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Computational analysis of triglyceride molecule involving in transesterification reaction

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Abstract. This present study deals with the quantum computational analysis of palmitic-oleic-stearic acid based triglyceride molecule available in waste animal fat, which involves in transesterification reaction during biodiesel production. From stereospecific analysis, stearic acid, oleic acid and palmitic acid, and were found at SN1, SN2 and SN3 positions respectively. The proposed triglyceride model was developed using Gaussian 09 and computational analyses were carried out using Density functional theory (DFT) method. Based on geometric optimization, the average bond length between C-C bond, C=C bond, C-H bond, C-O bond and C=O bond was measured as 1.53Å, 1.33Å, 1.09Å, 1.43Å and 1.23Å respectively. Average dipole moment of the triglyceride molecule was measured as 1.3010 Debye while electronic dislocation was noted in X+Z direction. In addition, the overall molecular energy was found to be -2522.7425 a.u. and optimization energy as -58.95 kJ/mol. Also, vibrational frequencies were analysed using the IR spectrum whereas electrostatic potential were mapped for the triglyceride molecule.

Key Words: Triglyceride, Quantum computational chemistry, Activation Energy, HOMO & LUMO, Electrostatic Potential, Vibration Frequencies and optimization energy.

1. Introduction

The increase in the demand for energy has been making the researchers to rely on self-sustaining biodiesel, which are renewable with lower emission characteristics and robust combustion features [1].To globalize this biofuel in world, the need for understanding its molecular properties is very primary need as these properties decides the overall nature of the fuel. But the market demands forces the experts to optimize the transesterification reaction to evaluate the production economy alone. Accordingly numerous researches have been carried out to optimize the transesterification reaction using various statistical & analytical techniques. The optimization of scum oil as feedstock for biodiesel was done using response surface methodology [2], whereas Taguchi method was implemented for evaluating the feasible production of biodiesel from *Manilkara zapota* (L.) seed oil [3]. Similarly, other high end tools like artificial neural network has been trained in MATLAB for auto optimization for any level of complexity involved in production. However, an effective optimization can be achieved only if the molecular properties of a molecule are analysed prior to the statistical analysis. Various molecular properties include molecular activation energy, electrostatic potential, molecular orbitals, vibrational frequencies etc. [4,5] which are decided based upon the bond length &

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angle, strength of the nucleus, electrons in the outermost orbital, spin quantum number etc. Understanding these properties helps one in calculating parameters which influences the rate of transesterification reaction, to a greater extent. However, very less work has been carried out to study these properties for a triglyceride molecule involved in transesterification reaction. Among these few, Asukama et al., 2009 has conducted a theoretical study on triglyceride molecule involved in transesterification reaction which predicted the reaction order for an ideal reaction [6]. The computational study of the above work was influenced based upon the quantum study done on a KDP crystal for its colouring using dye, where electrostatic potential distribution was studied to understand its colouring mechanism [4]. Similarly, thermochemical analysis was done on oleic acid using quantum computation approach to analyses its behavior during a transesterification reaction [7].

In this study, the molecular properties of triglycerides derived from waste animal fat has been studied using Gaussian View software tool V5.0 [8, 9], where the molecular activation energy, electrostatic potential distribution, vibrational frequencies were analysed completely.

2. Materials and Methods

2.1 Identification of fatty acids: Waste animal fat was collected from the animal wastes and was extracted using Soxhlet's extraction technique. The extracted fat was degummed using orthophosphoric acid, water washed and dried. Following that, the fat was mixed with hexane and was analysed using gas chromatography [10]. GC-MS spectra identified the dominant fatty acids present in the waste fat thereby helping in designing the triglyceride molecule.

2.2 Design of triglyceride molecule: The triglyceride molecule was designed using Avogadro software and was imported to Gaussian tool using mol.2 file format. Arrangement of fatty acids in the triglyceride molecule was based on the Stereoscopic Number. The molecular model was initially optimized using auto optimization tool for proper alignment of atoms in their respective positions. The optimized model was then submitted for molecular analysis.

2.3 Optimization and frequency Analysis of triglyceride molecule: The actual optimization and determination were calculated using Density Functional Theory (DFT) method of quantum mechanics. The molecule was considered to be in ground state and the default spin was assumed for spin state [11]. The parameters involved in optimization and frequency determination of triglyceride molecule is tabulated below in table 1.

2.4 Electrostatic potential of triglyceride molecule: The electrostatic potential distribution was determined using the Density Functional Theory (DFT) method of quantum mechanics under the job type- energy. The molecule was considered to be in ground state and the default spin was assumed for spin state [11]. The basis set used for determining the energy of molecule was 6-31G*, known for computing larger organic molecules. The parameters involved in determination of energy and electrostatic potential distribution of triglyceride molecule is tabulated below in table 1.

