Quantitative Structure-Properties Relationships and Molecular Dynamic Simulations of Some Lubricant Additives (LAs)

Usman Abdulfatai, Adamu Uzairu, Sani Uba, Gideon Shallangwa
Ahmadu Bello University, Department of Chemistry, P.M.B. 1044, Zaria, Nigeria

The degradation of this zinc-dialkyl-dithiophosphate (ZDDP), at a temperature less than 246K often leads to the release of phosphorus, sulphur, and zinc which are indirectly responsible for the emission of poisonous gas from the exhaust pipe of the motor cars. Four QSPR mathematical models were generated from 39 structures of lubricant additives (LAs) and the structural features were found to corresponds to the coefficients of; internal correlation (R^2) of 0.95, adjusted squared correlation (R^2adj) of 0.94, Cross-validation (Q2cv) of 0.90, and the external validation (R^2pred) of 0.54. The model suggests that new LAs with improved onset temperatures (T_{onset}) could be designed by interpreting and increasing the value of the molecular descriptor such as IC5 (Information Content index/neighborhood symmetry of 5-order) and Ve (V total size index/weighted by Sanderson electronegativity) and at the same time decreasing the values of RDF080m (Radial Distribution Function-080/weighted by mass), RDF110m (Radial Distribution Function-110/weighted by mass), P2v (2nd component shape directional WHIM index/weighted by Van der Waals volume) and R1e+ (R maximal autocorrelation of lag 1/weighted by Sanderson electronegativity). Moreover, the LAs with an experimental onset temperature of 351.6K agreed with the predicted onset temperature of 351.7K13a. And was also in agreement with the result of molecular dynamics simulations in which the LAs with the best dynamic binding energy of -2112.06 kcal/mol was tightly bounded on the simulated DLC mechanical coated boundary inter-surface and was also found to be better than the commercial LAs, ZDDP in term of binding energy and onset temperature. This investigation will help in rational additive design and synthesis of new and better selective Las

Keywords: Lubricant Additives (Las); Diamond-Like Carbon (DLC); DFT; GFA; Molecular Dynamic (MD); simulations; Quantitative Structure-Properties Relationships (QSPR)

Introduction

Research showed that energy loss from ineffective boundary lubrication of mechanical components is accounting for 25% of important energy needed while 15% of the loss in internal energy is due to mechanical frictional loss (Yanli, (2017), and Becker, (2004)). Innovative machine technology has made it clear that the requests put upon each viable oil were not met by even the monetarily accessible lubricants. To avoid friction and machine wearing, researchers are searching for reliable and less costly means to designs different types of lubricant additives (LAs) that could increase the known properties of lubricants and will not decompose easily when blended with the base stock at higher machines lubricating dynamic temperature (Kato, (2011); El-Eisawy *et al.*, (2015); Ahmad *et al.*, (2018); Podgornik, (2001); Moriguchi *et al.*, (2014)). LAs are chemical organic compounds used to increase the performance of base oil stock (Ahmad *et al.*, (2018); Podgornik, (2001)). LAs help to prolong the machine engine lifespan by providing the necessary performance for smooth and better operation (Kato, (2011); El-Eisawy *et al.*, (2015); Ahmad *et al.*, (2018); Podgornik, (2001)). Scientists have been effectively performing different researches on the association of different DLC boundary coatings with various kinds of LAs to acquire better machine tribology understanding of boundary interfaces (Neville *et al.*, (2007); Kano *et al.*, (2005); (2005), Kalin and Velkavrh, (2013); Aboulthana *et al.*, (2019); Forsberg *et al.*, (2013); Chiro *et al.*, (2010)). LAs such as Pyrimidine, natural acids, and pyrazines have emerged following the used zinc-dialkyl-dithiophosphate (ZDDP) as multifunctional LAs. This widely used ZDDP was reported to hurt the environment and was also reported to decompose at a temperature of less than 246K (Chiro *et al.*, (2010); Zhongyi *et al.*, (2020)). Therefore, urgent need to look for better and ecologically friendly LAs that can withstand diverse high lubricating working temperatures cannot be overemphasized. Quantitative Structure-Properties Relationships (QSPR) and molecular dynamics simulations are computational methods widely used as a research tool (Kubinyi, (1997); Robinson *et al.*, (1999); Ivanciuc *et al.*, (2000); Wong *et al.*, (2002)). QSPR relates molecular properties with its molecular structure of interest. The advantage of the QSPR technique is the capacity to figure the properties of new hypothetical chemical substance and it serves resources and gives direction before the real experimental study (Abdulfatai *et al.*, (2019a); Mohammad and Zohreh, (2013); Abdulfatai *et al.*, (2019b)).

