# Quantitative Structure-Properties Relationship of Lubricating Oil Additives and Molecular Dynamic Simulations Studies of Diamond-Like-Carbon (DLC)

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**ABSTRACT:** *Quantitative Structure-Properties Relationship (QSPR) and molecular dynamics simulations studies were carried out on the 53 lubricating oil additives and hydrogen-containing DLC (a-C: H). Good QSPR model was developed along with squared correlation coefficient ($R^2$), adjusted squared correlation coefficient ($R^2adj$), leave one out cross-validation coefficient ($Q^2$) and the external validation ($R^2ext$) of values 0.807208, 0.763674, 0.68867 and 0.6297 respectively which shows that model I was reliable and satisfactory. Molecular dynamics simulation binding energy calculations between the lubricant additives and the hydrogen-containing DLC (a-C: H) crystals surface revealed that the best molecular dynamic binding energy was found to be -2112.06 kcal/mol and was found to be better than the one reported by other researchers. Moreover, the lubricant additive with compound number 50** (S-(2-(benzo[d]thiazol-2-ylamino)-2-oxoethyl) O-hexyl carbonodithioate) was found to have the best molecular dynamic binding energy of -2112.06 kcal/mol which conformed with excellent best-normalized onset temperature ($T_{onset}$) 2.467K of the same compound. Moreover, Table 7 revealed that the time(s) used for every simulation varies from 12683.13s to 138841.09s for all the studied additives. This investigation will help in rational additive design and synthesis of new and better lubricant additives with predetermined promising binding energy and onset temperature ($T_{onset}$) and will provide valuable information for the understanding of dynamic binding energy between DLC substrate and the new compounds and will give the way toward the discovery of novel lubricating oil additives that can withstand high dynamic working temperature and also resist wearing and frictions.*

**KEYWORDS:** *QSPR; Lubricant additive: Diamond-Like-Carbon (DLC): Hydrogen-containing DLC (a-C: H): Density Functional Theory: Genetic Function Algorithm: Molecular dynamic.*

## INTRODUCTION

With the increase in the problem of friction and wear, unpleasant emissions and knocking of the engine during fluidic lubrication has dramatically increased a large number of lubricant energies usually consumed to overcome friction and wear on surfaces close to each other in recent years. The important problems in machines construction and operations are efficient lubrication assurance [1]. About 84-90% of productivity

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loss by machines and 50% of transport facilities energy consumed are usually lost by wear of friction origin. Researchers are now focusing their attention on using new technologies to designs non-poisonous materials and better lubricant additives that can withstand high lubricating working temperature in the automotive industries to save a huge amount of energy and reduce the release of hazardous chemicals into the already polluted environment [2-4].

Lubricating oil additives are substances formulated for improving the chemical and physical properties of base oils which results in enhancing the lubricant performance and thereby extending the equipment lifespan [4]. Lubricating oil additives help provide the necessary performance for smooth operation and prolonged engine life span. A lubricating oil package of typical multi-grade motor oil is usually comprised of 1- 25% of a typical lubricant oil additives (Detergent, friction modifier, viscosity modifiers, corrosion inhibiting, antioxidant, anti-wear, anti-foam, extreme pressure additives), and a base oil [3, 4]. Diamond-Lke Carbon (DLC) is an environmentally friendly and superior lubricative hard material with a low coefficient of friction, high hardness, good optical transparency and chemical stability [5]. DLC has been very effective in reducing the automobile engines fuel consumption by decreasing friction, being introduced as driving components and pump components to prevent seizure [5]. Coating improvements deposition methodologies enable the many productions of quality Diamond-Like Carbon (DLC) coatings at commercial scale and also increase their use in lubricated contacts. Moreover, the understanding of the interactions of different lubricating oil additives with this material is not yet fully developed [6-8].

To obtain better properties of tribological of the mechanical systems; researchers have been actively performing various investigations on the interaction of various DLC coatings with the different kinds of lubricants and lubricant additives [6–11]. Therefore, the need to search for better and environmentally friendly lubricating oil additives that can withstand different high lubricating working temperatures and overcome friction and wear on surfaces close to each other became an important challenge for engineers and scientists researchers. Quantitative Structural-Properties Relationships (QSPR) and molecular dynamics simulations are widely used in-silico methods in the fields of biochemistry, chemical engineering, toxicology, nanotechnology, environmental sciences and physical, organic, analytical, pharmaceutical, medicinal chemistry [12-14]. The advantage of the QSPR technique is the ability to estimate the properties of new chemical compounds without the need to carry out in-vitro and in-vivo studies while computational molecular dynamic simulations main success is the possibility to calculate the strength of binding energy of substances in close proximity accurately without the needs to carry out experimental study [15, 16]. Moreover, both QSPR and molecular dynamic simulations can save resources (energy, time and money) and accelerate the process of designing new molecules for use as materials, additives or any interest [15,16].

The objective of this research was to use QSPR method to design a novel and environmentally friendly lubricant additives that will be able to withstand high working temperatures in the automobile engine and to in-silico testing of the binding strength of these compounds on DLC coating sliding surfaces using molecular dynamics Simulations.

## EXPERIMENTAL SECTION

### *Data sets*

In this study, the lubricant additives compounds along with the decomposition temperatures were used and collected from some scientist's research kinds of literature [17-19]. Using the randomly selected method, the lubricant additive dataset was divided into training (74%) and test sets (26%). The training sets of 74% dataset were used to build the predictive QSPR model while the remaining test sets of 26% was used to evaluate the predictive ability of the developed QSPR model. The onset temperature of these lubricant additive compounds was measured as $T_{onset}$ (K) were normalized and expressed as logarithmic scale as $pT_{onset}$ ($pT_{onset} = \log T_{onset}$).

### Computational Learning method

*QSPR Model building Details*

The 2D chemical structure of each compound (lubricant additives) in the datasets were drawn with ChemDraw ultra V12.0, named and saved as *cdx file,