Table 1: Gaussian calculation setup for computational analyses

	Optimization and Frequency Analysis	Electrostatic Potential charge distribution	Activation Energy (Ground State)	Activation energy (Transition State)
Job Type	Opt + Freq	Energy	Energy	Energy
State	Ground State	Ground State	Ground State	Transition State

Method	DFT	DFT	DFT	DFT
Spin State	Default Spin	Default Spin	Default spin	Default spin
	B3LYP	B3LYP	B3LYP	B3LYP
Basis Set	6-31G*	6-31G*	6-31G*	6-31G*
Charge			0	1

2.5 Activation energy of triglyceride molecule: The activation energy was determined using the Density Function Theory (DFT) Method in quantum mechanics under the job type- energy. The molecule was considered to be in ground state and the default spin (B3LYP) was assumed for spin state. The basis set used for determining the energy of molecule was 6-31G*, also known for computing larger organic molecules. The charge of the molecule in ground state was found to 0 whereas charge in excited state was found to be +1[11].

3. Results and Discussion

The waste animal fat was rendered from the subcutaneous wastes and was characterized for fatty acids using GC-MS spectra ,which identified Stearic Acid (C18),Oleic Acid (C18:1) and Palmitic Acid (C16) as the most dominant fatty acids present in it. Figure 1 shows the GC spectra of waste animal fat. The position and order of the fatty acids in the triglyceride molecule were decided based upon the Stereoscopic Number System (SN) and degree of saturation [12]. Accordingly, unsaturated oleic acid was well placed at SN2 position. Meanwhile, saturated Stearic Acid and Palmitic Acid among the identified fatty acids, was positioned in SN1 and SN3 position.

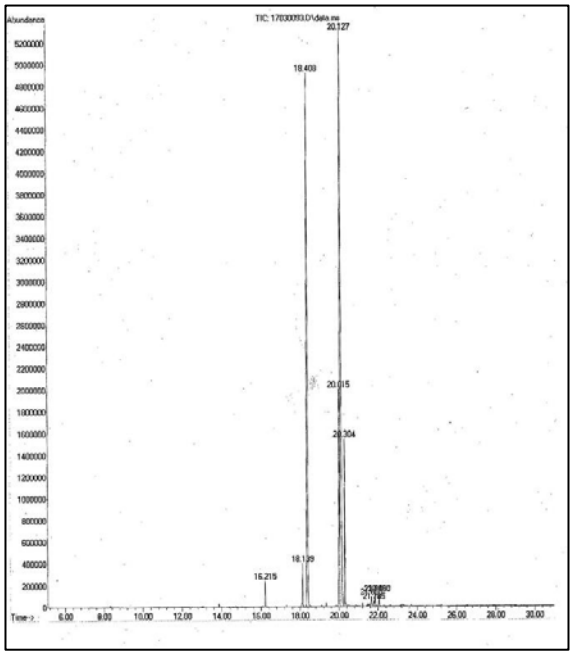

Figure 1: GC Spectra of waste animal fat based triglyceride molecule

Figure 2 shows the initial design model of the triglyceride molecule with no optimized geometry and ground state energy level. The model consisted of 168 atoms and 490 electrons in total and was arranged according to the tetravalency of the carbon with respect to hydrogen and oxygen and corresponding chain length of respective fatty acids.

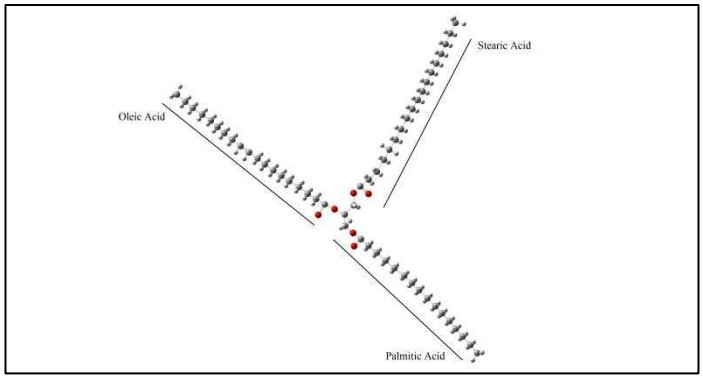

Figure 2: Initial molecular model of the triglyceride molecule (pre-optimization)

Figure 3 shows the optimized model of waste animal fat based triglyceride. The initial optimization was done using auto optimization tool which uses Merck Molecular Force Field (MMFF94(s)) method [13] where every individual atom in the molecule was considered as charged spheres with predetermined diameter and charges ,and were optimized based upon their interactions [11]. The overall energy required for optimizing the triglyceride molecule including the bond stretching energy, bond bending energy and torsional energy was estimated to be -58.95 kJ/mol. The final optimization of the triglyceride was optimized through Gaussian calculation setup using semi empirical method which works on successive iteration.

