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RECEIVED 30 September 2025

REVISED 05 December 2025

ACCEPTED 17 December 2025

PUBLISHED 09 January 2026

CITATION

Borges ID, Aguiar ASN, Camargo AJ and
Napolitano HB (2026) Biodiesel stabilization by
dibrominated dimethoxybenzaldehydes: a
comprehensive computational perspective.
Front. Chem. Eng. 7:1716732.
doi: 10.3389/fceng.2025.1716732

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Biodiesel stabilization by dibrominated dimethoxybenzaldehydes: a comprehensive computational perspective

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The oxidative instability of biodiesel remains a critical barrier to its widespread adoption despite its advantages as renewable, biodegradable, and low-emission fuel. Antioxidant additives are an established strategy to suppress free radical chain reactions, yet their efficiency is strongly modulated by molecular structure and solvent environment. This is the first comparative density functional theory study of dibrominated dimethoxybenzaldehydes and standard phenolic antioxidants under biodiesel-relevant solvent conditions using the conductor-like polarizable continuum model. Frontier molecular orbitals, Fukui index, ionization potentials, spin density distributions, and natural bond orbital hyperconjugations were systematically analyzed across polar and nonpolar environments. The computational results suggest that bromination is associated with increased electronic softness and electron transfer potential, while also leading to changes in the stability of radical intermediates, especially in ortho-substituted derivatives. Among the dibrominated compounds, IB1 exhibits the most balanced combination of computed properties, whereas IB3, although highly reactive *in silico*, is predicted to form comparatively less stable radical species. Compared with commercial benchmarks, these halogenated systems constitute a distinct mechanistic class governed by polarization rather than hydroxyl-centered resonance. These computational findings provide guidance for the rational design of next-generation biodiesel stabilizers, pending future experimental validation.

KEYWORDS

additives, antioxidant potential, biodiesel, fukui, stability

1 Introduction

The transition to sustainable energy sources is a central challenge for global energy security and environmental stewardship (Yusuf et al., 2011; Luque et al., 2010; Usmani et al., 2023). Increasing the efficiency and operational stability of renewable fuels is vital for accelerating the energy transition and achieving lower carbon emissions. Biodiesel, produced from renewable feedstocks such as vegetable oils, and animal fats, has emerged as a promising alternative to petroleum-derived fuels due to its biodegradability, low toxicity, and reduced greenhouse gas emissions compared with fossil fuels (Davis et al., 2018; Giakoumis et al., 2012). Integration of biodiesel into

TABLE 1 Reaction Rate (k_{OH}) for DMB derivatives and commercial antioxidants.

Compound	Reaction rate constant k_{OH} ($M^{-1}s^{-1}$)
IB1	5.22×10^9
IB2	4.64×10^9
IB3	5.22×10^9
GA	4.09×10^9
TBHQ	7.57×10^9
BHA	7.27×10^9
PG	1.11×10^{10}

existing and future energy infrastructures directly supports clean energy goals and sustainable process design. Despite these advantages, the large-scale deployment of biodiesel remains hindered by its intrinsic oxidative instability. Overcoming these process limitations is essential to enable the broader adoption of sustainable fuels within the context of advanced process engineering and reactor optimization for the energy transition. Oxidation during storage and use accelerates the formation of peroxides, acids, and polymers, leading to increased viscosity, corrosiveness, and sediment deposition, ultimately impairing both fuel quality and engine performance (Knothe, 2007; Pullen and Saeed, 2012; Saluja et al., 2016; Yang et al., 2013; Pullen and Saeed, 2014; Pantoja et al., 2013; Serqueira et al., 2021). This challenge is further exacerbated in tropical and subtropical climates such as those in Brazil (Alvares et al., 2013) (Köppen area A4), where elevated temperatures, humidity, and solar irradiation intensify oxidative degradation (Varatharajan and Pushparani, 2018). Agricultural operations are especially impacted: machinery exposed to these conditions and fueled by blends experiences more rapid loss of fuel quality and higher maintenance requirements (Arumugam et al., 2023; Cui et al., 2025; Ryu, 2009; Silva et al., 2025).