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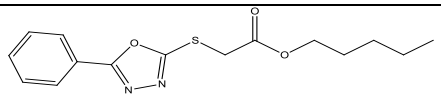
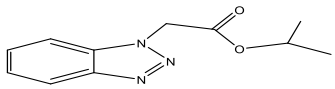
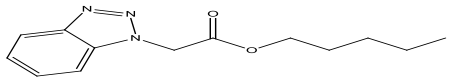
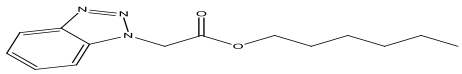
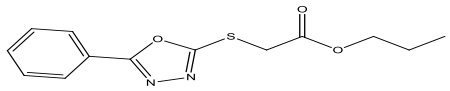
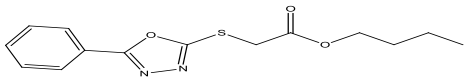
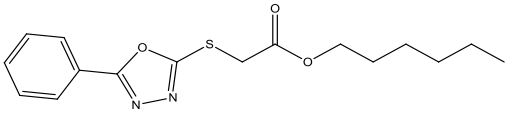
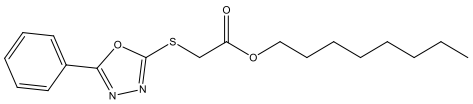
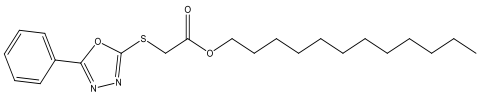
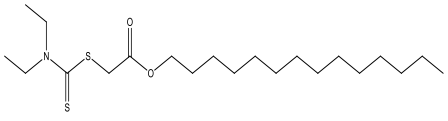
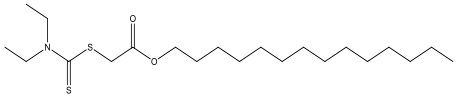
Moreover, the molecular dynamics simulations main success was the possibility to calculate the dynamic binding strength (binding energy) of a molecule on interfaces accurately before carrying out the complicated expensive experimental study (Abdulfatai *et al.*, (2019a); Mohammad and Zohreh, (2013); Abdulfatai *et al.*, (2019b)). This investigation was aimed at designing better LAs that can resist high dynamic boundary temperatures before it decomposes and to determine the dynamic binding strength of LAs in the boundary sliding interfaces via QSPR and MD.

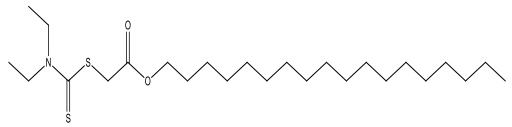
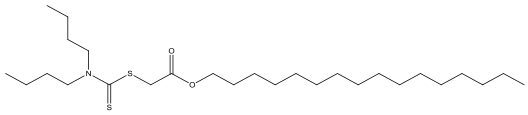
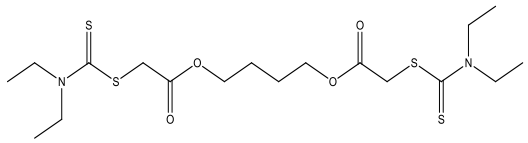
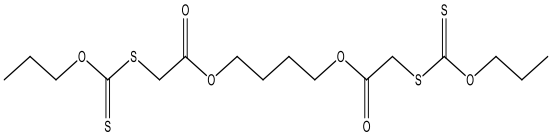
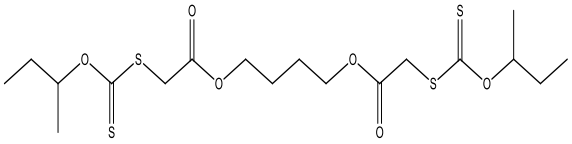
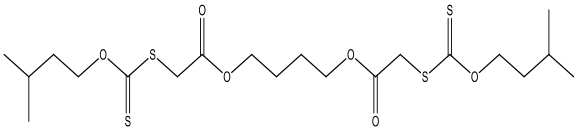
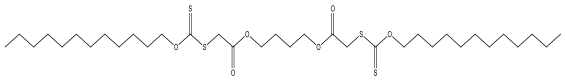
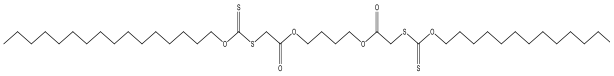
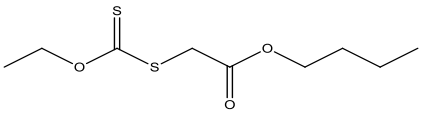
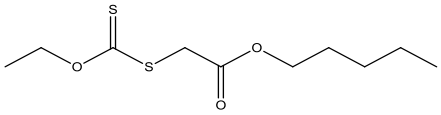
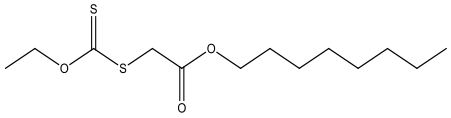
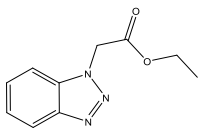
1 Materials and Methods

