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Research article

Molecular design of antioxidant lubricating oil additives via QSPR and analysis dynamic simulation method

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ABSTRACT

Alternatives antioxidant lubricant additives have been proposed by many researchers to replace long-time use of multifunctional lubricant additive, Zinc-dialkyl-dithiophosphate (ZDDP). Computational methods (QSPR and MD) were successfully used to design five novel anti-oxidant lubricating oil additives with improved properties and dynamic binding energies. The five novel antioxidant lubricant additives with improved properties and without sulfated ash, phosphorus, and sulfur (SAPS) were successfully designed. These group of newly designed additives were better than other similar research from the literature and could stop or terminate complete oxidation of the lubricant. Moreover, the result of molecular dynamics simulations (MD) in which 3-(2-(3-amino-4,5-dihydroxyphenyl)-3-chloro-4-oxoazetidin-1-yl)-2-argioquinazolin-4(3H)-one with the most promised dynamic binding energy of -1487.68 kcal/mol was found to be dynamically bound better on the simulated steel coated surface than the DLC coated surface and was also revealed to be excellently good when compared with commercially sold multifunctional additives, ZDDP (197.143 kcal/mol). These groups of five newly designed additives could be easily synthesized in the wet laboratory by adding –OH and or NH_2 around the ortho, meta and para position of the phenyl group of the structure template. This research will help designing new oxidation resistance lubricating oil additives with improved properties that will reduce the capacity of base oil to oxidize and form sludge during the autoxidation process of the lubricating oil.

1. Introduction

One of the fundamental human prerequisite and basic factors for progress and monetary improvement in current industrialization is energy. A literature search revealed that energy loss from machines due to in-effective lubricant is accounting for one-third of essential energy consumption while fifteen per cent of the total fuel energy in the modern internal combustion high-speed and duty engines is usually mechanically lost due to wear caused by oxidation of the lubricant [1, 2]. Antioxidants are specially designed additives used to enhance or improve the performance (chemical and physical properties) of lubricants and functional fluids at high temperatures by increasing/prolonging the oxidative resistance of the lubricating oil [3, 4]. At present, nearly all lubricating oil contains the minimum of one to two antioxidant lubricating oil additives for performance enhancement and stabilization purposes since lubricating oil degradation problem have been identified to be primarily caused by oxidation and that antioxidant lubricant additive could resist this lubricant oxidation by terminating the complete oxidation cycle at the propagation stage [5].

To avoid oxidation of lubricant and machine wearing, scientists and engineers are currently focusing their attention on using innovative technologies to designs very effective anti-oxidant lubricant additives that will enhance the existing lubricant properties by protecting the lubricant against oxidation [3, 4, 5, 6, 7]. Several antioxidant lubricant additives such as hindered phenol, amines, natural acids and Pyrazines have emerged globally to replace the widely used multifunctional lubricant additives, zinc-dialkyl dithiophosphate (ZDDP). ZDDP major problem was usually the generation of sulfated ash, phosphorus, and sulfur (SAPS) that usually poison the catalysts used for exhaust gas treatment thereby increasing the concentrations of carbon monoxide gas in the environment [8, 9]. Therefore, there is a need to scan for excellent and ecologically good anti-oxidant base oil additives that will act as either peroxide decomposers or that can trap free radical to prolong the lubricant oil lifespan by reducing or slowing the capacity of oil to oxidization and form sludge and acids [10]. Also, a crystallized filmed hydrogen-containing diamond-like carbon (DLC) and steel have been reported to be superior coating materials with a minimal coefficient of friction, and they have been excellently reliable in managing the motors

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fuel utilization by limiting mechanical [11, 12, 13, 14, 15].

Quantitative Structure-Properties Relationships (QSPR) and dynamic molecular simulations are commonly used computational technique that can preserve resources and accelerate the process of designing better molecules for use as additives [16]. This research work was aimed at designing more effective alternatives amine lubricant additives towards the enhancement of engine efficiency by slowing or delaying oxidation onset and prolongs the lifespan of lubricant in the machine sliding interfaces, and to determine the dynamic binding strength of the lubricant additives at different working conditions on.