A well-established strategy to counteract these effects is the incorporation of antioxidant additives, which suppress autoxidation, extend shelf life, and enhance operational reliability (Saxena et al., 2017; Rajamohan et al., 2022; Hosseinzadeh-Bandbafha et al., 2022). Phenolic compounds have been widely employed for this purpose because of their strong capacity to interrupt free radical chain reactions via electron or hydrogen donation (Schober and Mittelbach, 2004; Sundus et al., 2017; Lapuerta et al., 2012). However, the efficacy of phenolic antioxidants is strongly modulated by their molecular structure and the surrounding medium (Lau et al., 2024). Understanding these structure–activity relationships is therefore essential for rational design of efficient stabilizers. A robust understanding of these structure–activity relationships and their process implications is crucial for advancing energy technologies that align with the goals of cleaner production. Density Functional Theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) has become a powerful tool for elucidating the electronic and structural determinants of antioxidant performance. By probing reactivity descriptors, frontier orbital distributions, and ionization potentials, computational methods provide predictive insight into antioxidant activity under diverse conditions. Prior studies of commercial phenolic antioxidants including butylated hydroxyanisole (BHA), butylated

hydroxytoluene (BHT), gallic acid (GA), propyl gallate (PG), pyrogallol (PY), and tert butylhydroquinone (TBHQ) have established benchmark profiles of electron donating ability and radical stabilization.

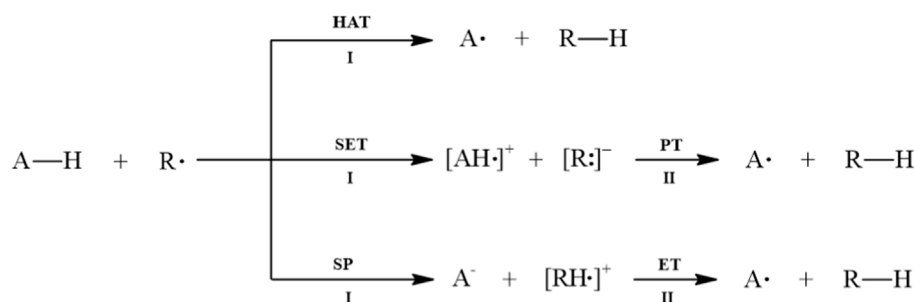
Within this broader landscape of potential stabilizers, phenolic antioxidants remain central because their radical scavenging efficiency has been consistently rationalized in terms of electronic descriptors. The commercial use of this class of compounds has established a robust theoretical benchmark, since their activity can be directly correlated with well-defined structure–activity relationships involving hydrogen donation and resonance stabilization of phenoxyl radicals (Yang et al., 2013; Yaakob et al., 2014; Mittelbach and Schober, 2003). This consolidated body of knowledge provides both a conceptual and computational framework against which new molecules can be evaluated. Dimethoxybenzaldehyde (DMB) derivatives extend this framework by combining methoxy groups, which enhance donation, with carbonyl and halogen substituents that introduce inductive influences capable of modulating frontier orbital energies and reactivity indices (Duarte et al., 2025; Wenceslau et al., 2025; Lee et al., 2020; Borges I. et al., 2022; Duarte et al., 2023; Aguiar et al., 2022a; Borges I. D. et al., 2022; Kim et al., 2011; Gawai et al., 2005). Bromine substitution, in particular, alters electron density distribution in ways that may enhance radical stabilization but also requires careful consideration regarding fuel compatibility. Positioning DMB derivatives in direct comparison with well-characterized phenolic antioxidants therefore establishes a coherent theoretical basis for probing how substituent effects govern antioxidant performance in biodiesel (Christensen and McCormick, 2023; Amran et al., 2022; Sterpu et al., 2024).