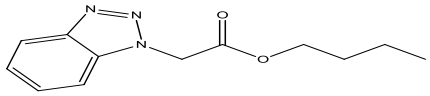
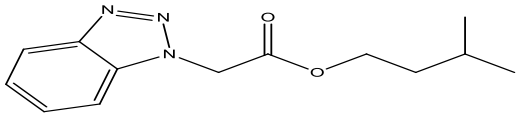
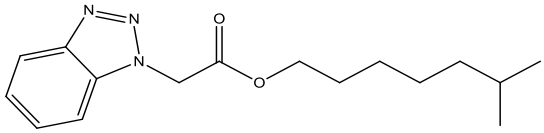
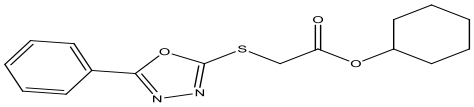
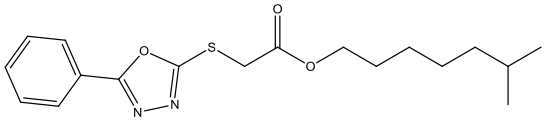
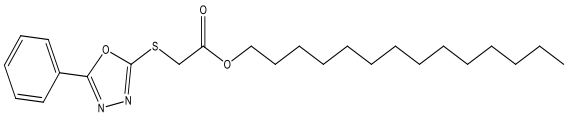
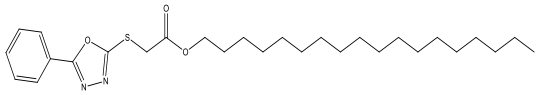
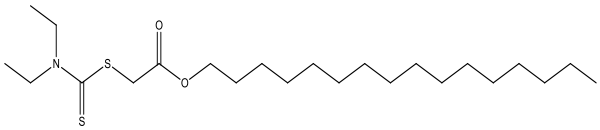
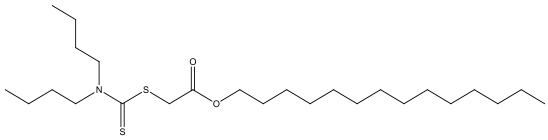
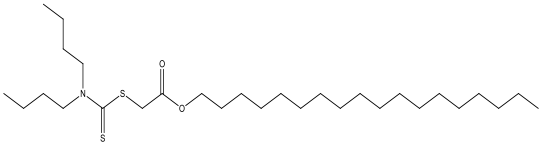
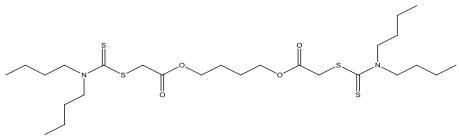
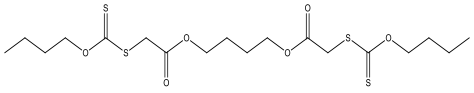
1.1 Data sets, Molecular Descriptors Generation, and model building

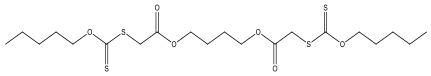
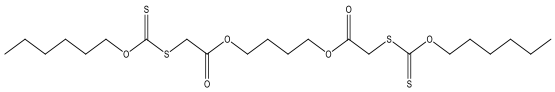
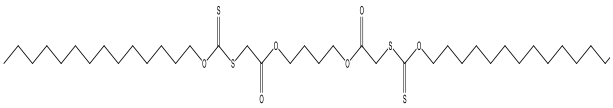
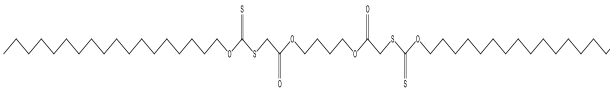
The 2D structure of LAs (**Table 1**) with their onset temperatures were retrieved from the literature and used for this research (Deng, (2009); Jeng, (2009); Jiao, (2011)).

