10% in volume) bioethanol (Boluda et al., 2019).

In 2020, the number of vehicles authorized to circulate amounted to 2 361 175, and this trend continued in 2021, reaching 2 535 853 cars. Statistics show that 11% are vehicles that run on diesel, and the remaining 89% are vehicles that run on gasoline or are

hybrids (Arcentales et al., 2023). Although the technical specifications of new vehicles suggest a 95-octane gasoline, most cars in Ecuador use EcoPlus or EcoPaís. However, sports or high-end vehicles with high-compression engines need gasoline with a higher octane number to prevent engine knocking (Selim, 2004).

Ecuadorian fuel market offers 89 octane EcoPlus gasoline and 96 octane Super Premium gasoline from October 2022; this gasoline is being analyzed in structural and chemical forms, the three-dimensional spatial conformation for studying structural stability, and intermolecular interactions (Chiriboga et al., 2023; Rojas-Reinoso et al., 2023).

II. Materials and Methods

Characterization of Ecuadorian Oil

Through the review, the types of crude oil in the world were represented in comparative tables and graphs, delimiting the data to those found in the American continent; consequently, they were contrasted with the individual variables reported for Ecuadorian oil.

Fossil Fuels Traded in Ecuador

Petroecuador, well known as The Public Company of Hydrocarbons of Ecuador, develops its business management by maximizing the value of energy resources.

Contrasted data from regular gasoline indicated the type of hydrocarbon obtained from the refinery and the combinations used to improve fuel quality.

Quality Indices – Octane - Cetane

Corroborate octane ratings for regular gasoline and cetane for diesel through international fuel reports and analysis of their data sheets, by contrast with what was reported by Petrocomercial, a subsidiary of Petroecuador, allowed a direct comparison of the quality of the fuels sold in the Ecuadorian market. The octane number analysis shows that it directly influences engine combustion and affects the import of vehicles with engines optimized for higher-quality fuels.

Composition of Regular Gasoline - 89 Octane

The report on the composition of regular gasoline in the Ecuadorian market was made based on data provided annually by Petrocomercial, a subsidiary of Petroecuador. Percentages or equivalents of organic components are tabulated. The data was also statistically analyzed to determine which are the most representative and how they influence the general behavior of the hydrocarbon mixture.

Prediction of 3D Structural Conformations

With the list of the most representative components of the mixture, we proceeded to graph them linearly in 2D using chemical

grapher software. Subsequently, for the correct use of these hydrocarbons, they were saved in (.mol) format; these files can store spatial coordinates in compound libraries. Using the free software Avogadro 1.2.0 and the self-optimization tool, the MMFF94 force field model is used to analyze hydrocarbon molecules and visualize molecular geometry, bond lengths of link, and dihedral angles, among others.

Prediction of Stability in Octane Molecules

The range of compounds derived from octane was generated, thus having the most stable isomers, applying the Cahn-Ingold-Prelog rules through the well-known Newman projections. All Newman projections and their conversions to 3D representations explain the stability of octane isomeric molecules (Khalilian et al., 2016).

Prediction of Intermolecular Interactions

Since all the molecules analyzed were hydrocarbons, the lipophilicity data provided valuable information on how they interact with cell membranes in biological elements. In the same way, solubility, solvation, and polarity generated reports of how the contribution of each molecule to the predominant molecular interactions in the mixtures occurs. Considering Van der Waals interactions in the study of dipoles, detailing how lipophilicity contributes mainly to London interactions, and solubility focused on hydrogen bonds and generated instantaneous dipoles.

III. Results and Discussion

Ecuadorian Oil

The ranking of producing countries in South America is detailed in Table 1, reflecting the millions of barrels extracted daily (Pan et al., 2023). In South America, the largest oil producers are Brazil, with 54%, followed by Colombia, at 14%, Venezuela, at 11%, and Argentina and Ecuador at 9% each.