Here, we extend the computational framework to three dibrominated dimethoxybenzaldehyde derivatives 4,5 dibromo 2,3 dimethoxybenzaldehyde (IB1), 2,3 dibromo 5,6 dimethoxybenzaldehyde (IB2), and 4,6 dibromo 2,3 dimethoxybenzaldehyde (IB3) whose antioxidant potential has not been systematically investigated. The antioxidant properties and fuel stabilization potential of dibrominated DMBs derivatives remain largely unknown, as their mechanisms and synergistic effects have not been systematically evaluated in biodiesel contexts. This study addresses this gap by computationally investigating their electronic structure and radical-scavenging efficiency relative to established phenolic antioxidants. Their performance was evaluated through comparison with commercial phenolics, focusing on ionization potential, frontier orbital distributions, Fukui reactivity indices, spin density mapping, and Natural Bond Orbital (NBO) hyperconjugation analysis. By integrating molecular modeling with comparative benchmarking, this study provides a mechanistic basis for assessing brominated derivatives as potential biodiesel stabilizers. The comparative evaluation of DMBs derivatives and commercial phenolics reveals key structure–activity relationships that determine radical scavenging efficiency.

2 Computational procedures

2.1 Electron density calculations

All theoretical calculations were performed using the Gaussian 16 (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Molecular



SCHEME 1
Diagram of free radical scavenging mechanisms.

geometries were optimized at the hybrid M06-2X (Zhao and Truhlar, 2008), which incorporates long-range exchange corrections and is widely used for thermochemistry, kinetics, and noncovalent interactions. Studies have demonstrated that this functional reliably describes mid-range electronic correlation effects, and non-covalent interactions and is one of the best-performing functionals for modeling the thermodynamics of chemical processes (Arumugam et al., 2023; Cui et al., 2025). Furthermore, this functional has shown good results in analyses of the antioxidant activity of compounds (Mendes et al., 2024; Thuy and Son, 2022; de Aguiar et al., 2025). Self-consistent field (SCF) calculations employed tight convergence criteria and an ultrafine integration grid. Geometry optimizations maintained stringent thresholds, and vibrational frequency analyses confirmed that all structures represent true minimum, with no imaginary frequencies. Unless otherwise specified, thermal corrections were obtained at 298.15 K and 1 atm.

Electronic structures were analyzed in terms of Frontier Molecular Orbitals (FMOs) (Zhang and Musgrave, 2007): the Highest Occupied Molecular Orbital (HOMO), associated with electron-donating ability, and the Lowest Unoccupied Molecular Orbital (LUMO), associated with electron-accepting ability (KEBİROGLU and AK, 2023; Rocha et al., 2015; Freitas et al., 2024; NC et al., 2023). Within conceptual DFT, the central descriptors are defined from the total electronic energy $E(N, \nu)$ as functions of the number of electrons N under a fixed external potential ν . The chemical potential (Equation 1) (Pearson, 1992),

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{\nu} = -\frac{I + A}{2} = -\chi, \quad (1)$$

the chemical hardness (Equation 2) (Pearson, 1992; Pearson, 2005)

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu} = \frac{I - A}{2}, \quad (2)$$

and the global electrophilicity index (ω) (Equation 3) (Parr et al., 1999)

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

were calculated to obtain information about the chemical reactivity of the compounds studied in this work. In this context, E is the total electronic energy, N is the number of electrons, and ν is the external

potential (arising from the nuclei and any fixed fields). The chemical potential (μ) is related to electronegativity (χ) by $\chi = -\mu$, the ionization energy (I) is approximated as $I \cong -E_{\text{HOMO}}$, and the electron affinity (A) as $A \cong -E_{\text{LUMO}}$. The chemical hardness (η) measures the resistance of the electronic cloud to deformation during charge transfer, while the global electrophilicity index (ω) quantifies the stabilization achieved upon electron acquisition.

2.2 Antioxidant analysis

The Fukui index f^0 (Fukui, 1982; Li and Evans, 1995) was applied to identify molecular sites most susceptible to radical attack. Atomic charges were obtained through natural population analysis, and finite-difference approximations were used to derive the reactivity indices. These indices guided the generation of radical species, which were subsequently optimized at the same theoretical level (Weinhold et al., 2016; Reed et al., 1985; Barrera et al., 2025; Yamauchi et al., 2024). There are several methods for determining the antioxidant activity of compounds (Wenceslau et al., 2025), and to determine these property of the dibrominated DMBs derivatives, thermodynamic descriptors were calculated in the gas phase, in the same level of theory. Two main mechanisms can explain the antioxidant activity of compounds. The first, the hydrogen atom transfer (HAT) and the other, proton transfer (Lee et al., 2020; Borges I. et al., 2022). Hydrogen transfer processes can occur through homolytic or heterolytic scission of hydrogen atoms. The heterolytic pathway involves either a single electron transfer followed by proton transfer (SET-PT) or sequential proton loss followed by electron transfer (SPLET). The schematic representation of both mechanisms is shown in Scheme 1.