Table 1 Experimental, Normalized and Predictive Lubricant Additives Onset Temperature (T_{onset})

S/N	Lubricating Oil Additives	Experimental (T_{onset})	Predicted (T_{onset})
1a		261.5	239
2a		193.82	193
3a		193.22	193.4
4b		201.78	210
5b		296.7	270
6b		272.9	268
7b		312.7	315
8b		300.7	298
9a		309	313
10b		332.8	334
11b		327.8	327.2

12		298.3	297.4
13a		351.6	351.7
14a		311.9	315.2
15b		262.8	269
16a		259.6	259.3
17b		267.6	269
18b		270.8	270.3
19b		273	273
20b		224.49	224.8
21a		224.95	224.67
22b		247.11	248
23b		213.39	216.4

24b		242.1		249
25a		251.5		254
26b		258.93		259
27a		220.9	220.3	
28b		265.23		268.3
29b		270.53		271.2
30b		167.85		169.0
31b		198.85		198.85
32b		202.9		200.4
33a		231.84		231.4
34b		195.13		195.14
35b		164.65		165.83

36a		225.8	225.6
37a		295.9	296.3
38b		312.2	309
39a		319.8	320.6

[b]**Training sets:** [a]**Test sets**

The 2D structures of all the 39 LAs were drawn with ChemDraw software and later transferred and converted to 3D by Spartan'14 version 1.1.2 software. Using molecular mechanics (MMFF), these 3D structures of all the LAs were then subjected to energy minimization (Hashem, (2011)) after which complete geometry optimization was carried out with Density Functional Theory (B3LYP/6-311++ G**). The optimized LAs were transferred to Dragon 6.0 software toolkits (Todeschini *et al.*, (2017)) where about 3556 molecular descriptors were generated. The onset temperature of these LA compounds was measured as $T_{onset}(K)$ were normalized and further expressed as p^{Tonset}. Using a random selection method, all the LAs were grouped into 25 and 14 sets. Material studio version 8.0 software was utilized to carry out correlation analysis and development of the QSPR models with the genetic function algorithm method (GFA). GFA as a method, as the ability to incorporate the idea of natural evolution (Rogers and Hopfinger, (1999); Ching-Wen *et al.*, (2014)). The quality assurance of the generated QSPR mathematical models was accessed by internal (R^2, Q^2 R^2_{adj},) and predictive (R^2_{pred}.) validation parameters (Equations 1-4) in comparison with the acceptable QSPR parameters (Ravinchandran *et al.*, (2011)). The relative relevance of every generated descriptor contribution to the developed model was calculated in-term of mean effect (MF) value in equation 5 (Ravinchandran *et al.*, (2011)).

$$R^2 = 1 - \frac{\sum(Yobserved - Ypredicted)^2}{\sum(Yobserved - Ytraining)^2} \quad (1)$$

$$Q^2 = 1 - \frac{\sum(Yp - Y)^2}{\sum(Y - Ym)^2} \quad (2)$$

$$R^2_{adj} = \frac{(N-1)R^2 - P}{N-1-P} \quad (3)$$

$$R^2_{pred.} = 1 - \frac{\sum[Yobs(test) - Ypred(test)]^2}{\sum[Yobs(test) - Ym(training)]^2} \quad (4)$$

$$MF_j = \frac{\beta_j \sum_{i=1}^{i=n} d_{ij}}{\sum_j^m \beta_j \sum_{i=1}^{i=n} d_{ij}} \quad (5)$$

Where Y_{obs}=observed/experimental training set properties, Y_{calc}=calculated/predicted training set properties, $Y_{obs(test)}$= observed/experimental properties for the test set, $Y_{pred(test)}$ = predicted test set properties, N= number of molecules in the data, Yp =represent the predicted properties of the training set, Y=observed properties of the training set, Y_m the mean activity value of the training set, R^2=determination coefficient, p=number of descriptors in the QSPR model, N-1-p= degree of freedom, j= model's generated descriptor, βj = descriptor's coefficient, dij= training set's data matrix descriptor value, m = sum of model's descriptors while n = summation of training set's molecules.