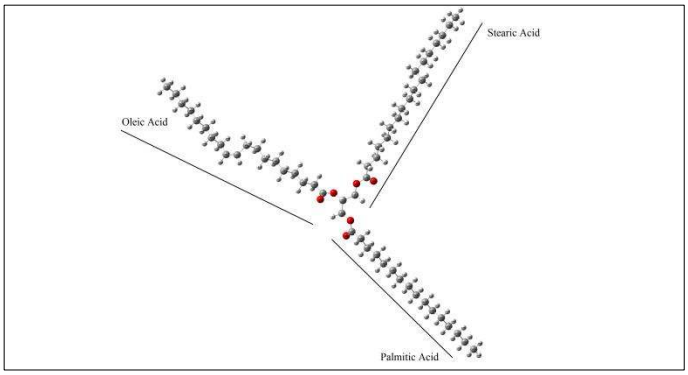

Figure 3: Optimized model of the triglyceride molecule (post-optimization)

Figure 4 and 5 depicts the variation in the geometry between the auto optimized model and mathematically optimized model. The latter model was computed based upon the Gaussian calculation setup→optimization job type, where it was solved until the interatomic distances between two carbon atoms were brought to the closer range of accuracy. This was achieved using semi empirical method of quantum mechanics, where all the physical dimensions related to the model was optimized based on successive iterations. Total number of iterations taken to solve this model was 67 and the energy was found to be -0.770 Hartee (2021.64 kJ/mol). The RMS gradient norm was bought nearly to 0 after 67 iterations and in addition, the deviation was with negligible difference post 50th iteration, thereby indicating that any value considered beyond 50th iteration was accurate with minimum variation. Figure 6 and 7 shows the energy curve and RMS Gradient Curve.

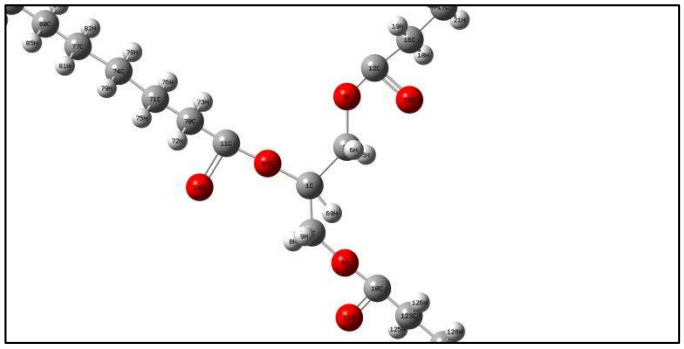

Figure 4: Auto Optimized model of triglyceride molecule (Glyceride spine)

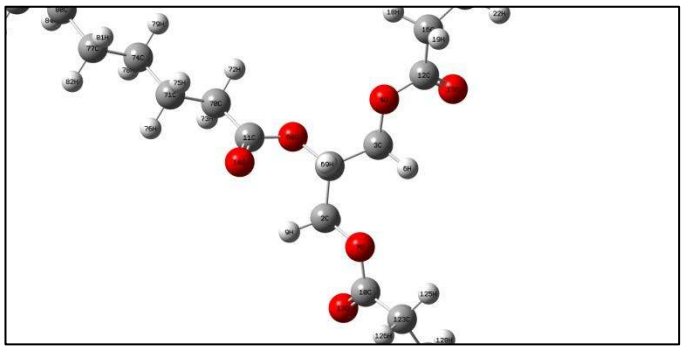

Figure 5: Mathematically Optimized model of triglyceride molecule (Glyceride spine)

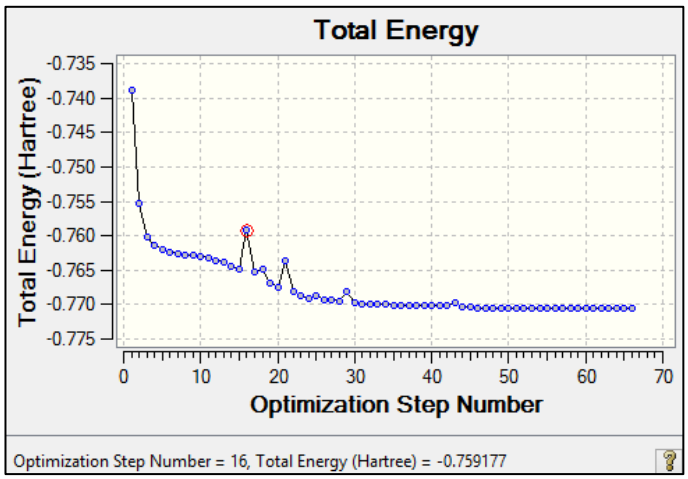

Figure 6: Energy Curve of Optimized Triglyceride molecule (in steps)