Table 1

Oil-producing countries in South America

Ranking	Country	Mb/d
9	Brazil	2 905 000
21	Colombia	736 000
25	Venezuela	595 000
28	Argentina	507 000
29	Ecuador	473 000
40	Guyana	110 000
54	Perú	38 000
63	Bolivia	31 000
70	Suriname	15 000
81	Chile	1 900

Note. Adapted from (Pan et al., 2023)

Fossil Fuels in Ecuador

Refining involves separation, transformation, and purification processes to convert crude oil into multi-use products to meet the population's needs. In Ecuador, there are three refineries: 1) Esmeraldas, 2) La Libertad, and 3) Shushufindi where the operational capacity of the three is 175 000 barrels per day, where the products that are processed are naphthas

(gasoline), diesel 1, 2 and Premium, jet A-1, fuel oil, Liquefied Petroleum Gas (LPG), asphalt, sulfur, solvents, absorb oil, residue (Harring et al., 2023; Parra et al., 2023).

Octane Number

On July 12, 2022, Ecuador, through Petroecuador, announced the production, distribution, and implementation of two types of gasoline, EcoPlus 89 and Super Premium 95 octane, which are compatible with the Euro 3 technical standard, sufficient for vehicles that require Euro 4 and Euro 5 (Yakubov & Suyarov, 2023). The increase in octane number and decrease in the amount of sulfur will benefit the automotive sector; EcoPlus 89 octane gasoline will contain 200 ppm sulfur and 8% ethanol, which is considered more friendly with the environment and will be light green, while Super Premium 95 octane gasoline will have a yellow color (Valdivia, 2023).

Gasoline - 89 Octane Composition

EcoPlus 89 octane gasoline is a mixture of naphtha and kerosene, also called a fraction of petroleum ether (C_5 to C_7), with the reported formula C_5H_{10} to C_9H_{18} (Ortega Gallegos et al., 2022). When consolidating the conformation list, it was possible to observe that the most significant contribution to the mixture is made up of four representative fractions: xylenes, paraffin, and naphthene, all in a range between 20-25%, (Table 2); which allows us to delimit them as the organic components that predominate and that have the most outstanding contribution in terms

of intermolecular interactions, thus reflecting the properties of this blended gasoline (Llanes Cedeño et al., 2018).

Table 2

Gasoline - 89 octane composition

Organic compound	Percent
Aromatic	2%
Benzene	<1%
Naphthenes	≈20%
<i>n</i> -hexane	<7%
Olefins (alkenes)	3%
Paraffin	≈25%
Toluene	20–25%
Xylenes	20–25%
Total	100%

Note. Adapted from (Llanes Cedeño et al., 2018)

3D Structural Conformations

The 2D representation of each component was developed using the MarvinSketch 22.11.0 chemical structure plotter, where each of the organic components was designed individually. Thus, the aromatic components biphenyl **1**, phenanthrene **2**, benzo[*pqr*] tetrafen **3**, phenanthrene **4**, and anthracene **5** are the most reported in the literature, as seen in Figure 1. Likewise, Figure 2 shows the 3D conformation of compound **3** as an example of 2D to 3D conversion.

Figure 1

Aromatic components of EcoPlus gasoline.

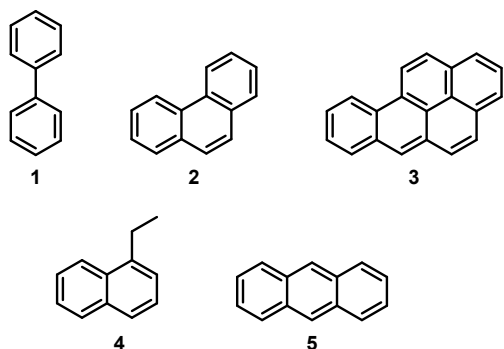
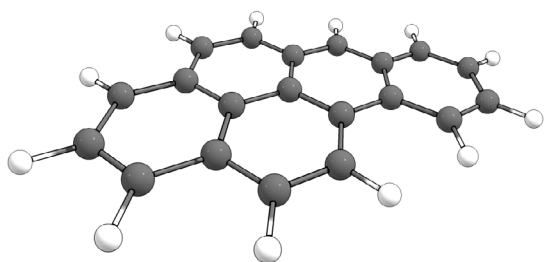


Figure 2

3D optimization of compound 3.