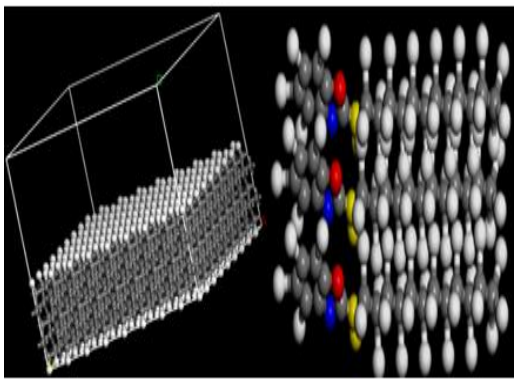


Fig. 1 3D structures of DLC substrate and LAs

1.2 Molecular dynamics (MD) simulation research

To understand, access the structural and dynamic binding energy between the DLC simulated coated interfacial sliding surfaces and potentially designed lubricant anti-oxidant additives, molecular dynamics (MD) simulation investigation was studied (Wymyslowski *et al.*, (2008)). The 3D structure (**Figure 1)** of hydrogen-containing DLC crystal surface which was reported in many works of literature (Wymyslowski *et al.*, (2008)) to be better allotropy of carbon in term of wearing resistance ability and antioxidant in the sliding interface was constructed from the carbon (C) model using Materials studio 8.0 simulation software. This was done by cleaving the carbon surface at point 1.1 .0 (Height, Breadth Length), Top (1.006 Å), and Thickness (24.121 Å) into the crystal unit. Moreover, the repeated units (supercell) of the carbon crystal units were formed at (Height) U (9) and (Breadth) and V (8) while hydrogenation of the supercell, vacuum slab, and geometric optimization was performed. Similar steps were also followed to build steel. The 2D structures of the lubricant antioxidant additives were drawn with Chemdraw software and were then converted to 3D structures by materials studio version 8.0 simulations Program, then optimized and saved by the same software (Fig. 1). COMPASS II which is a strong and well-created power field (than COMPASS) that was determined dependent on the fitting capacity against a wide scope of inorganic and synthetic organic compounds (Wymyslowski *et al.*, 2008) was selected in the Materials studio 8.0 Software. Molecular Dynamic (MD) simulation binding energy (B.E) calculations were done subsequent after presenting the minimized additive compound into the simulation vacuum slab of optimized steel and 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 interaction binding energy of all the designed additives on the diamond like carbon (DLC), was determined by using equation 6 (Zhao *et al.*, (2014)).

$$\boldsymbol{E}_{Dynamic\ Binding\ Energy}=\boldsymbol{E}_{total}-(\boldsymbol{E}_{LubricantAdditive}+\boldsymbol{E}_{DLC\ Surface}) \quad (6)$$

2 Results and discussion

2.1 Analysis of QSPR

After using the Genetic Function Algorithm (GFA) method, GFA in material studio software to carefully developed the QSPR model from 39 structures of LAs and the onset properties, four QSPR mathematical models were generated. All these generated mathematical models along with their statistical correlation coefficients were subsequently subjected to QSPR validation parameters (Ravinchandran *et al.*, (2011)). The first, second, third and fourth models were found to have coefficients of; internal correlation (R^2) of 0.95, 0.94, 0.94, 0.94, adjusted squared correlation (R^2adj) of 0.40, 0.93, 0.93, 0.92, Cross-validation (Q^2) of 0.90, 0.90, 0.80, 0.89, and the external validation (R^2pred) of 0.54, 0.52, 0.52, 0.51, respectively. But after careful comparison, the 1st model was revealed to better comply with the standard validation requirements (Ravinchandran *et al.*, 2011).

Model 1:

$$p^{(T_{onset})} = 0.07^{*}IC5 - 0.02^{*}RDF080m - 0.09^{*}RDF110m - 1.23^{*}p2v + 0.00002^{*}Ve - 3.22^{*}R1e + +2.56.\,\mathrm{R2} = 0.95, \mathrm{R2ext} = 0.54,\ \mathrm{R2adj} = 0.94, \mathrm{Q2cv} = 0.90.$$

Model 2:

$$p^{(T_{onset})} = 0.08^{*}IC5 - 0.02^{*}RDF080m - 0.009^{*}RDF0800m - 1.27^{*}RDF110 + 0.00002^{*}P2v - 3.28^{*}R1e + +2.55.\,\mathrm{R2} = 0.94, \mathrm{R2ext} = 0.52, \mathrm{R2adj} = 0.93, \mathrm{Q2cv} = 0.90.$$