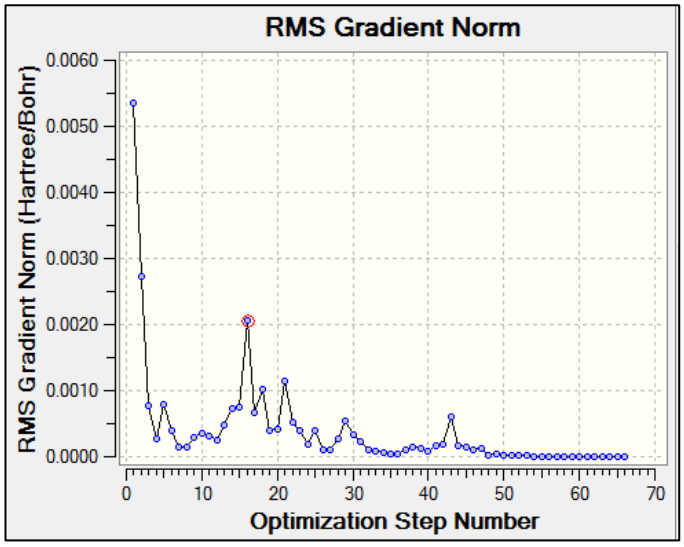

Figure 7: RMS Gradient Norm Curve of Optimized Triglyceride molecule (in steps)

Figure 8 and 9 depicts the modification in the spatial geometry of the double bond in fatty acid at SN2 position in the triglyceride molecule. The bend in the optimized model was because of the Cis-Configuration type isomerism, which is usually recorded for an ideal optimized oleic acid. The angle between C92 and C89 atoms was found to be 127.321° and the same was measured between C97 and C95 atoms because of its geometrical symmetricity. Similarly, the other carbon atoms were aligned based upon their spatial alignment with another carbon atom and their respective hydrogen atoms.

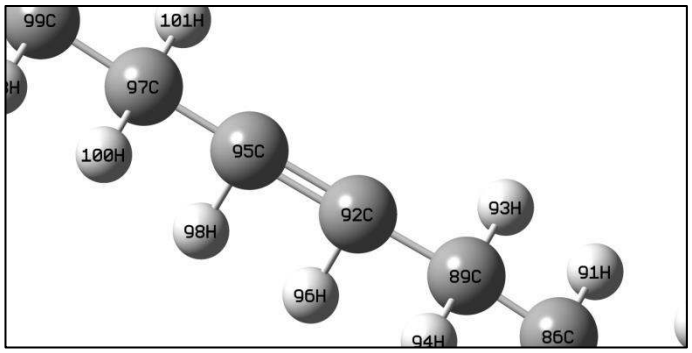

Figure 8: Double Bond in Oleic Acid (Pre-optimization)

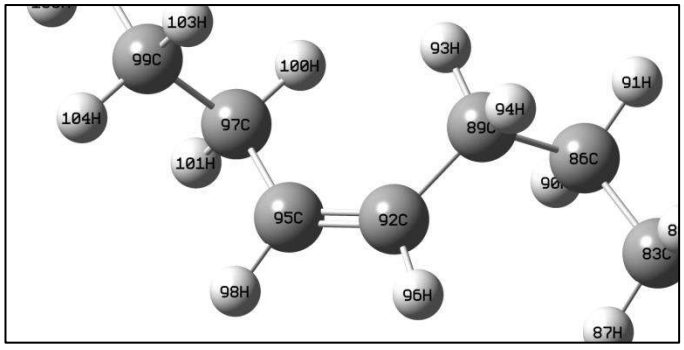

Figure 9: Double Bond in Oleic Acid (Post-optimization)

Figure 10-15 explains the optimization of majorly concentrated bonds which influences the transesterification reaction carried out later. The optimized bond length between C95-C92, C1-C2 and C1-C3 was found to be 1.3382Å, 1.533361Å and 1.53178Å respectively, whereas C2-O7, C1-O68 and C3-O4 were found to be 1.45096Å, 1.46109Å and 1.45141Å respectively. On average, it can be concluded the bond length between two saturated carbon atoms were found to be 1.53Å whereas for an unsaturated carbon bond it was found to be 1.33Å. The average bond length between the saturated bond between carbon and oxygen was found to be in order of 1.45Å. These bond lengths impart major role in transesterification reaction, where increased bond length imparts higher activity in reaction. Table 2 summarizes the bond length before and after Gaussian optimization.