In the same way, with a minor composition, benzene **6**, which, despite being also aromatic, is a functional unit for formulating organic components of concatenated cycles. Its 2D structure can be seen in Figure 3, and its 3D structure in Figure 4.

Figure 3

Benzene in Gasoline EcoPlus.

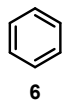
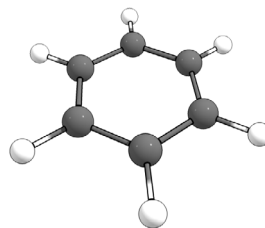


Figure 4

3D optimization of compound 6.



Additionally, the naphthene with the majority composition in the gasoline are shown, thus being in order (Figure 5): cyclohexane **7**, methylcyclohexane **8**, ethylcyclohexane **9**, 1,2,4-trimethylcyclohexane **10**, decahydronaphthalene **11**, isopropylcyclopentane **12**, 1,1-dimethylcyclopentane **13**., represent in 3D form in Figure 6.

Figure 5

Naphthene in gasoline.

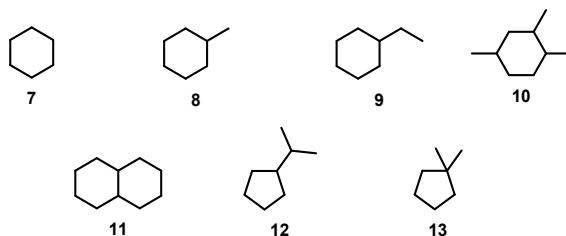
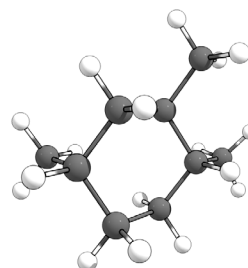


Figure 6

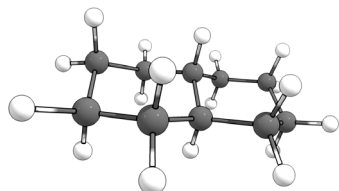
3D optimization of compound 10.



Because it differs from the base compounds in Figure 7, compound **11**, a double cycloalkane, is also detailed.

Figure 7

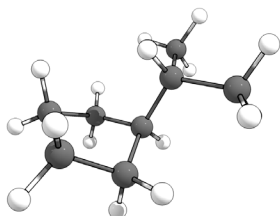
3D optimization of compound 11.



Compound **12** is also mentioned since it is an alkane cycle of five carbon atoms with an isopropyl substituent, as displayed in Figure 8.

Figure 8

3D optimization of compound 12.



On the other hand, an aliphatic fraction such as *n*-hexane **14** is found in a maximum of 7%, and in the same way, there are its isomers within the category of hexanes: 2-methylpentane **15**, 2,3-dimethylbutane **16**, 3-methylpentane **17**. As shown in Figure 9, compound **14** is chosen to show their 3D conformations in Figure 10.

Figure 9

Hexanes isomers.

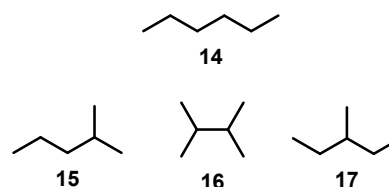
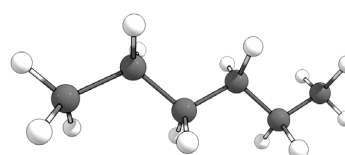


Figure 10

3D optimization of compound 14.



Among the most energetic molecules, highlight olefins these alkenes represent around 3% of the total mixture and are ethene **18**, propylene **19**, 1-butene **20**, (*E*)-2-butene **21** and (*Z*)-2-butene **22**. As reported in Figure 11, compound **21** was chosen to show its spatial conformation in Figure 12.

Figure 11

Olefins.