Model 3:

$$p^{(T_{onset})} = 0.12^{*}IC5 - 0.03^{*}RDF080m - 0.03^{*}Mor11e + 0.38^{*}Dv + 0.18^{*}H3p - 2.47^{*}R1e + +1.91.\ \mathrm{R2} = 0.94, \mathrm{R2ext} = 0.52,\quad \mathrm{R2adj} = 0.93, \mathrm{Q2cv} = 0.90$$

Model 4:

$$p^{(T_{onset})} = 0.08^{*}IC5 - 0.024^{*}RDF080m - 0.012^{*}RDF110 - 1.32^{*}P2v + 0.00002^{*}Vm - 3.325^{*}R1e + +2.56.\,\mathrm{R2} = 0.94, \mathrm{R2ext} = 0.51, \mathrm{R2adj} = 0.92, \mathrm{Q2cv} = 0.89.$$

The confirmation assessment further proved that the 1st model's internal coefficient prediction (R^2) of 0.95 value conformed with R^2 coefficient (training set graph) of 0.95 (**Figure 2**) and the external coefficient of the predicted (R^2) of 0.54 value was also in conformity with R^2 (test set graph) value of 0.54 in the plotted

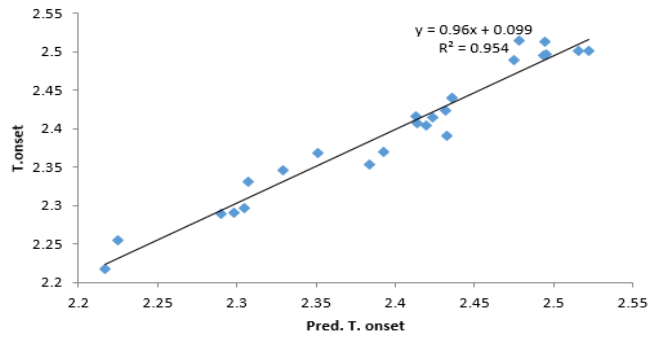


Fig. 2 Plot of training set

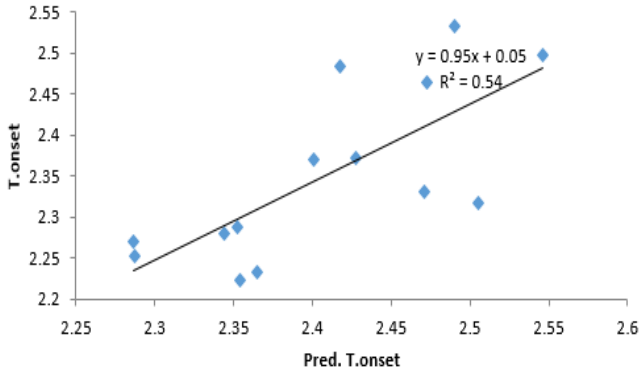


Fig. 3 Plot of test sets

graph (**Figure 3**). Moreover, there was no problem of multi-colinearity since model 1's descriptors coefficient correlation was very low (**Table 2**) (David *et al.*, (2004); Costa *et al.*, (2014)). Therefore, in QSPR model 1, the positive coefficient signs in the molecular descriptors such as IC5 and *Ve* while the negative coefficient sign of RDF080m, RDF110m, *P2v*, and *R1e+* implies that increase in former and decrease in latter descriptors will increase the onset temperatures (T_{onset}) properties at which the lubricant additives decompose during the mechanical boundary lubrication. Since all the required statistical analysis carried out have proved that most of the 39 LAs used in this study can withstand high temperature without being decomposing easily during mechanical boundary lubrication of machine of interest. It is also important to know those that can enhance the properties of base oil at high onset temperature. Applicability domain (AD) was a help in this case. AD statistical analysis was performed to determine the set of molecular additives found within the domain and the outliers/influential additives compounds outside the domain or danger boundary, *h**(*Eqn.* 7) (Netzeva *et al.*, (2005)). Where *m*=number of descriptors that appear in a QSPR linear model, *n*=number of training set molecule only.

$$\boldsymbol{h} * = \frac{\mathbf{3}(\boldsymbol{m}+\mathbf{1})}{\boldsymbol{n}} \qquad (7)$$

A closed look at **Figure 4** shows that all the LAs were found within the domain of the graph except additive with serial number 39 (Table 1) that was noticed to be outside the danger limit (*h**) of 0.83. Therefore, this compound is called outlier and it cannot be used as a template to design other LAs because it is not reliable and its property may be gotten in error during the experimental characterization (Netzeva *et al.*, (2005)).