***Table 1: Experimental lubricant additives onset temperature ($T_{onset}$).***

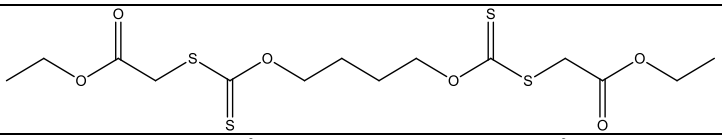
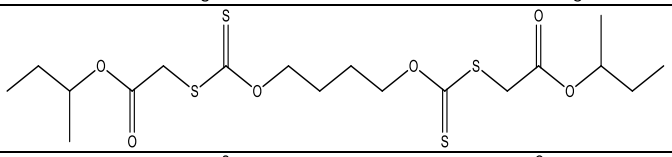
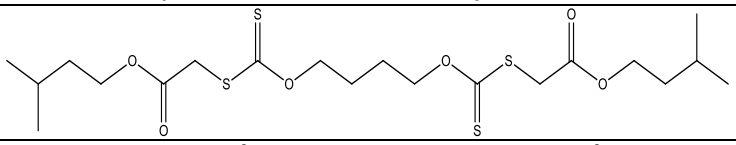
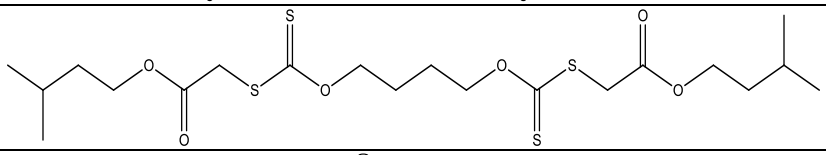
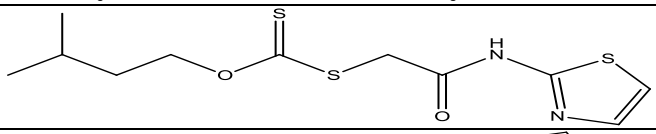
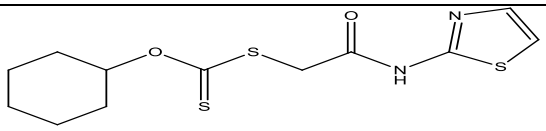
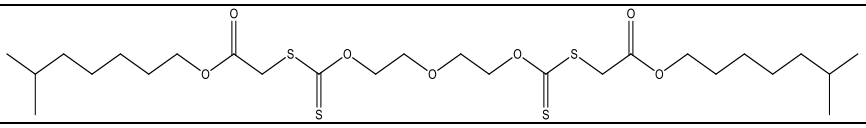
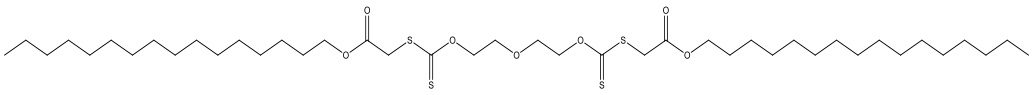
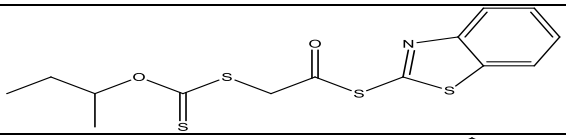
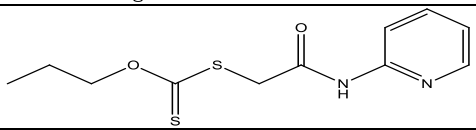
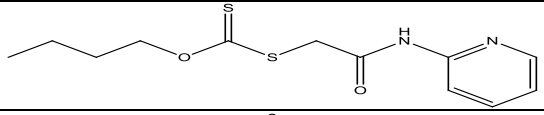
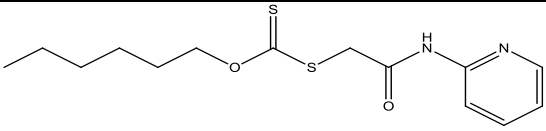
| S/N | 2D Structures of Lubricating Oil Additives | EXP. $T_{onset}$ |
|---|---|---|
| 1* |  | 2.38 |
| 2** |  | 2.385 |
| 3** |  | 2.40 |
| 4** |  | 2.407 |
| 5** |  | 2.381 |
| 6** |  | 2.417 |
| 7* |  | 2.288 |
| 8** |  | 2.242 |
| 9** |  | 2.286 |
| 12* |  | 2.432 |
| 13** |  | 2.43 |
| 14** |  | 6 |

***Table 1: Experimental lubricant additives onset temperature ($T_{onset}$ ), (Countinued).***

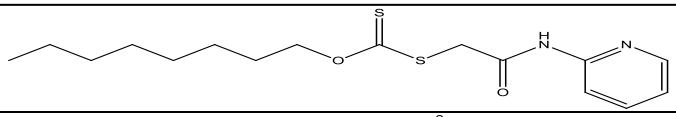
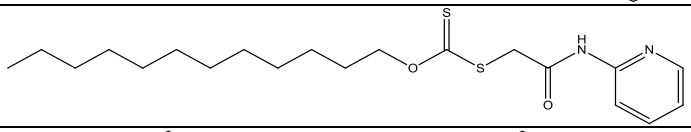
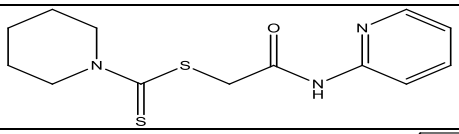
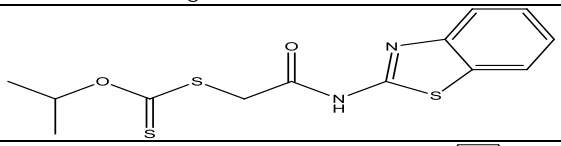
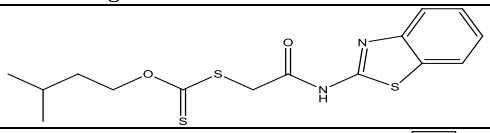
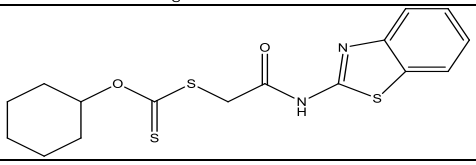
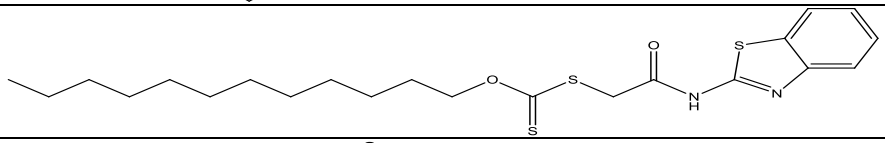
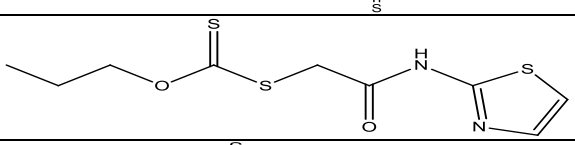
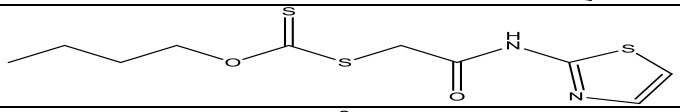
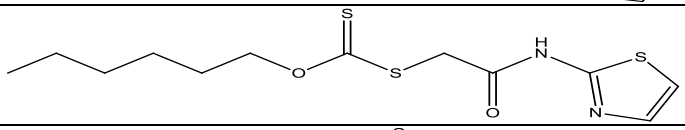
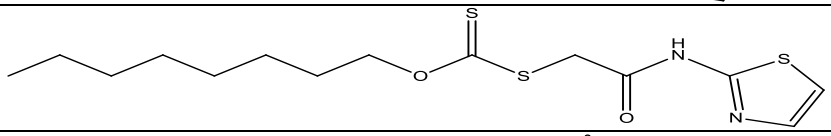
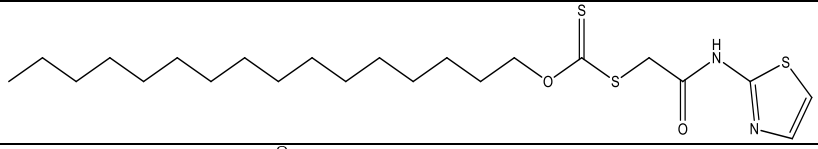
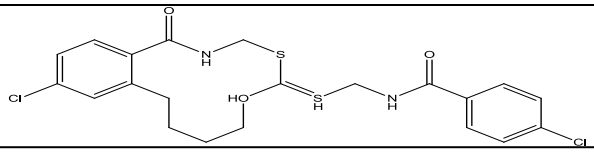
| | | |
|---|---|---|
| 15** |  | 2.253 |
| 16** |  | 2.226 |
| 17* |  | 2.251 |
| 18** |  | 2.271 |
| 19** |  | 2.361 |
| 20** |  | 2.253 |
| 21* |  | 2.254 |
| 22** |  | 2.292 |
| 23** |  | 2.326 |
| 24** |  | 2.258 |
| 25** |  | 2.276 |
| 26** |  | 2.270 |
| 27* |  | 2.352 |