Since IB1, IB2, and IB3 have no phenolic groups, the antioxidant activity calculations were conducted only using the ET mechanism, in which one electron was removed from each structure and the ionization potential of the dibrominated DMBs derivatives was calculated using Equation 4,

$$\text{IP} = H_{[\text{AH}\cdot]^+} + H_e - H_{\text{AH}}, \quad (4)$$

in which H_{AH} , $H_{[\text{AH}\cdot]^+}$, and H_e are the dibrominated DMBs derivatives, radical cation formed after free radical scavenging, and electron enthalpies. The lower the IP value, the greater the antioxidant activity of the azine. The results were tabulated and

compared. Furthermore, spin density distributions were obtained to predict the stability of the radicals formed.

To investigate the influence of the medium on the electron-transfer step, the ionization potentials (IP) were calculated in different solvation environments. For this purpose, the implicit conductor-like polarizable continuum (CPCM) model (Takano and Houk, 2005) was employed, using solvents with distinct dielectric constants to represent hydrophobic and hydrophilic microenvironments relevant to biodiesel-like systems. Benzene ($\epsilon = 2.27$) and toluene ($\epsilon = 2.37$) were selected as representatives of nonpolar media because their polarity is similar to the hydrophobic matrix of biodiesel, which is predominantly composed of fatty acid esters with dielectric constants between 3 and 4.5. These solvents therefore allow the low-polarity microenvironment in which antioxidant additives operate to be reasonably mimicked. The inclusion of ethanol ($\epsilon = 24.85$) was intended to model residual polar components that may remain from the transesterification process, affecting local polarity and the solvation profile of the compounds (Patiño-Camino et al., 2021; Plácido and Capareda, 2016). Water ($\epsilon = 78.35$) was also considered due to the hygroscopic nature of biodiesel (Etim et al., 2022; He et al., 2007), which enables the incorporation of small amounts of this contaminant and can substantially alter the dielectric properties of the medium. In this manner, it becomes possible to assess how different physicochemical environments influence the ionization process without anticipating any interpretation regarding antioxidant performance.

Radical stabilization was further investigated by spin density distribution and NBO analysis (Weinhold and Landis, 2012; Weinhold and Landis, 2001) through the donor-acceptor hyperconjugation (Alabugin et al., 2011) obtained by the second-order perturbation formula (Equation 5),

$$E_{i \rightarrow j}^{(2)} = -n_{\sigma} \frac{\langle \sigma_i | \hat{F} | \sigma_j^* \rangle^2}{\epsilon_j^* - \epsilon_i} = -n_{\sigma} \frac{F_{ij}^2}{\epsilon_j^* - \epsilon_i}, \quad (5)$$

where $\langle \sigma_i | \hat{F} | \sigma_j^* \rangle^2$ or F_{ij}^2 is the Fock matrix element between the natural bond orbitals i and j ; ϵ_{σ^*} is the energy of the antibonding orbital σ^* , and ϵ_{σ} is the energy of the bonding orbital σ ; n_{σ} represents the population occupation of the σ donor orbital.

To complement these quantum descriptors, a machine learning approach was adopted for estimating radical reaction rate constants (k_{OH}). Calculations leveraged the pySIRC (Sanches-Neto et al., 2021) framework, employing Morgan fingerprints and the XGBoost algorithm to predict k_{OH} for each target molecule under oxidative attack by hydroxyl radicals in model biodiesel environments. Performance benchmarks and method validation followed protocols previously reported (Jenkin and Hayman, 1999). This allowed direct computational comparison of dibrominated DMBs (IB1, IB2, IB3) and reference commercial antioxidants (BHT, TBHQ, BHA, PG, PY, GA) (Figure 1), supporting a predictive ranking of radical-trapping potentials in biodiesel-relevant conditions.