Table 2 Model I descriptors inter-correlation matrix

Descriptor	IC5	RDF080m	RDF110m	*P2v*	*Ve*	*R1e+*
IC5	1					
RDF080m	-0.23	1				
RDF110m	-0.19	0.45	1			
P2v	-0.59	0.48	-0.007	1		
Ve	-0.30	0.42	0.93	0.12	1	
R1e+	0.28	-0.73	-0.56	-0.50	-0.52	1

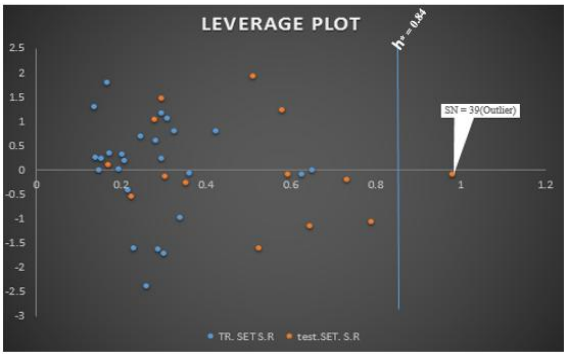


Fig. 4 The Plot of Standardized Residual versus Leverage for the Best Model

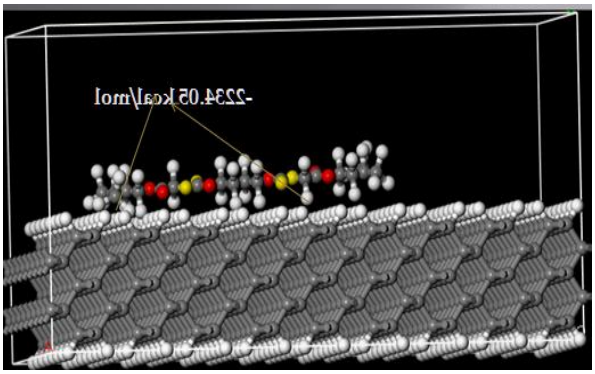


Fig. 5 Side view of Lubricant Additive-DLC Complex

2.2 Molecular Dynamic Simulation Analysis

To determine the dynamic binding energies of all the LAs under investigation, computational MD simulation studies were carried out between LAs and the boundary DLC coated surface. The binding energy scores in **Table 3** show the individual binding energies of lubricant additives, DLC, total and binding energies of the complex. All the lubricating oil additive compounds (Table 3) were found to bind strongly with the DLC mechanical sliding interface. Besides, LAs with serial number 13a and with a dynamic binding energy of -2234.05 kcal/mol was found to show excellent binding energy than other co-lubricant additives. This study revealed that this LA with serial number 13a could form a stable film on the surface of the DLC boundary coated surface than other co-additives. **Figure 5** shows the best LA- DLC complex with the best binding energy. This binding energy of -2234.05kcal/mol generated was found to be better than the one reported by Costa and his co-workers in 2011 (Costa *et al.*, (2011)) and it was also better than the dynamic binding energy of ZDDP (Table 3).