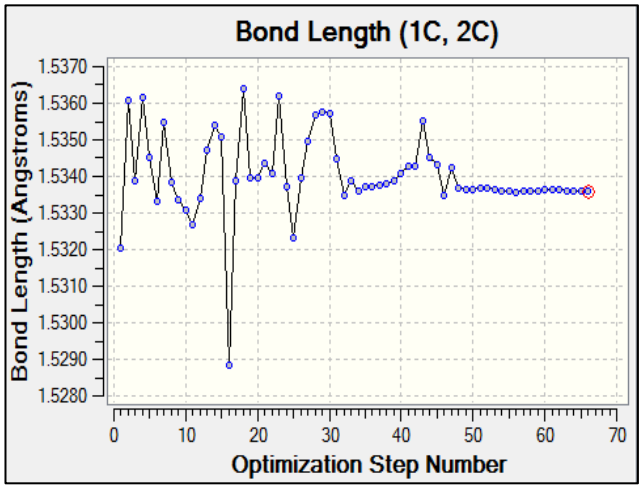

Figure 10: Optimization of Bond length for C1-C2 bond using Gaussian iteration

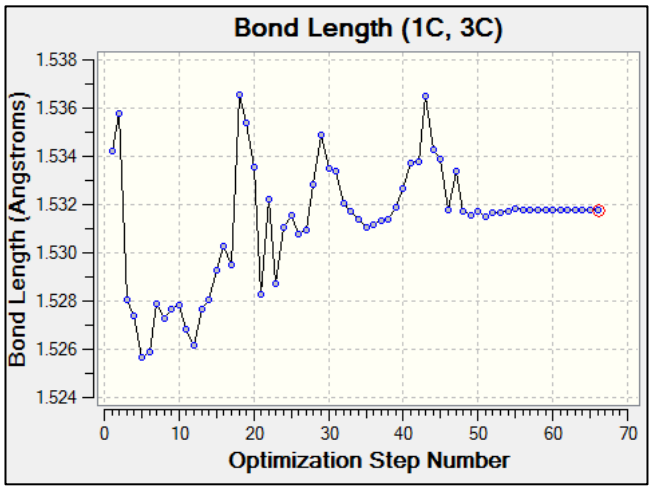

Figure 11: Optimization of Bond length for C1-C3 bond using Gaussian iteration

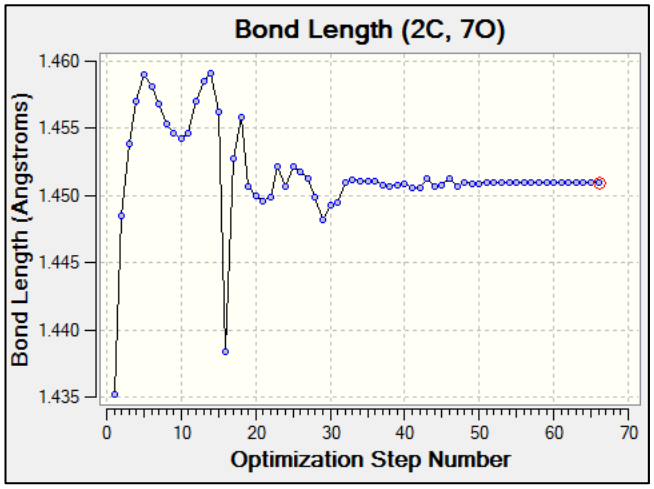

Figure 12: Optimization of Bond length for C2-O7 bond using Gaussian iteration

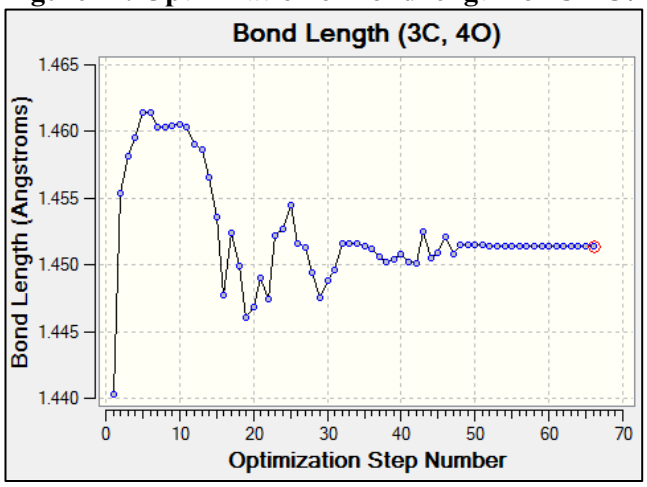

Figure 13: Optimization of Bond length for C3-O4 bond using Gaussian iteration

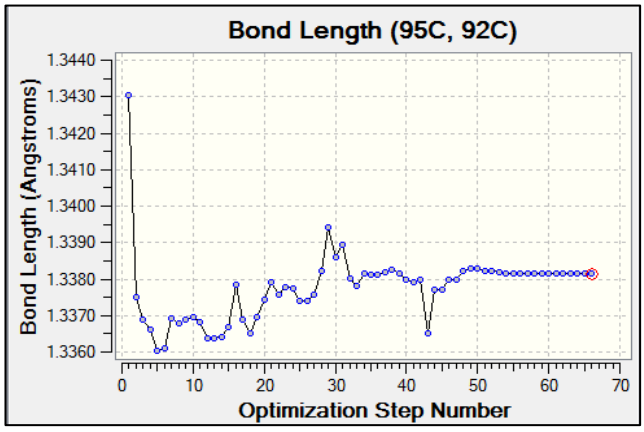

Figure 14: Optimization of Bond length for C92-C95 bond using Gaussian iteration)

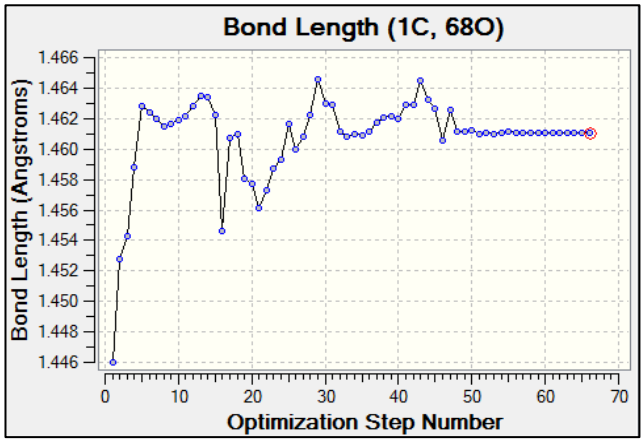

Figure 15: Optimization of Bond length for C1-O68 bond using Gaussian iteration

Table 2: Bond length before and after Gaussian optimization

s.no	Interested bond	Bond length (Å) Pre-optimization	Bond length (Å) Post-optimization
1	C95-C92	1.3430	1.3382