2. Materials and methods

2.1. Datasets (antioxidant lubricant additives)

The dataset (Suppl. Table 1) of the lubricant additives together with their anti-oxidant (acid value KOH/g oil) values were selected from the literature [17, 18] and used in this research work. Using Kennard-Stone algorithm software technique, the lubricating base oil additives data-set was group into training 17 (77.27%) and 5 (22.727%) test-sets. The training set was used for the construction of the QSPR models while test sets were used to check the predictive ability of the generated models. The ALA (anti-oxidant lubricant additive) values of these molecular lubricating oil additives represent the inhibition efficiency of the lubricants and were expressed as predictive antioxidant lubricant additives (pALA).

2.2. Molecular descriptors generations and QSPR model development

The two dimensional structures of all the lubricating base oil additives were drawn with the ChemDraw ultra V12.0 software, converted to three dimensional and optimized by Spartan software version 1.1.2 software using density functional theory (B3LYP/6–31 G*) [19], and about 3475 molecular descriptors were generated with the help of Dragon 6.0 software toolkits [20]. Moreover, Material studio software version 8.0 software was used to develop the predictive QSPR model with the genetic function algorithm (GFA) method. The quality assurance (reliability and predictive ability) of the developed QSPR model were accessed by internal (R^2, R^2_{adj}, Q^2_{cv}) and external (R^2_{ext}) validation parameters. Furthermore, these validation parameters were contrasted and the base standard prescribed for the standard acceptable QSPR parameters [21].

2.3. Virtual lubricant additives design and development

Virtual template-based design method is an in-silico screening method for designing better active lubricant compounds. This QSPR virtual method is usually used to screen and design a compound with better properties of interest by relating experimental properties of the compound to their structures. In this case, the structure of chemical compound with about 99% pure and anti-oxidant property of 5.2 acid value KOH/g oil in supplementary Table 1 was found to be within minimal residual value and also within the best domain of applicability and was thereafter chosen as additive template to which further structural alterations were made with the assistance of molecular descriptors from the produced QSPR mathematical model 1 [21].

2.4. Molecular dynamics simulation studies

Dynamics simulation calculations were performed to describe and determine the interaction between the lubricant additives molecules and the DLC and steel sliding interfaces. The sub-atomistic dynamic program from Accelrys in the Materials Studio software version 8.0 s was used for the simulation calculations of the dynamic binding strengths that existed between the lubricant additives (Suppl. Table 1) and the prepared hydrogen-containing *DLC (a-C: H)* and steel crystal surfaces.

2.4.1. Molecular dynamics simulation computational details

In Materials studio 8.0 Software, the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II (COMPASS II) force field method which is a robust and better-developed (than COMPASS) force field was derived based on fitting against a wide range of experimental data set for organic and inorganic compounds [22] was selected and used for the molecular dynamics simulation. 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 and steel crystal (24.82 Å × 24.82 Å × 45.27 Å) surfaces at 350.15 K and over a range of inter-surface separations. Using equation 1and 2, the dynamic binding energy-strength was calculated for both the DLC and Steel crystals respectively [23].

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

$$\text{Binding Energy} = E_{total} - (E_{\text{Lubricant Additive}} + E_{\text{Steel Surface}}) \quad (2)$$

3. Results and discussion

3.1. Analysis and validation

3.1.1. Best QSPR model

p(ALA) = - 0.631624082 * nBondsS3 + 3.303960124 * MLFER_BH + 4.834698113 * MLFER_S - 5.152278264 * Wnu2.unity +2.960271, R^2 of 0.954433, R^2_{adj} of 0.939244, Q^2_{cv} of 0.917263 and R^2pred 0.7572.

Model 1 out of the other numerous internally generated QSPR models by the Materials studio 8.0 Software was found to be conformed to the minimum requirements for a reliable, predictive and robust QSPR model [21] and therefore, it was termed as the best QSPR model for predictions and designs of better novel ant-oxidant lubricant additive compounds as it has the highest squared correlation coefficient (R^2) of 0.954433, adjusted squared correlation coefficient (R^2_{adj}) value of 0.939244, Cross-validation coefficient (Q^2_{cv}) value of 0.917263 and the external validation (R^2pred) of 0.7572. Furthermore, these results of the statistical parameters revealed that all the experimental 2D structures and their antioxidant additive properties used for the development of the QSPR model were reliable [17, 18].