Table 3 Lubricant Additives Binding Energies

Comp. No	$E_{LAdditives}$ (kcal/mol)	E_{DLC} (kcal/mol)	E_{Total} (kcal/mol)	$E_{Binding\ Energy}$ (kcal/mol)
1a	-35.29	-970.04	-1024.3	-1959.06
2a	41.46	-970.04	-940.75	-1952.25
3a	56.30	-970.04	-933.49	-1959.83
4b	56.42	-970.04	-937.16	-1963.62
5b	91.98	-970.04	-893.3	-1955.32
6b	91.49	-970.04	-788.57	-1850.09
7b	91.59	-970.04	1710.13	648.50
8b	91.20	-970.04	-832.65	-1893.89
9a	238.43	-970.04	-785	-1993.47
10b	-4.81	-970.04	-94.29	-1059.51
11b	-4.62	-970.04	36.47	-928.947
12	-4.63	-970.04	-74.51	-1039.91
13a	240.21	-970.04	-1023.8	-2234.05
14a	-26.00	-970.04	605.39	-338.65
15b	36.90	-970.04	-951.42	-1958.36
16a	33.5	-970.04	832.03	-171.50
17b	23.95	-970.04	3443.24	2449.25
18b	29.23	-970.04	3285.99	2286.71
19b	35.46	-970.04	722.96	-282.54
20b	16.10	-970.04	-972.93	-1959.07
21a	14.31	-970.04	-1011.7	-1996.09
22b	13.95	-970.04	-965.21	-1949.2
23b	54.28	-970.04	-929.46	-1953.77
24b	56.79	-970.04	-915.82	-1942.64
25a	52.14	-970.04	-923.42	-1945.61
26b	53.46	-970.04	-921.24	-1944.73
27a	83.19	-970.04	-652.05	-1705.29
28b	144.34	-970.04	853.375	-261
29b	195.17	-970.04	-742.07	-1907.28
30b	104.80	-970.04	7487.52	6412.68
31b	94.97	-970.04	3557.07	2492.06
32b	2.99	-970.04	6379.47	5406.43
33a	275.67	-970.04	2736.1	1490.40
34b	-9.43	-970.04	7769.77	6809.17
35b	34.90	-970.04	-969.17	-1974.12
36a	20.14	-970.04	-973.15	-1963.33
37a	33.22	-970.04	-983.84	-1987.09
38b	31.17	-970.04	1640.3	639.09
39a	36.80	-970.04	727.42	-279.41
ZDDP	262.62	-970.04	18502.31	24365.40

$EL._{Additives}$=Lubricant Additives **E_{DLC} = Diamond Like-Carbon, E_{Total} = Total Energy of the complex** **[b]Training set: [a]Test set**

Conclusions

QSPR's principle which was based on chemical properties-structure relationship and MD simulation which was based on the calculation of dynamic binding energy of compound of interest were used to carry out the onset temperature of LAs study. Four QSPR mathematical models were generated from 39 structures of LAs and the onset properties. The 1st model was found to better comply with the standard validation requirements. The generated physicochemical descriptors from the model correspond to the structural features and were found to have coefficients of; internal correlation (R^2) of 0.95, adjusted squared correlation (R^2 adj) of 0.94, Cross-validation (Q^2_{cv}) of 0.90, and the external validation (R^2pred) of 0.54. The model suggests that new LAs with improved onset temperatures (T_{onset}) could be designed by interpreting and increasing the value of the molecular descriptor such as IC5 and *Ve* and at the same time decreasing the values of RDF080m, RDF110m, *P2v*, and *R1e+*. Moreover, the LAs with an experimental onset temperature of 3 51.6 K agreed with the predicted onset temperature of 351.7 K (13a, Table 1). And was also in agreement with the result of molecular dynamics simulations in which lubricating oil additive number 13a, Table 3, with the best dynamic binding energy of -2112.06 kcal/mol. These two methods could be adopted by researchers and industrialists/engineers to design an improved lubricant additive property before wet experiments since they have proven to be good research tools due to the structure-properties correlation capability.

Nomenclature

QSPR	=Structure-Properties Relationships	[-]
DLC	=Diamond like carbon	[-]
$DLC_{Lubricant\ additive}$	=Energy of the diamond like carbon	[-]
Dv	=D total accessibility index / weighted by Van der Waals volume	[-]
E	=Energy	[Kcal/mole]
$E_{Lubricant\ additive}$	=Energy of the lubricant additive	[Kcal/mole]
E_{Total}	=Total Energy	[Kcal/mole]
GFA	=Genetic function algorithm	[-]
IC5	=Information Content index/neighborhood symmetry of 5-order	[-]
LAs	=Lubricant additives	[-]
MD	=Molecular dynamic	[-]
P2v	=2nd component shape directional WHIM index / weighted by Van der Waals volume	[-]
Q2cv	=Cross-validation	[-]
RDF	=Radial Distribution Function	[A^o]
RDF080m	=Radial Distribution Function - 080 / weighted by mass	[-]
RDF110m	=Radial Distribution Function - 110 / weighted by mass	[-]
R1e+	=(R maximal autocorrelation of lag 1 / weighted by Sanderson electro negativity	[-]
R1e	=R autocorrelation of lag 1 / weighted by Sanderson electro negativity	[-]
T_{onset}	=Onset temperature	[-]
Ve	=V total size index / weighted by Sanderson electro negativity	[-]
Vm	=V total size index / weighted by mass	[-]

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