2	C1-C2	1.5320	1.5334
3	C1-C3	1.5342	1.5318
4	C2-O7	1.4352	1.4510
5	C1-O68	1.4460	1.4611
6	C3-O4	1.4403	1.4514

Figure 16 a&b depicts the electrostatic potential mapping of the triglyceride molecule. The electrostatic map shows the overall charge distribution throughout the triglyceride molecule and their related properties as well. The net charge of the molecule was found to be 0 since all atoms were paired and electrons shared covalently, in other words the model was a molecule .The spin state was considered as singlet and the whole iteration was computed based upon the DFT with 6-31G* as its basis set. Overall energy for the molecule was calculated to be -2522.7425 a.u.(-10999.1573*10-18 J) and the dipole moment was found to be 1.3875 debaye (0.287 eÅ).

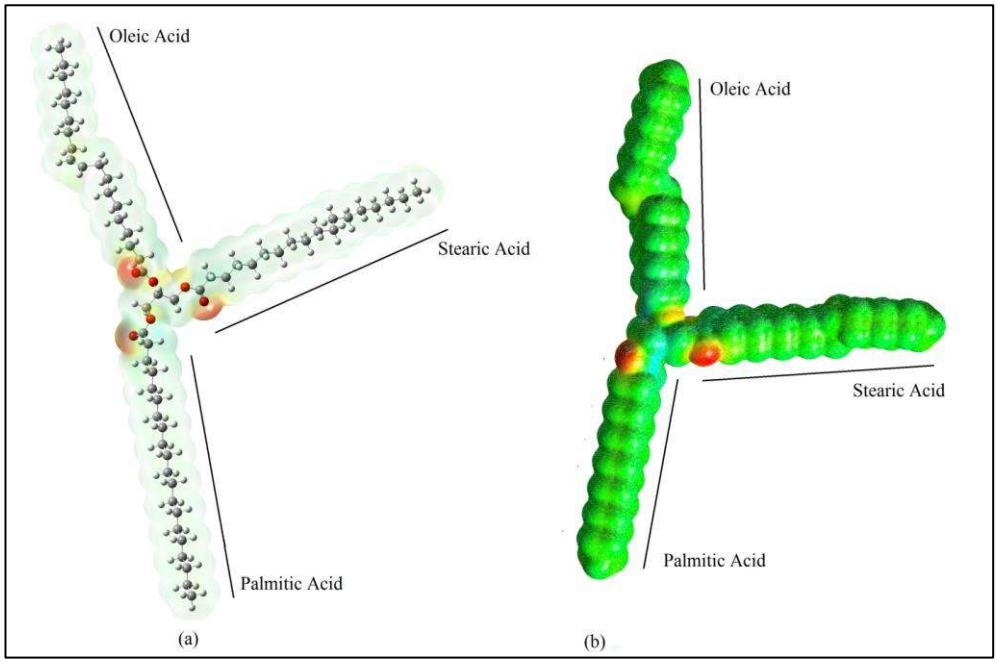

Figure 16: Electrostatic potential mapping of the triglyceride molecule (a) transparent surface (b) wireframe surface