3 Results and discussion

3.1 Molecular modeling analysis

The spatial distributions of the HOMO and LUMO (Figure 2) provide computational insights into the reactivity profiles of the studied compounds (Ganiev et al., 2023; Kim et al., 2013). In IB1, the

computed HOMO is extensively delocalized over the aromatic backbone and adjacent methoxy and bromine substituents, indicating a pronounced propensity for electron donation from these conjugated regions. The LUMO is primarily localized on the brominated and methoxylated sites, suggestive of a substituent-directed capacity for charge acceptance that may modulate interaction with radical species. IB3, conversely, exhibits both HOMO and LUMO densities that are distinctly more localized, confined to specific aromatic and substituent positions; this spatial restriction is associated with decreased π -delocalization and enhanced electronic softness, factors that favor increased reactivity but potentially at the cost of reduced radical stabilization. IB2 displays intermediate behavior, with modest orbital delocalization and energetic descriptors that fall between IB1 and IB3.

Among phenolic benchmarks, BHA and BHT show HOMO density highly concentrated on the hydroxyl moieties and ortho/para positions of the aromatic core. This canonical distribution aligns with classical mechanisms for HAT, where delocalized spin upon oxidation stabilizes the resulting phenoxyl radicals. In contrast, GA, PG, and PY each exhibit broader orbital delocalization in their HOMOs, spanning multiple hydroxyl sites and aromatic centers, which enhances radical stabilization but may slow initial scavenging kinetics (Varatharajan and Pushparani, 2018; França et al., 2017). The complementary LUMO maps reveal diffuse and, in some cases, spatially extended character particularly pronounced in PG, PY, and TBHQ. For these molecules, the computed LUMOs exhibit substantial electron density expansion beyond the aromatic moiety into peripherally located regions, a hallmark indication of Rydberg orbital character. The presence of these Rydberg orbitals endows TBHQ, PY, and BHA with alternative electron-accepting channels and non-classical stabilization pathways for radicals, as observed in both computational theory and experimental radical chemistry.

Quantitative descriptors (Supplementary Table S1) consistently support these qualitative trends. IB1 displays the highest HOMO energy (~ -8.39 eV) among the DMB derivatives, reflecting its strong electron-donating profile and increased electronic hardness. By contrast, IB3, characterized by the narrowest HOMO–LUMO gap (~ 6.53 eV) and lowest ionization energy (~ 7.89 eV), is definitively the most electronically “soft” and computationally reactive member within the new inhibitor series. IB2 presents an intermediate electronic configuration. Solvent-dependent analyses further suggest that while IB1 and IB2 maintain their electronic features across environments of varying polarity, IB3’s descriptors, especially its electronic gap and ionization potential, are substantially modulated by medium, reflecting a heightened sensitivity to environmental changes as predicted within the computational protocol. This effect may have implications for radical persistence under operational biodiesel conditions, but experimental corroboration is warranted.

Commercial antioxidants define well-established mechanistic archetypes: GA and PG have the largest calculated HOMO–LUMO gaps (~ 7.26 – 7.37 eV) and highest calculated hardness, which typically correlate with enhanced kinetic stability but lower inherent reactivity. BHA and BHT, with moderate gaps (~ 6.80 – 6.96 eV) and the lowest ionization energy (~ 6.99 – 7.12 eV), are computationally positioned as rapid radical quenchers. TBHQ,