***Table 1: Experimental lubricant additives onset temperature ($T_{onset}$ ), (Countinued).***

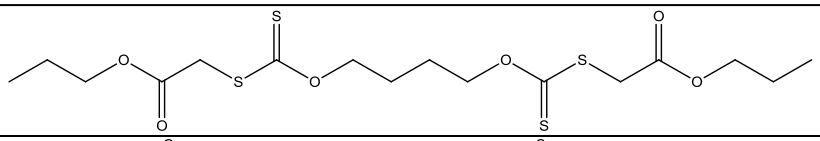
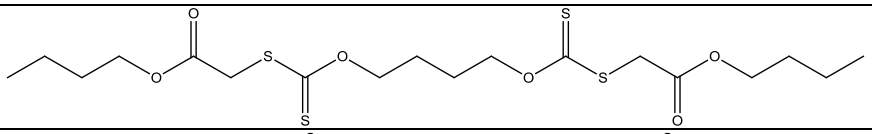
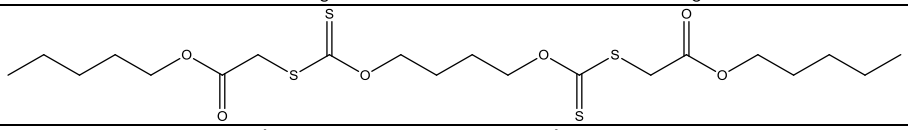
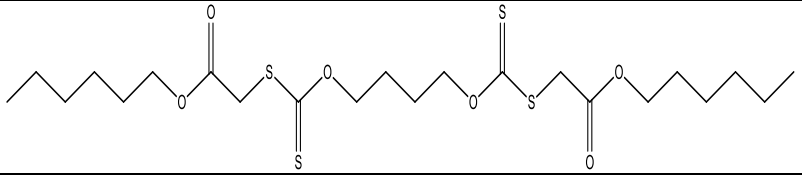
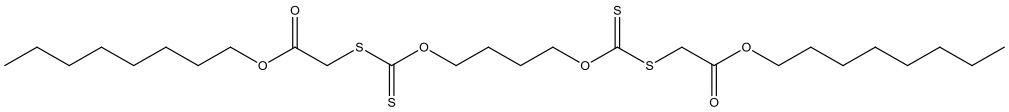
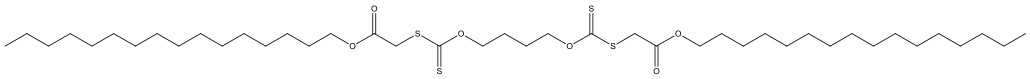
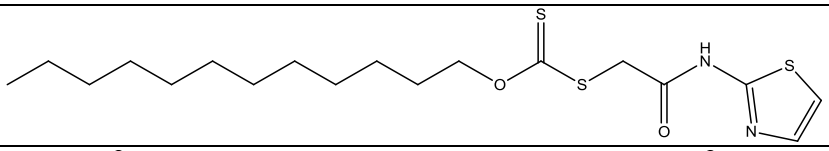
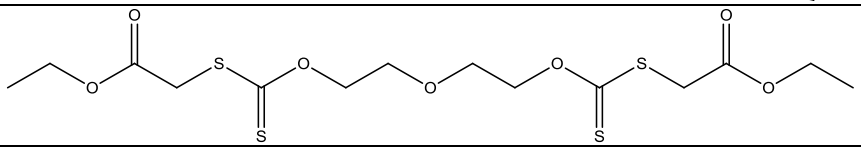
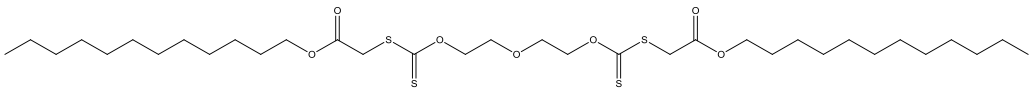
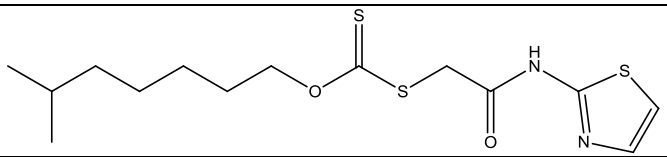
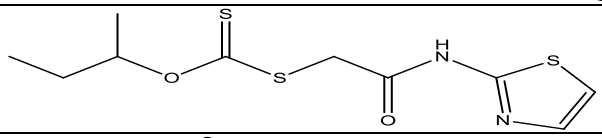
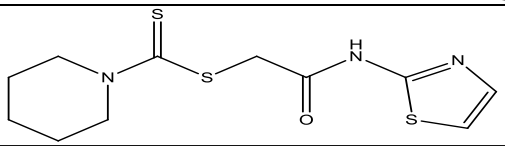
| | | |
|---|---|---|
| 28** |  | 2.392 |
| 29** |  | 2.329 |
| 30* |  | 2.383 |
| 31** |  | 2.400 |
| 32* |  | 2.413 |
| 33** |  | 2.410 |
| 34* |  | 2.408 |
| 35** |  | 2.413 |
| 36** |  | 2.344 |
| 37** |  | 2.307 |
| 38* |  | 2.365 |
| 39** |  | 2.290 |