3.2. Analysis of designed anti-oxidant lubricant additives

To be sure of the additives to use as a design template for further structural modifications since the robustness of the QSPR model alone cannot be enough to predict accurately the properties of all the compounds within the chemical space [24]. In supplementary figure 1, William's plot which is the applicability domain's leverage plot was calculated and found to contain leverage danger, h* of 0.882. This plot revealed that about five compounds (4, 22, 8, 5 and 18) that go beyond the leverage danger were termed as influential antioxidant lubricating additives [25]. These influential antioxidant lubricant additives are compounds that go beyond the danger leverage lines/chemical space and therefore, such compound cannot be used as design template [25]. The compound with serial number 14 (Suppl.Table 1) has 0.1 residual value and was statistically found to be within the chemical space of William's plot with an excellent leverage value (Suppl. fig. 1) was selected as the amazing template after which further modification was made (Fig. 1). Moreover, to avoid statistical misinterpretation error during designing of novel additives, mean effect [26] calculation was also carried out. From the mean effect statistical calculation in supplementary Table 2, MLFER_BH (Overall or summation solute hydrogen bond basicity) molecular descriptor [27] was found to be more significant toward the development and designing of better novel antioxidant lubricant additives. The addition of compounds of base origin like –OH, $–NH_2$ around the ortho, meta and para position of the phenyl group of the structure

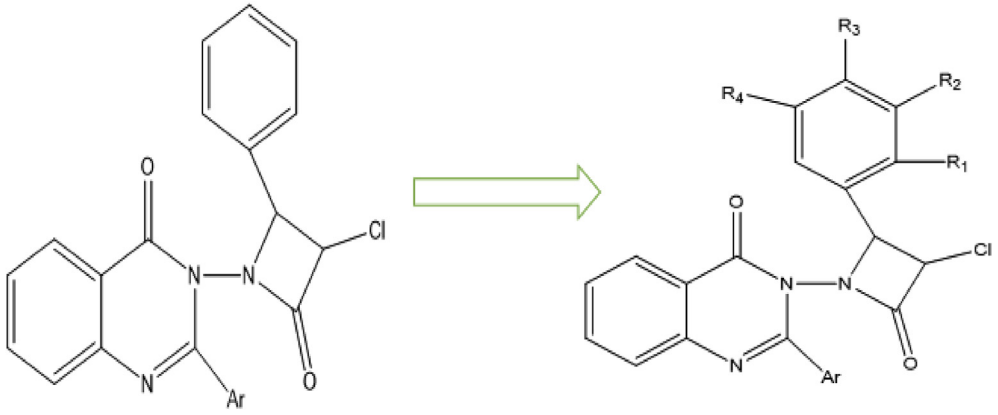

Fig. 1. ALA Template structure.

Table 1
Designed Antioxidant Lubricant Additives (ALA) substituents and their predicted properties.

S/N	R_1	R_2	R_3	R_4	Predicted ALA (Acid value gm KOH/g oil)
1	$-NH_2$	-H	-H	-H	1.813985
2	$-NH_2$	-H	$-NH_2$	-H	3.846586
3	-OH	$-NH_2$	-OH	-OH	2.557055
4	$-NH_2$	$-NH_2$	-OH	$-NH_2$	2.55703
5	-H	$-NH_2$	-OH	-OH	3.063552

template as shown in Fig. 1 was noticed to increases the hydrogen bonding of all the five designed additives thereby increasing their lubricant antioxidant properties by lowering the coefficients of lubricant antioxidant additive (Table 1).

Fifteen novel anti-oxidant lubricant additives were designed out of which 3-(2-(2-aminophenyl)-3-chloro-4-oxoazetidin-1-yl)-2-argioquinazolin-4(3H)-one, 2-argio-3-(3-chloro-2-(2,4-diaminophenyl)-4-oxoazetidin-1-yl)quinazolin-4(3H)-one,3-(2-(3-amino-2,4,5-trihydroxyphenyl)-3-chloro-4-oxoazetidin-1-yl)-2-argioquinazolin-4(3H)-one, 2-argio-3-(3-chloro-2-oxo-4-(2,3,5-triamino-4-hydroxyphenyl)azetidin-1-yl)quinazolin-4(3H)-one and 3-(2-(3-amino-4,5-dihydroxyphenyl)-3-chloro-4-oxoazetidin-1-yl)-2-argioquinazolin-4(3H)-one (Table 1) were reported because they were found to have better predicted anti-oxidant lubricant additive (ALA) properties of 1.813985, 3.846586, 2.557055, 2.55703 and 3.063552 (acid value KOH/g oil) respectively than the properties of the experimental anti-oxidant lubricant additives in supplementary Table 1. Lower Antioxidant Lubricant Additive coefficients have been reported somewhere to have better lubricating oil oxidation resistance potentials [18].