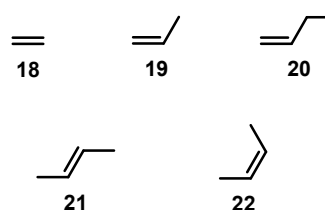
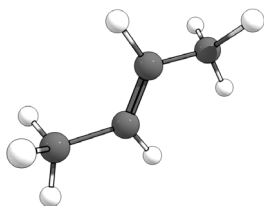


Figure 12

3D optimization of compound 21.



Paraffin, linear alkanes with the conventional formula C_nH_{2n+2} , are present from C_5 to C_{11} (23-33), (Figure 13). As a representative molecule of this group, the 3D configuration of compound 23 is shown in Figure 14.

Figure 13

Linear alkanes.

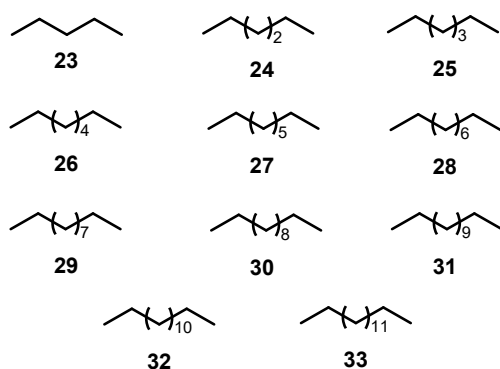
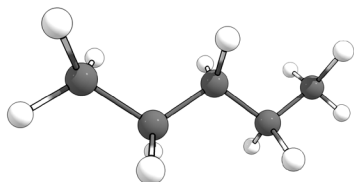


Figure 14

3D optimization of compound 23.

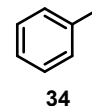


One of the most used solvents at an industrial level is toluene 34, which is present in a liquid state inside the fuel and exudes its

characteristic odor. It is shown in Figure 15.

Figure 15

Toluene 34.



Compound 34, considering its methylation, gives rise to xylenes, non-polar molecules of the following description: *o*-xylene 35, *m*-xylene 36, and *p*-xylene 37 can be seen in Figure 16. Compound 36 is representative, showing its 3D spatial conformation in Figure 17.

Figure 16

Xylenes.

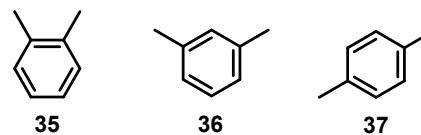
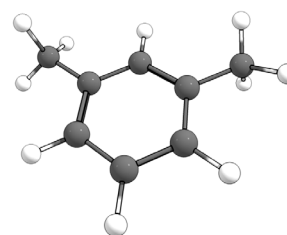


Figure 17

3D optimization of compound 37.



Stability in Octane Molecules

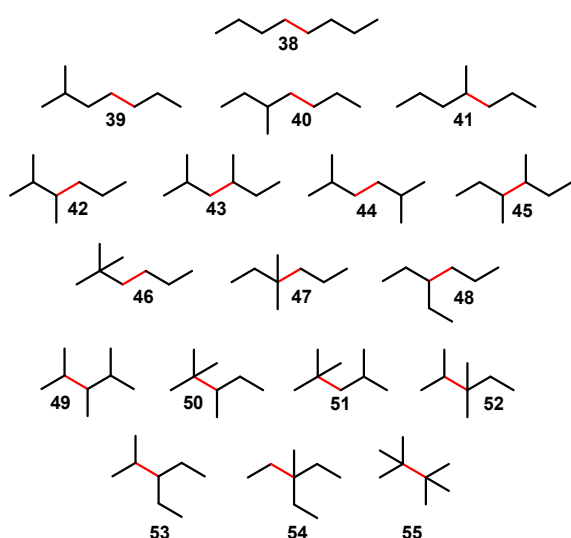
For the prediction of the stability of octane molecules, their 18 positional isomers were considered, identifying, according to the *Cahn-Ingold-Prelog* theory, a symmetrical

axis to project it in space through the analysis of its 3D structures (Hanson et al., 2018).