***Table 1: Experimental lubricant additives onset temperature ($T_{onset}$), (Continued).***

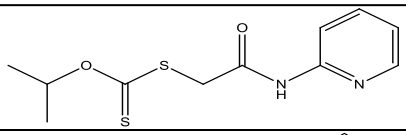
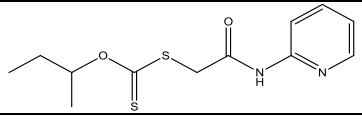
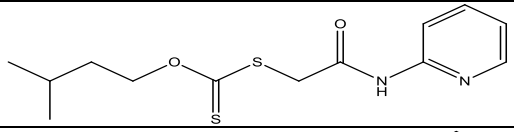
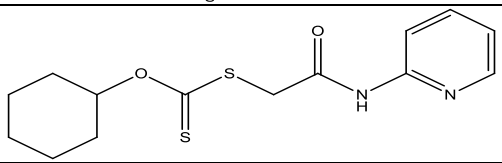
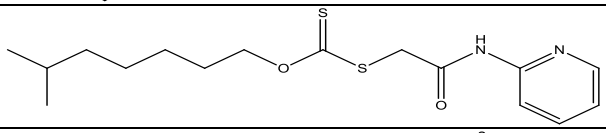
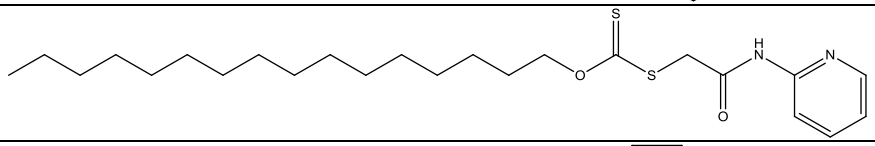
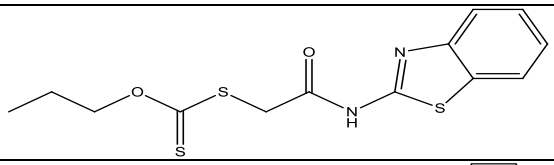
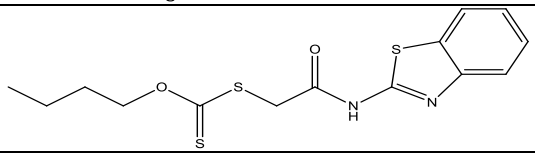
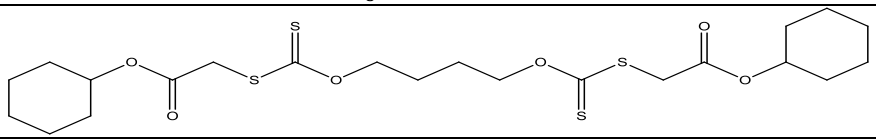
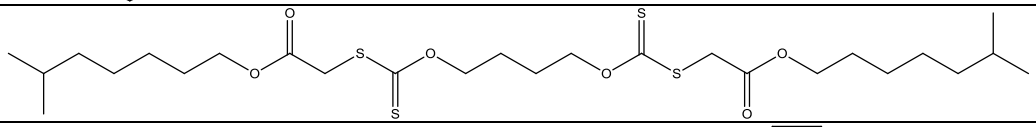
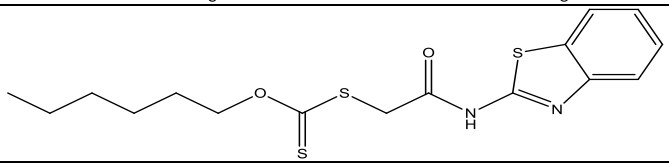
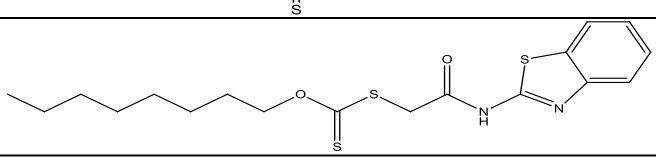
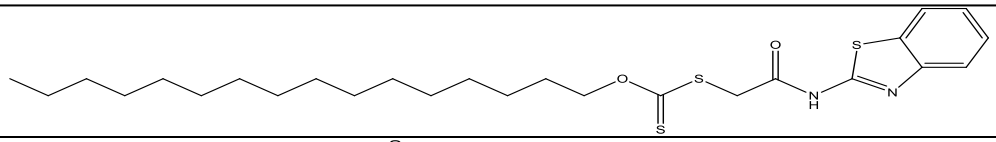
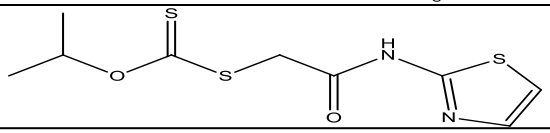
| | | |
|---|---|---|
| 40* |  | 2.415 |
| 41* |  | 2.423 |
| 42** |  | 2.216 |
| 43** |  | 2.219 |
| 44** |  | 2.263 |
| 45** |  | 2.239 |
| 46* |  | 2.268 |
| 47* |  | 2.239 |
| 48** |  | 2.236 |
| 49** |  | 2.258 |
| 50** |  | 2.467 |
| 51** |  | 2.408 |

***Table 1: Experimental lubricant additives onset temperature ($T_{onset}$), (Continued).***

| | | |
|---|---|---|
| 52** |  | 2.319 |
| 53** |  | 2.320 |

***Training set.*
**Test set.*

***Table 2: Minimum recommended value of Validation Parameters for a generally acceptable QSAR model.***

| Name and Symbol | Value |
|---|---|
| Coefficient of determination $R^2$ | ≥ 0.6 |
| Confidence interval at 95% confidence level $P_{(95\%)}$ | < 0.05 |
| Cross-validation coefficient $Q^2$ | ≥ 0.5 |
| Difference between $R^2$ and $Q^2$ $R^2 - Q^2$ | ≤ 0.3 |
| Minimum number of external test set $Next_{. test\ set}$ | ≥ 5 |
| Coefficient of determination for external test set $R^2_{ext}$ | ≥ 0.6 |

after which the 2D structures were converted to 3D structures and geometry optimization/ energy minimization was carried out with Spartan'14 version 1.1.2 quantum chemistry package using density functional theory ( B3LYP/6-311++ G**) [20]. The geometrically optimized compounds were saved in sdf format and transferred to Dragon 6.0 software toolkits [21] where about 3665 generated descriptors were reduced after removing all the redundant descriptors. The Material studio software version 8.0 was used to perform the correlation analysis between the onset temperature values of the molecules and the calculated descriptors. Moreover, the Material studio software version 8.0 was used to develop the predictive QSPR model with the genetic function algorithm (GFA) method and quality assurance of the predictive parameters of the models were carried out. Furthermore, these validation parameters were compared with the minimum recommended value for the QSPR acceptable parameters (Table 2) [22].