3.3. Dynamic molecular simulation generation and analysis

Dynamic molecular simulation calculations were carried out between all the designed and commercially sold multifunctional lubricant additives, zinc-dialkyl dithiophosphate (ZDDP) on the hydrogen-containing DLC (a-C: H) and steel surfaces to determine the dynamic binding energies/strength using Eqs. (1) and (2). The five novel designed anti-oxidant lubricant additives with serial number of 1,2,3,4,5 (Table 2) were found to have dynamic binding strength of 18.79 kcal/mol, -24.27 kcal/mol, -164.79 kcal/mol, -70.502 kcal/mol, -127.81 kcal/mol on DLC crystal surface and -1221.59 kcal/mol, -1401.87 kcal/mol, 1254.982 kcal/mol, -1170.53 kcal/mol and -1487.68 kcal/mol on steel surface respectively. The results of this dynamic simulation (Table 2) revealed that four out of the five designed additives were found to be bound better to the surface of the simulated coated steel than on the DLC coated crystal surface.

4. Conclusions

Computational methods (QSPR and MD) were successfully used to design five novel anti-oxidant lubricating oil additives with improved better properties and dynamic binding energies. The anti-oxidant improved properties (1.813985, 3.846586, 2.557055, 2.55703 and 3.063552 acid value KOH/g oil) of some of our designed additives were better than the additives experimental anti-oxidant lubricant properties reported by our previous research [28] and by Habib and his co-researchers in 2014 and 2012 [17,18,29]. These lower ALA properties have been reported somewhere to have better lubricating oil oxidation resistance potentials and that could stop or terminate complete oxidation of the lubricant [5, 18]. Moreover, the result of molecular dynamics simulations in which 3-(2-(3-amino-4,5-dihydroxyphenyl)-3--chloro-4-oxoazetidin-1-yl)-2-argioquinazolin-4(3H)-one (Table 2) with

Table 2
Molecular dynamic simulations of antioxidant lubricant additives.

S/N	E_{ALA} (kcal/mol)	E_{Fe} (kcal/mol)	Steel- ALA Complex		E_{DLC} (kcal/mol)	DLC- ALA Complex	
			E_{Total} (kcal/mol)	Binding Energy (kcal/mol)		E_{Total} (kcal/mol)	Binding Energy (kcal/mol)
1	61.290	-85300.4	-86460.7	-1221.59	-6126.4	-6046.320	18.79
2	62.877	-85300.4	-86639.4	-1401.87	-6126.4	-6087.793	-24.27
3	78.582	-85300.4	-86476.8	1254.982	-6126.4	-6212.608	-164.79
4	65.128	-85300.4	-86405.8	-1170.53	-6126.4	-6131.774	-70.502
5	71.484	-85300.4	-86716.6	-1487.68	-6126.4	-6182.734	-127.81

ALA = Antioxidant Lubricant Additive.

the most promised binding dynamic energy of -1487.68 kcal/mol was found to be dynamically bound better on the simulated steel coated surface than the DLC surface and was also revealed to be excellently good when compared with commercially sold multifunctional additives, ZDDP (197.143 kcal/mol) [29,30]. The group of five newly designed additives could be easily synthesized in the wet laboratory by adding –OH and or NH_2 around the ortho, meta and para position of the phenyl group of the structure template as shown in Fig. 1. This research will help designing new oxidation resistance lubricating oil additives with improved properties that will reduce the capacity of base oil to oxidize and form sludge during the autoxidation process of the lubricating oil.

Declarations

Author contribution statement

Adamu Uzairu, Gideon Shallangwa, Sani Uba: Analyzed and interpreted the data.

Usman Abdulfatai: Conceived and designed the analysis; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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