Figure 17a & b shows the electrostatic potential map in form of transparent surface and meshed surface at glycerol spine. The variation in charge distribution at molecule from electrostatic potential map was identified using the colour code variation. The energy scale ranged from -0.273846 a.u. (718.99 KJ/mol) to 0.318700 a.u. (836.746914 KJ/mol), where the oxygen molecule, which readily involves in reaction is in the range of -0.27 a.u. (-718 KJ/mol) exhibiting negative charge whereas the inert carbon atoms is in the range of 0.31 a.u. (837 KJ/mol) carries the positive charges. The O68 atom has the highest negative charge, thereby making the positively charged alkyl ion to attack it first, followed by the remaining oxygen molecules based on magnitude of their charges. Table 3 shows the charge of individual atoms that involves in reaction.

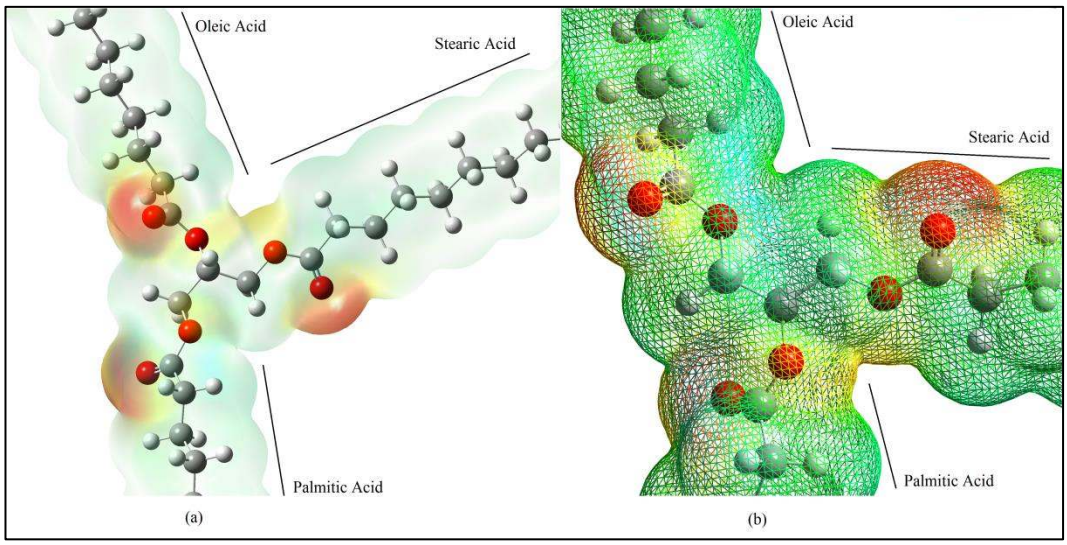

Figure 17: Electrostatic Potential Mapping at Glycerol Spine (a) Transparent surface (b) Wireframe Surface

Table 3: Atomic charge of individual atoms involving in transesterification reaction

Atom Number	Atomic Charge (in a.u.)	Atomic Charge (in KJ/mol)
O15	-0.273846	-7.4517
O4	-0.262573	-7.1449
C12	0.316875	8.6226
C10	0.318700	8.6722
O7	-0.263718	-7.1761
O13	-0.271112	-7.3773
C11	0.318486	8.6664
O14	-0.273373	-7.4388
O68	-0.263721	-7.17621

The activation energy of the triglyceride molecule was studied by computing the energy levels at the ground state and excited state of the molecule. The energy level in the ground state was found to be -2539.06 a.u. (6666302.54 KJ/mol) whereas for the excited state, it was found to be -2538.860 a.u. (6665777.44 KJ/mol). Similarly, the dipole moment varied from 1. 3010 to 18.0651 Debaye.

ΔE= 2539.06 -2538.860 a.u. = 0.2 a u or 525.1 KJ/mol

The variation in energy predicts the amount of energy required to activate the triglyceride molecule for the reaction from it ground state. The data related to the activation energy is tabulated in table 4.

Table 4: Energy and dipole moment of molecule in ground and transition state

Ground state		Transition state (charge:1, spin: doublet)	
Energy	-2539.06 a.u.	Energy	-2538.860 a.u.
Dipole moment	1.3010 debaye	Dipole moment	18.0651 debaye

Figure 18 represents the HOMO and LUMO plot of triglyceride molecule. It can be concluded that the HOMO mapping was higher at SN2 position, and then followed by SN3 position and SN1 position. The LUMO position was occupied at the unsaturated bond between carbon-carbon atoms belonging to fatty acids in SN2 position.