**Molecular dynamics simulation studies**

Molecular dynamics calculations were performed to describe and determine the interaction between the lubricant additives molecules [17-19] and the Diamond-like Carbon (DLC) surface. The dynamic module implemented in the Materials studio 8.0 software from Accelrys was used for the simulation calculations.

*Preparation of the* hydrogen-containing *DLC (a-C: H) crystals*

The 3D structure of hydrogen-containing DLC crystal substrate (Fig.2) was built from the carbon (C) model in Materials studio 8.0 simulation software. This was done by cleaving the carbon surface at point 1.1 .0 (h k l), Top (1.006 Å) and Thickness (25.221 Å) into the crystal unit. Moreover, the repeated units (supercell) of the carbon crystal units were formed at U (9) and V (8) while hydrogenation of the supercell, vacuum slab and geometric optimization were performed.

*Preparation of the 3D lubricant additives*

The 2D structures of the lubricant additives compounds were drawn with ChemDraw software and were then converted to 3D structures (Fig.2) by Materials studio 8.0 simulations Software optimized and saved by the same software.

*Analysis of dynamics simulation*

The COMPASS II which is a robust and well-developed (than COMPASS) force field that was derived

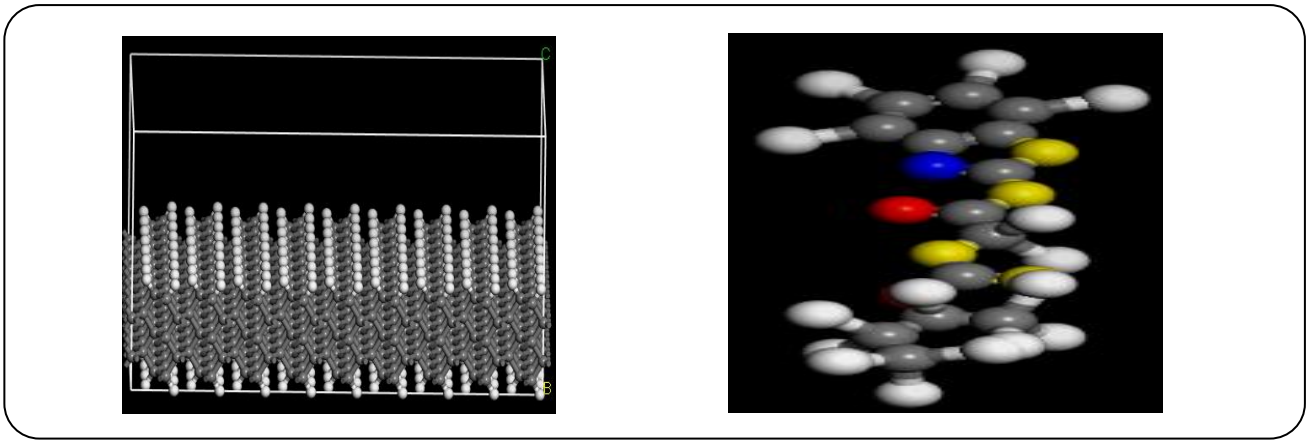


***Fig. 1: A) Prepared 3D a-C: H Substrate, B) Prepared 3D Lubricant Additive.***

based on fitting against a wide range of experimental data for organic and inorganic compounds [23]. The Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II (COMPASS II) force field method in Materials studio 8.0 Software was selected and used for carrying out optimization on both the lubricant additives and DLC crystal. By selecting Dynamic (density functional theory) method from the studio of the materials 8.0 Software, The dynamic simulation calculations were carried out after introducing the optimized lubricant additive compound into the simulation vacuum slab of geometrically optimized hydrogen-containing DLC crystal (24.82 Å ×24.82 Å ×45.27 Å) surface at 350.15 K and over a range of inter-surface separations. The binding energy was calculated by using equation 1 [24]

$$\text{Binding Energy} = E_{\text{total}} - (E_{\text{Lubricant Additive}} + E_{\text{DLC Surface}}) \quad (1)$$

## RESULTS AND DISCUSSIO

### *QSPR Studies*

*Model I*

$p(T_{onset})$ = 0.525100536 * PJI2 + 0.022827404 * VRm1 + 0.067375036 * Mor21m + 0.109901196* BLTF96 - 0.032319313 * F04[C-N] - 0.037025650 * F05[C-O] - 0.031488379 * F05 [O-S] + 1.901236 $R^2$ =0.807208, $R^2_{ext}$ =0.6297, $R^2_{adj}$ =0.763674, $Q^2_{cv}$ =0.68867 and Computed experimental error = 0.00

*Model II*

$p(T_{onset})$ = 0.525100536 * PJI2 + 0.022827404 * VRZ1 + 0.067375036 * Mor21m + 0.109901196* BLTF96 - 0.032319313 * F04[C-N]- 0.037025650 * F05[C-O]- 0.031488379 * F05[O-S] + 1.901236, $R^2$ = 0.807208, $R^2_{ext}$ =0.6170, $R^2_{adj}$ = 0.763674, $Q^2_{cv}$ = 0.68867 and Computed experimental error = 0.00

*Model III*

$p(T_{onset})$ = 0.524707490 * PJI2 + 0.022826879 * VRD1 + 0.067368971 * Mor21m + 0.109886383 * BLTF96 - 0.032288435 * F04[C-N] - 0.037035978 * F05[C-O]- 0.031482808 * F05[O-S]+ 1.90159 and Computed experimental error = 0.00

Due to the statistical significance and base on the recommendation of the standard validation parameters for the acceptable QSPR models (Table 2), the model I among the three models was identified and selected as the best QSPR model for the better prediction of lubricant additives onset temperatures. The highest squared correlation coefficient ($R^2$), adjusted squared correlation coefficient ($R^2$adj), Leave one out cross-validation coefficient ($Q^2$) and the external validation ($R^2$ext) of values 0.807208, 0.763674, 0.68867 and 0.6297 respectively shows that these modelled lubricating oil additives can withstand high working lubricating temperatures before they can decompose and loses the chemical properties that enable them to reduces the coefficient of friction between the sliding contacts.