The isomers to be analyzed are: *n*-octane **38**, 2-methylheptane **39**, 3-methylheptane **40**, 4-methylheptane **41**, 2,3-dimethylhexane **42**, 2,4-dimethylhexane **43**, 2,5-dimethylhexane **44**, 3,4-dimethylhexane **45**, 2,2-dimethylhexane **46**, 3,3-dimethylhexane **47**, 3-ethylhexane **48**, 2,3,4-trimethylpentane **49**, 2,2,3-trimethylpentane **50**, 2,2,4-trimethylpentane **51**, 2,3,3-trimethylpentane **52**, 3-ethyl-2-methylpentane **53**, 3-ethyl-3-methylpentane **54**, 2,2,3,3-tetramethylbutane **55**, the proposed axes of symmetry are in red, which identifies the section closest to a potential provisional axis of symmetry from which the Newman projections were generated, shown in Figure 18.

Figure 18

N-octane isomers.



Three-dimensional structures were obtained to analyze compounds **38-55**, and these 18 isomers were later identified and plotted.

Applying spatial optimization with an MMFF94 force field ensures compliance with the suggested conditions for obtaining 3D coordinates in hydrocarbons. They are shown in Table 3.

Table 3

Theoretical optimization energies for compounds 38-55

Compound	Energy [kJ/mol]	Compound	Energy [kJ/mol]
38	-24.6429	47	48.5500
39	-1.8594	48	20.1649
40	-12.0648	49	79.1602
41	-13.3462	50	93.4867
42	42.8410	51	78.2345
43	-51.2007	52	91.0836
44	23.4995	53	52.0903
45	60.3501	54	71.4076
46	41.4090	55	124.6100

In the group of compounds shown in Figure 19, to better identify the axis of symmetry, the front carbon was determined as **F** (*front*) and the back carbon as **B** (*back*). All structures present alternate configurations: compounds **38**, **39**, **40**, and **43** are the least bulky aliphatic groups. Meanwhile, compounds **41** and **42** have greater tension with each other because of the two aliphatic substituents.

Figure 19

3D optimizations and Newman projections for compounds 38-43.