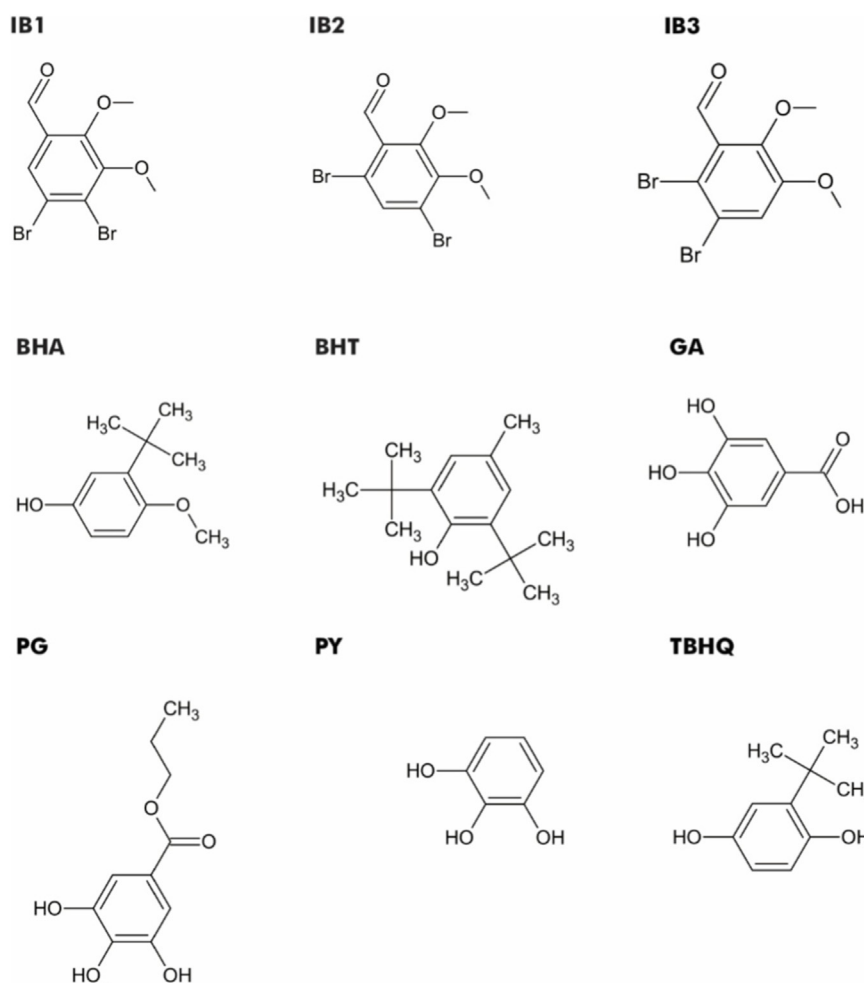


FIGURE 1
Structural formula of the dibrominated DMBs derivatives investigated (IB1, IB2, IB3) and commercial antioxidants used as benchmarks (BHA, BHT, GA, PG, PY, TBHQ).

sharing a moderate gap and showing pronounced solvent modulation, reflects practical efficiency in nonpolar biodiesel systems.

3.2 Antioxidant potential

Spin density mapping reveals the spatial distribution of unpaired electrons following radical formation. For the dibrominated derivatives (IB1–IB3), the unpaired electron preferentially localizes on carbons adjacent to brominated positions, with partial delocalization into the aromatic π -system (Figure 3). In IB1, spin density is found mainly on C2, C3, and C5; IB2 concentrates spin density at C3 and C6, reflecting a more localized distribution but still partially extended across the aromatic ring. IB3 exhibits localization at C3 and C5, but with reduced overlap into the π -framework, consistent with the structural distortion imposed by ortho bromination.

Commercial antioxidants display distinct but complementary stabilization strategies. BHA and BHT show spin densities centered on the phenolic oxygen and adjacent carbons, directly benefiting

from strong O–H to π conjugation, which efficiently stabilizes the radical cation. GA and PG exhibit broader spin distribution patterns, associated with their multiple hydroxyl substitutions, while PY and TBHQ exhibit intermediate patterns, with spin density distributed between oxygen substituents and aromatic carbons, reflecting their capacity to quench radicals efficiently in biodiesel-like environments (Lapuerta et al., 2012; Fernandes et al., 2012; Rizwanul Fattah et al., 2014; Sui et al., 2021; Ileri and Koçar, 2014; Rodrigues et al., 2020; Almeida et al., 2011). The spin density analysis consolidates the mechanistic framework of the dibrominated series: antioxidant activity is mediated by electron transfer, but the efficiency of radical stabilization is strongly modulated by substitution geometry. In contrast, commercial antioxidants achieve stabilization primarily through well-established O–H centered delocalization pathways, underscoring the advantage of phenolic hydroxyl groups over halogen substitution in ensuring persistent radical quenching.