From the best QSPR model I, increase in the molecular descriptors such as PJI2, VRm1, Mor21m, BLTF96 and decrease in F04[C-N], F05[C-O] and F05[O-S] will increase the onset temperatures ($T_{onset}$) at which the lubricating oil additives decompose during the fluidic lubrication. The predicted $R^2$ 0.807208 value

***Table 3: Internal validation of Model I.***

| | Equation 1 | Equation 2 | Equation 3 |
|---|---|---|---|
| Friedman LOF | 0.005375 | 0.005375 | 0.005375 |
| R-squared | 0.807208 | 0.807208 | 0.807203 |
| Adjusted R-squared | 0.763674 | 0.763674 | 0.763668 |
| Cross-validated R-squared | 0.68867 | 0.68867 | 0.688653 |
| Significant Regression | Yes | Yes | Yes |
| Significance-of-regression F-value | 18.5421 | 18.5421 | 18.54151 |
| Critical SOR F-value (95%) | 2.331629 | 2.331629 | 2.331629 |
| Replicate points | 0 | 0 | 0 |
| Computed experimental error | 0 | 0 | 0 |
| Lack-of-fit points | 31 | 31 | 31 |
| Min expt. error for non-significant LOF (95%) | 0.028385 | 0.028385 | 0.028386 |

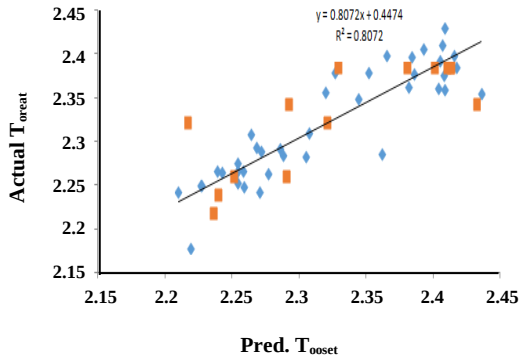



***Figure 2: The plot of actual versus predicted of the training and test set's $T_{onset}$ of the model I.***

which was in agreement with $R^2$ value of 0.8072 recorded in the plotted graph (Fig.2) of actual onset temperatures ($T_{onset}$) against predicted onset temperatures ($T_{onset}$) of both training and test sets confirmed the reliability of the developed model (best QSPR model).

The internal and external validation parameters of the generated and calculated values in Tables 3 and 4 shows that the lubricating oil additives have the thermal ability to withstand high fluidic working temperature. The result from the correlation matrix of Table 5 shows clearly that the correlation coefficients between each pair of descriptors are very low. This implied that no problem of multicollinearity among the descriptors used in building the model [25 and 26]. Moreover, on comparing the actual, predicted and residual of the training and test set's $T_{onset}$ (Table 6) shows that the high predictability of developed QSPR model I was evidenced by the low residual values observed in the Table.

*Molecular Dynamic Simulation Analysis*

Molecular dynamics simulation studies were carried out between the lubricant additives and the hydrogen-containing DLC (a-C: H) crystals surface. All the lubricating oil additive compounds (Table 7) were found to bond strongly with the DLC surface except for compounds 15(7543.395 kcal/mol), 19 (86.499 kcal/mol), 37 (2970 kcal/mol) and 39 (201.936 kcal/mol) which shows low binding energies. In addition, lubricant additive compound number 50** (S-(2-(benzo[d]thiazol-2-ylamino)-2-oxoethyl) O-hexyl carbonodithioate) with dynamic binding energy of -2112.06 kcal/mol showed better binding energy than other co-additives.

*Binding mode of lubricating oil additives*

In Table 7, the Lubricant additives with compound number 50** were found to bound tightly with the hydrogen-containing DLC substrate to generate the overall best binding energy result of -2112.06 kcal/mol. Fig. 3 shows the best lubricant additives- DLC complex with the best binding energy of -2112.06 kcal/mol which was found to be better than the one reported by coastal and his co-workers in 2011 [27].

***Table 4: External validation of Model I.***

| Comp. No | PJI2 | VRm1 | Mor21m | BLTF96 | F04[CN] | F05[CO] | F05[OS] | Predicted $T_{onset}$ | Actual $T_{onset}$ | Residual |
|---|---|---|---|---|---|---|---|---|---|---|
| 41* | 0.857 | 0.976 | -0.043 | 0 | 0 | 1 | 3 | 2.3230 | 2.217 | -0.108 |
| 46* | 1 | 1.025 | 0.268 | 0 | 0 | 1 | 2 | 2.2400 | 2.239 | -2.9E-04 |
| 52* | 1 | 0.972 | 0.368 | 0 | 0 | 1 | 0 | 2.3230 | 2.321 | -0.002 |
| 17* | 1 | 0.226 | 0.494 | 1 | 0 | 2 | 4 | 2.2608 | 2.251 | -0.009 |
| 21* | 0.833 | 0.245 | 0.2 | 1 | 1 | 2 | 2 | 2.343 | 2.29 | -0.051 |
| 1* | 0.9 | 22.56 | -0.473 | -2.33 | 0 | 0 | 4 | 2.3853 | 2.38 | -0.005 |
| 32* | 0.958 | 0.972 | -0.007 | 0 | 0 | 0 | 6 | 2.3853 | 2.410 | 0.0250 |
| 38* | 0.833 | 1.028 | 0.288 | 1 | 0 | 1 | 2 | 2.2608 | 2.290 | 0.0294 |
| 30* | 0.929 | 0.955 | 0.658 | 0 | 0 | 0 | 6 | 2.3853 | 2.401 | 0.0156 |
| 12* | 1 | 0.238 | 0.416 | 1 | 0 | 2 | 2 | 2.3438 | 2.43 | 0.0881 |
| 31* | 0.938 | 0.96 | 0.674 | 0 | 0 | 0 | 6 | 2.3853 | 2.41 | 0.0276 |
| 27* | 0.917 | 0.185 | 0.073 | 0 | 0 | 0 | 0 | 2.3853 | 2.321 | -0.056 |
| 47* | 0.917 | 1.016 | 0.835 | 0 | 0 | 0 | 8 | 2.2193 | 2.2360 | 0.0166 |
| 34* | 1 | 0.942 | 0.572 | 0 | 2 | 0 | 2 | 2.385 | 2.4131 | 0.0277 |

***Table 5: Model I descriptors inter-correlation matrix***

| Descriptor | PJI2 | VRm1 | Mor21m | BLTF96 | F04[CN] | F05[CO] | F05[OS] |
|---|---|---|---|---|---|---|---|
| PJI2 | 1 | | | | | | |
| VRm1 | -0.16027 | 1 | | | | | |
| Mor21m | 0.327873 | -0.64096 | 1 | | | | |
| BLTF96 | 0.012462 | -0.85482 | 0.523809 | 1 | | | |
| F04[C-N] | 0.063371 | -0.10904 | 0.160449 | 0.10126 | 1 | | |
| F05[C-O] | 0.017523 | -0.2817 | 0.003541 | 0.642277 | -0.023 | 1 | |
| F05[O-S] | -0.06629 | 0.098804 | 0.329187 | -0.18698 | -0.2249 | -0.40958 | 1 |