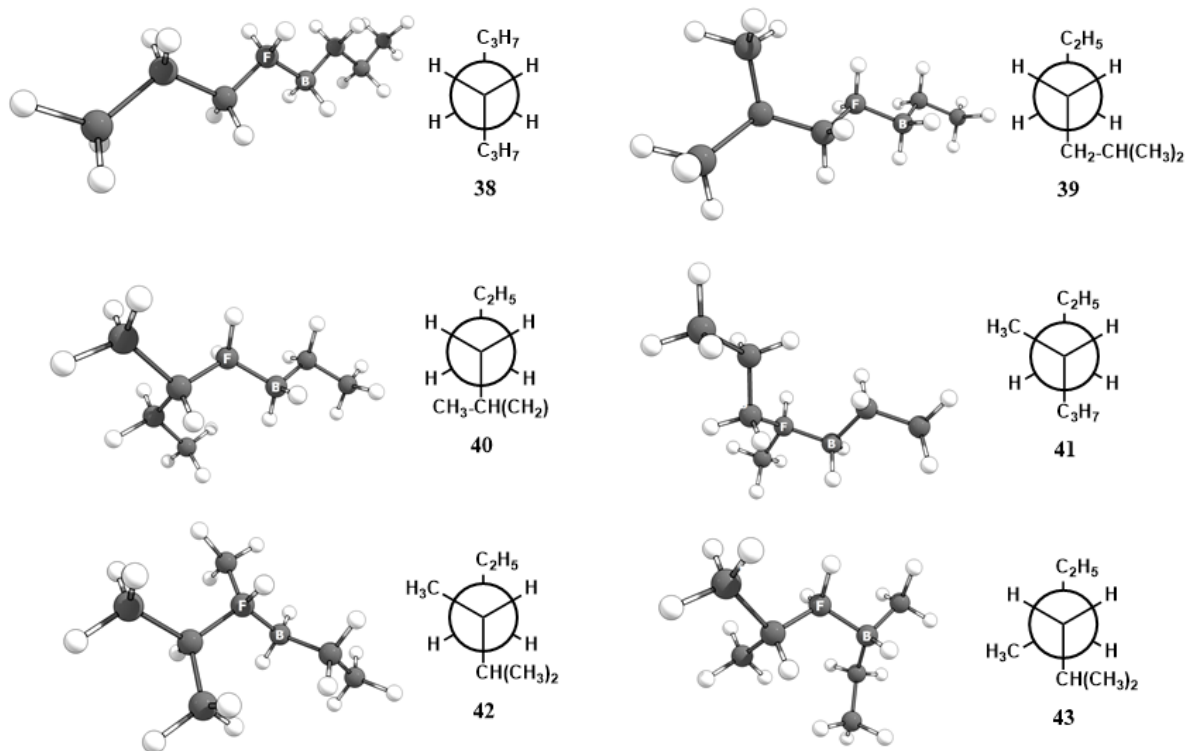


Figure 20

3D optimizations and Newman projections for compounds 44-49.