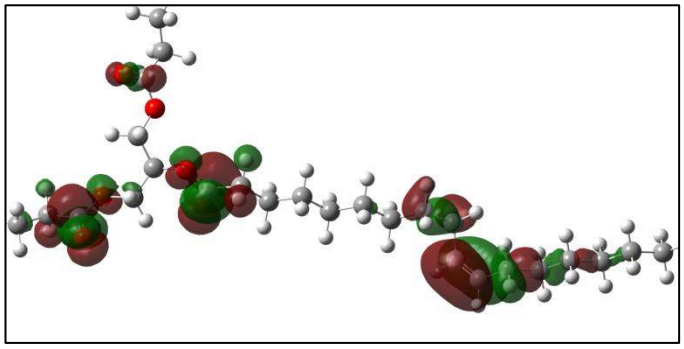

Figure 18: HOMO & LUMO Mapping of Triglyceride Molecule

Figure 19 shows the Infrared (IR) Spectrum of the triglyceride molecule. The major dominant peaks are 1819.08 cm^{-1},1821.88 cm^{-1} and 2694.50cm^{-1} whose corresponding Dipole strengths were 588.4613, 301.5978, 541.2702 $10^{-40}esu^2cm^2$. The Bond with a wavelength of 1819.08 cm^{-1} represents the carbon and oxygen (C=O) stretching, 1821.88 cm^{-1} represents the C=O stretching and 2694.50cm^{-1} represents carbon and hydrogen (C-H) stretching [14]. The table 5 consolidates the IR spectra for corresponding frequencies and Dipole strength.

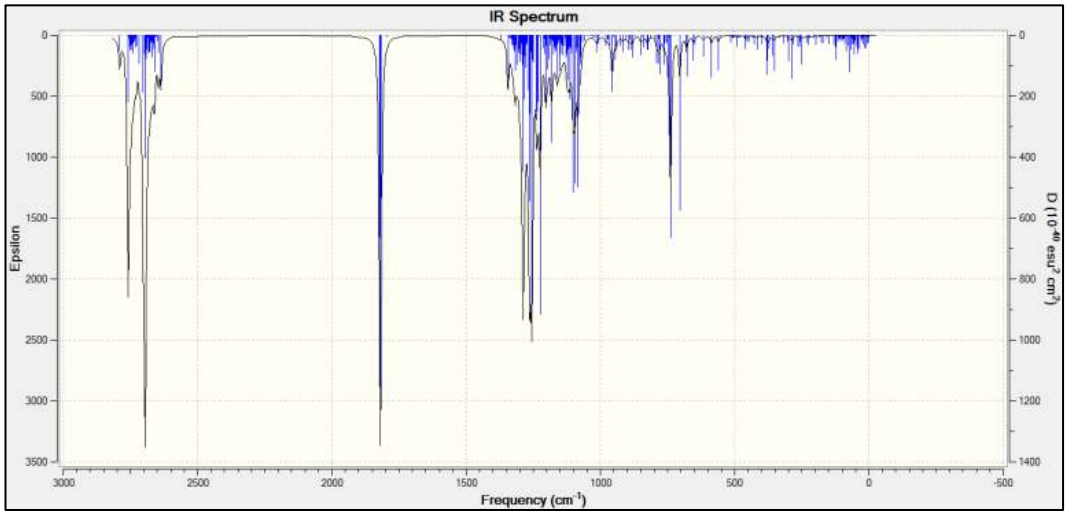

Figure 19: Infrared (IR) Spectrum of the Triglyceride molecule

Table 5: Spectral data of Dominant peaks and their corresponding strengths

Frequency (cm^{-1})	Dipole strength (10-40 esu^2cm^2)
1819.08	588.4613
1821.88	301.5978
2694.98	541.2702
1254.85	276.9249
1256.19	232.5961
2758.27	126.5725
2759.06	144.9754
2759.37	152.9581

4. Conclusions

The quantum computational study of the triglyceride molecule extracted from waste animal fat was studied successfully. The most dominant fatty acids present in it were found as stearic acid, oleic acid and Palmitic acid. The energy of the triglyceride molecule was found as -2522.7425 a.u. (10999.1573*10-18 J) and the dipole moment was found to be 1. 3010 debaye (0.287 eÅ). The IR spectrum revealed the bond behaviour between the carbon and hydrogen atoms and carbon and oxygen atoms in addition with carbon and carbon atoms. The activation energy required for the triglyceride to respond a reaction was found to be 0.2 a.u. Understanding these molecular properties of the molecules helps one in understanding properties and its role in reaction.

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