When dynamic binding energy (kcal/mol) of lubricant additives was plotted against the time(s) of every successful operation (Fig. 4), the peak for lubricant additive 50** (-2112.06) was found to be cleared. This is because it took more time (138841.09s) than other LAs for the dynamic binding energy of this lubricant additive on the crystal surface of DLC to converge/calculate. Moreover, Table 7 revealed that the time(s) used for every simulation varies from 12683.13s to 138841.09s

## CONCLUSIONS

This research has clearly shown that the approach used was successful in finding novel lubricant additives that can withstand a fluidic dynamic working temperature from the data set developed by these in-silico methods. The developed QSPR model from various physicochemical descriptors corresponds to the important structural features of lubricant additives found to have a significant correlation coefficient of determination ($R^2$) of 0.807208 values with DLC surface. Increase in the molecular descriptors such as PJI2, VRm1, Mor21m, BLTF96 and decrease in F04[C-N, F05[C-O] and F05 [O-S] will reduce the coefficients of friction and increases its anti-wear ability during the fluidic lubrication by increases the onset temperatures ($T_{onset}$) at which the lubricating oil additives decompose. This is in agreement with the result of molecular dynamic simulations in which lubricating oil additive number

***Table 6: Model I of the actual, predicted and residual of the training and test set's $T_{onset}$.***

| Comp. No | Actual $T_{onset}$ | predicted $T_{onset}$ | Residual | Comp. No | Actual $T_{onset}$ | predicted $T_{onset}$ | Residual |
|---|---|---|---|---|---|---|---|
| 42** | 2.21932 | 2.1791 | 0.04022 | 6** | 2.41747 | 2.386063 | 0.031407 |
| 44** | 2.239 | 2.266365 | -0.02737 | 10** | 2.305 | 2.284252 | 0.020748 |
| 45** | 2.2685 | 2.294609 | -0.02611 | 23** | 2.2582 | 2.266954 | -0.00875 |
| 46** | 2.25864 | 2.248394 | 0.010246 | 26** | 2.3929 | 2.406135 | -0.01324 |
| 47** | 2.404 | 2.361814 | 0.042186 | 35** | 2.3442 | 2.349363 | -0.00516 |
| 48** | 2.4088 | 2.360286 | 0.048514 | 39** | 2.4155 | 2.398897 | 0.016603 |
| 13** | 2.436 | 2.355939 | 0.080061 | 43** | 2.264 | 2.309176 | -0.04518 |
| 14** | 2.227 | 2.249961 | -0.02296 | 51** | 2.31994 | 2.35705 | -0.03711 |
| 15** | 2.254 | 2.253176 | 8.24E-04 | 19** | 2.2541 | 2.266857 | -0.01276 |
| 18** | 2.272 | 2.289366 | -0.01737 | 11** | 2.21 | 2.243613 | -0.03361 |
| 18** | 2.362 | 2.287093 | 0.074907 | 9** | 2.286052 | 2.293078 | -0.00703 |
| 20** | 2.2541 | 2.275428 | -0.02133 | 7** | 2.288026 | 2.284409 | 0.003617 |
| 22** | 2.32695 | 2.378971 | -0.05202 | 41* | 2.217 | 2.323081 | -0.10608 |
| 24** | 2.277 | 2.264031 | 0.012969 | 46* | 2.2398 | 2.240089 | -2.89E04 |
| 25** | 2.2704 | 2.243178 | 0.027222 | 52* | 2.321 | 2.323081 | -0.00208 |
| 2** | 2.3859 | 2.378109 | 0.007791 | 17* | 2.2512 | 2.260837 | -0.00964 |
| 3** | 2.4052 | 2.39267 | 0.01253 | 21* | 2.292 | 2.343829 | -0.05183 |
| 5** | 2.382 | 2.362511 | 0.019489 | 1* | 2.3803 | 2.385325 | -0.00503 |
| 33** | 2.4084 | 2.376082 | 0.032318 | 32* | 2.4104 | 2.385325 | 0.025075 |
| 36** | 2.3072 | 2.310309 | -0.00311 | 38* | 2.29032 | 2.260837 | 0.029483 |
| 37** | 2.3652 | 2.399547 | -0.03435 | 30* | 2.401 | 2.385325 | 0.015675 |
| 40** | 2.40875 | 2.429968 | -0.02122 | 12* | 2.4326 | 2.343829 | 0.088771 |
| 26** | 2.35209 | 2.379368 | -0.02728 | 31* | 2.413 | 2.385325 | 0.027675 |
| 29** | 2.384 | 2.397738 | -0.01374 | 27* | 2.3291 | 2.385325 | -0.05623 |
| 16** | 2.2269 | 2.250624 | -0.02372 | 47* | 2.236033 | 2.219341 | 0.016692 |
| 4** | 2.407 | 2.411804 | -0.0048 | 34* | 2.413115 | 2.385325 | 0.027791 |
| 8** | 2.24254 | 2.265986 | -0.02345 | | | | |