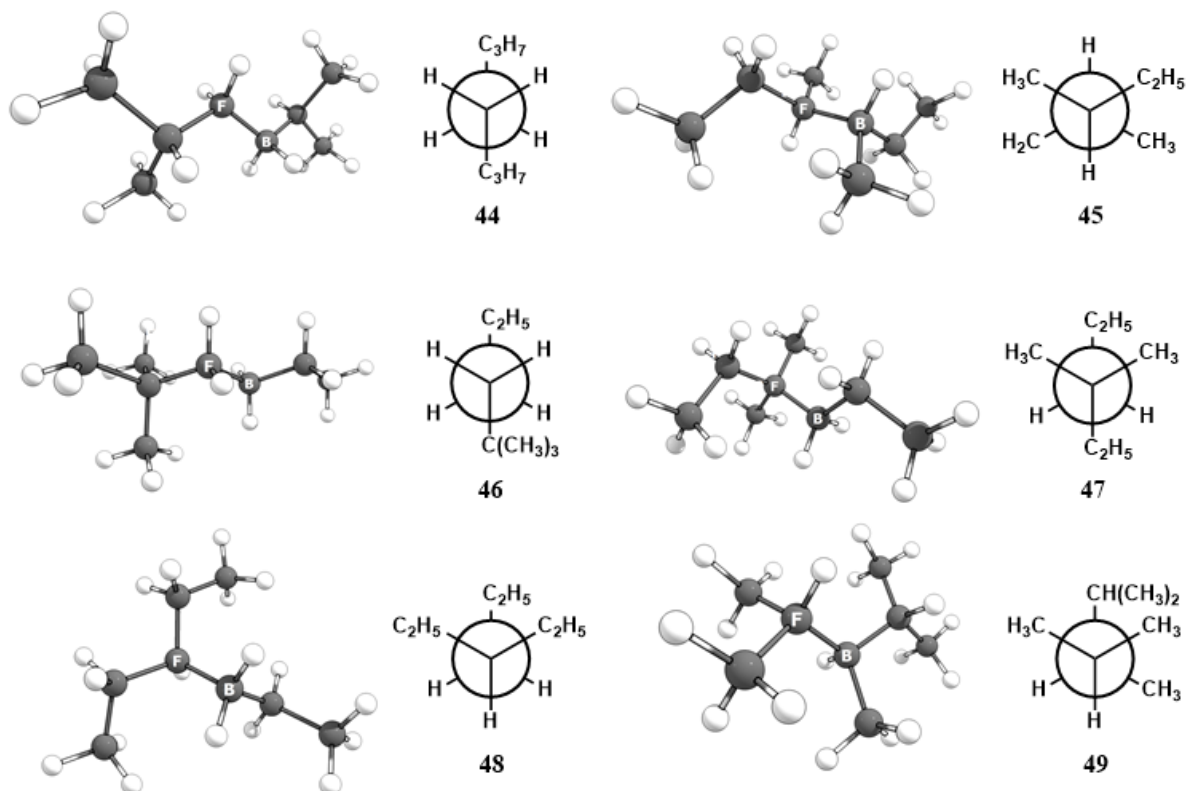
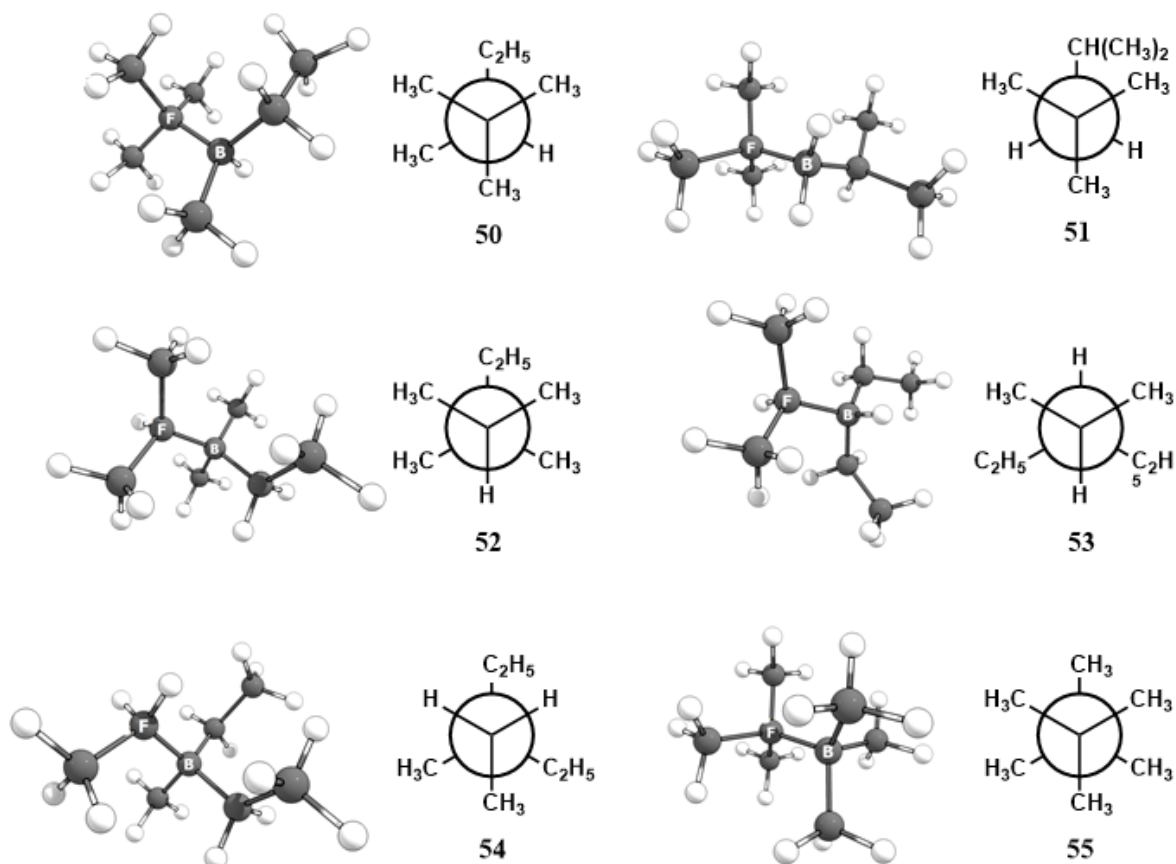


Figure 21

3D optimizations and Newman projections for compounds 50-55.



For the compounds shown in Figure 20, it can be seen that the most stable compounds are **41** and **46**, which only offer one aliphatic substituent. Followed by compounds **47-49**, those that add aliphatic substituents to the carbons adjacent to the symmetry bond.

Finally, compound **45** is the most stressed because all its substituents differ from the hydrogen atom, presenting aliphatic sections.