***Table 7: Lubricant Additives Binding Energies.***

| Comp. No | $E_{L.Additives}$ (kcal/mol) | $E_{DLC}$ (kcal/mol) | $E_{Total}$ (kcal/mol) | Binding Energy (kcal/mol) | Time (s) |
|---|---|---|---|---|---|
| 1* | 22.623 | -970.04 | -871.43 | -1864.1 | 13683.92 |
| 2** | 23.73 | -970.04 | -963.64 | -1957.4 | 13683 |
| 3** | 19.634 | -970.04 | -976.96 | -1966.6 | 13943.92 |
| 4** | 19.936 | -970.04 | -980.6 | -1970.6 | 13563.69 |
| 5** | -23.308 | -970.04 | -1023.3 | -1970 | 13684.58 |
| 6** | -23.346 | -970.04 | -1006.1 | -1952.8 | 13573.46 |
| 7* | 22.848 | -970.04 | -28.787 | -1021.7 | 13563.73 |
| 8** | 41.029 | -970.04 | -985.22 | -1996.3 | 13764 |
| 9** | 32.995 | -970.04 | -958.59 | -1961.6 | 13273.73 |
| 10** | -27.335 | -970.04 | -958.04 | -1900.7 | 12983.13 |
| 11** | 93.974 | -970.04 | -1022.4 | -2086.5 | 13823.75 |
| 12* | -43.846 | -970.04 | -97.421 | -1023.6 | 13483.72 |
| 13** | -42.949 | -970.04 | -1031.4 | -1958.5 | 13643.22 |
| 14** | -47.609 | -970.04 | -1030.1 | -1952.5 | 13683.62 |
| 15** | -42.02 | -970.04 | 8471.41 | 7543.4 | 13984 |
| 16** | -47.304 | -970.04 | -943.65 | -1866.4 | 13284.68 |
| 17* | -57.581 | -970.04 | -127.23 | -1039.7 | 13883.58 |
| 18** | -18.33 | -970.04 | -1016 | -1967.7 | 13884.09 |
| 19** | -14.916 | -970.04 | 1041.62 | 86.499 | 13876.46 |
| 20** | 238.59 | -970.04 | -74.858 | -1283.5 | 13983.84 |
| 21* | -12.023 | -970.04 | -777.88 | -1735.9 | 12786 |
| 22** | -29.966 | -970.04 | -1015.3 | -1955.4 | 13083.13 |
| 23** | -26.177 | -970.04 | -1019.5 | -1963.4 | 13983.15 |
| 24** | -33.306 | -970.04 | -1027.6 | -1964.3 | 13973.13 |
| 25** | -26.161 | -970.04 | -1029.5 | -1973.3 | 12683.13 |
| 26** | -29.011 | -970.04 | -1043.1 | -1984.1 | 15683.13 |
| 27* | -4.653 | -970.04 | -1012.3 | -1977.7 | 12983.03 |
| 28** | 28.997 | -970.04 | -45.444 | -1044.5 | 13284.68 |
| 29** | 28.527 | -970.04 | -960.93 | -1959.5 | 13823.75 |
| 30* | 24.726 | -970.04 | -963.35 | -1958.1 | 13883.58 |
| 31** | 24.816 | -970.04 | -978.4 | -1973.3 | 13983.15 |
| 32* | 23.931 | -970.04 | -980.7 | -1974.7 | 13483.72 |
| 33** | 27.835 | -970.04 | -974.15 | -1972 | 13884.09 |
| 34* | -36.805 | -970.04 | -1036 | -1969.3 | 13883.58 |
| 35** | 38.154 | -970.04 | -966.46 | -1974.7 | 13683.92 |
| 36** | 35.184 | -970.04 | -865.18 | -1870.4 | 12786.98 |

***Table 7: Lubricant Additives Binding Energies, (Continued).***

| | | | | | |
|---|---|---|---|---|---|
| 37** | 120.903 | -970.04 | 4061.59 | 2970.65 | 13563 |
| 38* | -32.702 | -970.04 | 1139.27 | 201.936 | 13643.22 |
| 39** | -56.172 | -970.04 | 697.046 | -216.82 | 13973 |
| 40* | -53.391 | -970.04 | -1032.5 | -1949.2 | 13573.46 |
| 41* | -43.231 | -970.04 | -1036.2 | -1963 | 13689.07 |
| 42** | -47.611 | -970.04 | -1043.2 | -1965.7 | 13993.15 |
| 43** | -40.072 | -970.04 | -1038.5 | -1968.5 | 13643.22 |
| 44** | -46.671 | -970.04 | -1035.5 | -1958.8 | 13684.58 |
| 45** | -44.542 | -970.04 | -1048.3 | -1973.8 | 13284.68 |
| 46* | -9.195 | -970.04 | -990.22 | -1951.1 | 13883.45 |
| 47* | -13.169 | -970.04 | -1002.2 | -1959.1 | 13884.04 |
| 48** | 9.556 | -970.04 | 1555.78 | 576.187 | 13083.13 |
| 49** | 23.89 | -970.04 | -987.16 | -1981.1 | 13884.09 |
| 50** | 127.772 | -970.04 | -1014.3 | -2112.1 | 138841.1 |
| 51** | -8.85 | -970.04 | -84.209 | -1045.4 | 13483.32 |
| 52** | -14.815 | -970.04 | -1025.4 | -1980.6 | 12786.75 |
| 53** | -38.223 | -970.04 | -1022.6 | -1954.4 | 13883.58 |

$E_{L.Additives}$ = *Lubricant Additives* $E_{DLC}$ = *Diamond Like-Carbon*
$E_{Total}$ = *Total Energy of the complex* ***Training set:* *Test set.*

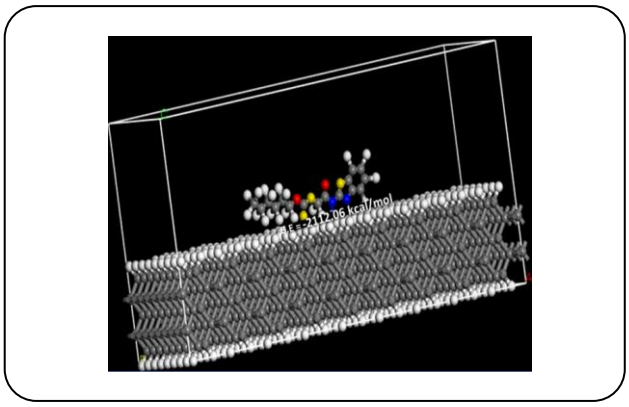



***Fig. 3: Side view of Lubricant Additive-DLC Complex.***

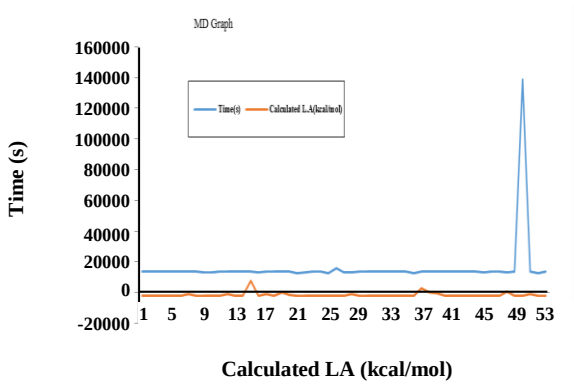



***Fig. 4: Molecular Dynamic Simulation's Graph.***

50**(Table 7) with the best dynamic binding energy of -2112.06 kcal/mol was found to be tightly bound with the hydrogen-containing DLC surface (Fig. 3) and was found to be better than the one reported by *Costal* and his co-researchers in 2011 [27].

Moreover, the lubricant additive with compound number 50** was found to have the best molecular dynamic binding energy of -2112.06 kcal/mol which conformed with the same compound number 50** that have overall best-normalized onset temperature ($T_{onset}$) of 2.467K (Table 1). This investigation will help in rational additive design and synthesis of new and better lubricant additives with predetermined promising binding energy and onset temperature ($T_{onset}$) and will provides valuable information for the understanding of dynamic binding energy between DLC surface and the new compounds and will give the way toward discovery of novel lubricating oil additives that can withstand high dynamic

working temperature and also resist wearing and frictions in coating sliding surfaces.

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