The last six octane isomers reported in Figure 21 have variable aliphatic substituents, highlighting that the most stable compounds are **51** and **54**, presenting only two hydrogen atom substitutes, allowing the substituents due to the steric effect; they accommodated in

space with a little more ease (Santana-Romo et al., 2020).

In contrast, **50** and **52** only have a hydrogen atom substituent; consequently, compounds **53** and **55** are tended the more, being stated as saturated by aliphatic groups.

Intermolecular Interactions

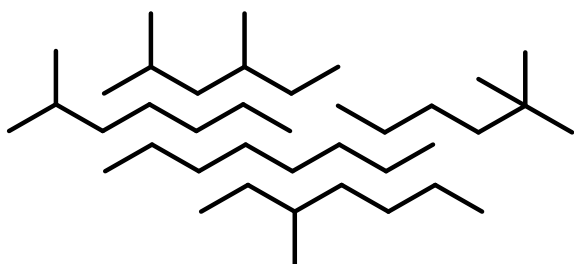
Considering the 3D structures obtained previously, as they are compounds of the hydrocarbon type, which present diversity in the composition of EcoPlus gasoline, those intermolecular interactions of the Van der Waals type, precisely the London (Figure 22), predominate in the alkanes as a product

of instantaneous dipoles.

These interactions of the non-polar type are considered permanent dipoles and all the variants of instantaneous dipoles for attraction between opposite poles/ions.

Figure 22

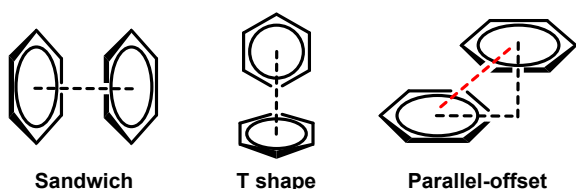
London non-polar interactions.



On the other hand, there are aromatic-type compounds whose fundamental characteristic is their electronic cloud. Without metals (*cations*) and non-metals (*anions*), they will not present π -cation and π -anion interactions, respectively. Nevertheless, overlapping the aromatic fragments will generate the expected π - π stacking interactions (Figure 23).

Figure 23

π - π stacking interactions.

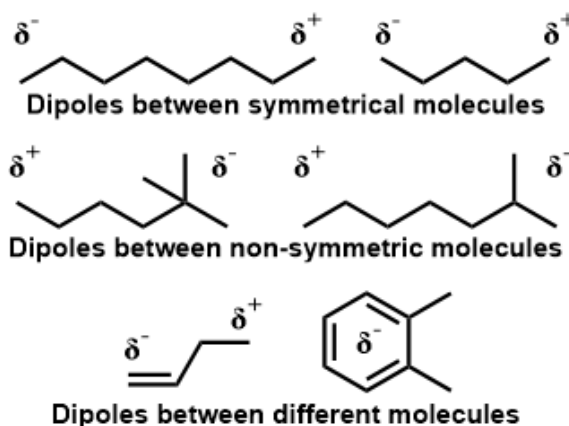


Due to their asymmetry, most compounds will also present momentary dipole-type interactions (Figure 24), thus inducing even symmetrical hydrocarbons to offer a partial

charge on their peripheries, therefore giving rise to the range of dipoles typical of Van der Waals intermolecular interactions.

Figure 24

Interactions between symmetric and non-symmetric molecules.



IV. Conclusions

The standard 3D configuration assigned by the plotters does not correspond to the spatial optimization given by the assignment of an appropriate force field for hydrocarbons. The coordinates (x,y,z) are displaced due to the steric effect between substituents, whose repulsions generate modified dihedral angles in their molecular geometry.

The study of the octane isomers showed in its spatial optimization, and after assigning an axis of symmetry, all the molecules adopt the alternate configuration in the Newman projection. Ecuadorian fuel market (89 octane gasoline) presents questionable quality concerning international standards; even so, the composition is like other gasoline, varying only the autoignition capacity in the engine chamber, decreasing the useful life of the

components associated with the conversion of chemical to mechanical energy.

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