The NBO analysis (Supplementary Table S2–S4) revealed that the O_2 and O_3 atoms experience the least stabilization due to the hyperconjugations occurring in the radicals. Notably, IB3 exhibits hyperconjugation from $\pi(C_1-C_6) \rightarrow \pi^*(O_2-C_2)$ with a stabilizing

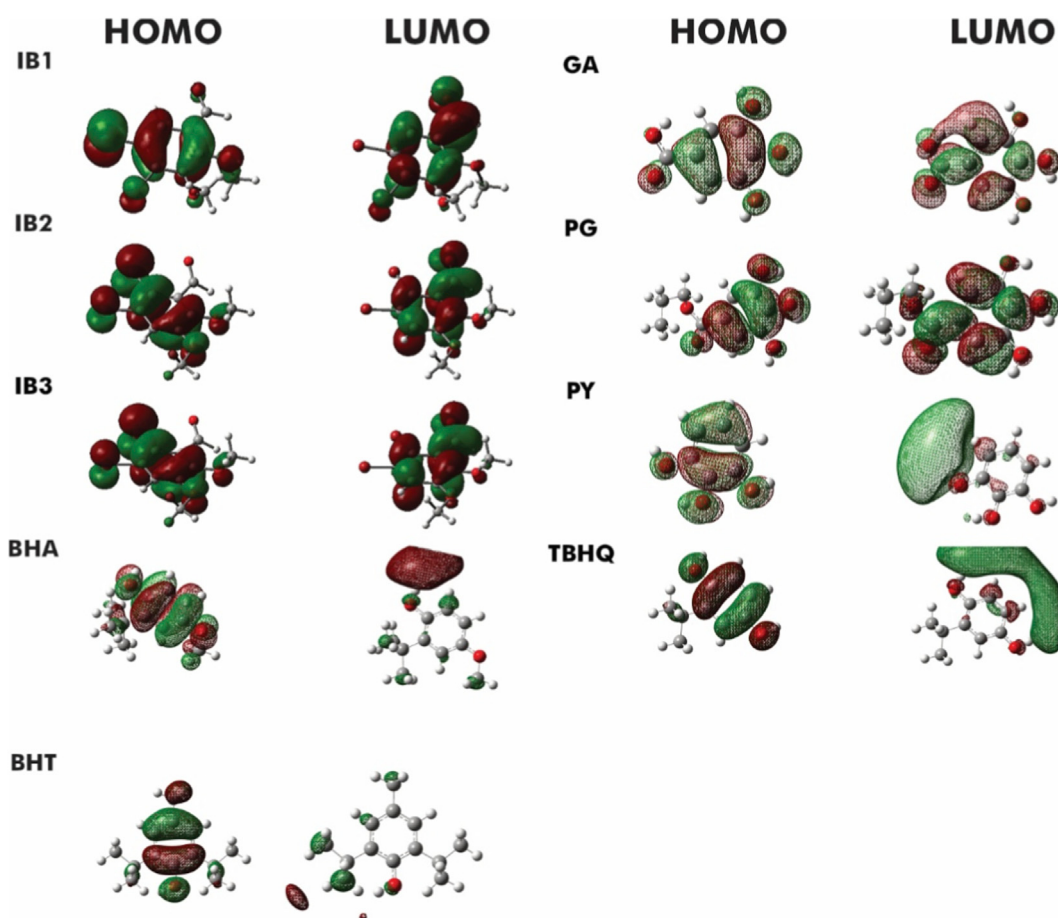


FIGURE 2
Isosurface representations of HOMO and LUMO for phenolic biodiesel additives and dibrominated DMBs (IB1–IB3). Energy values are shown in eV, as computed using the M06-2X/6-311+G (d,p) level of theory (isovalue = 0.002) in the gas phase.

energy of ≈ 1.07 eV, effectively stabilizing the radical on the O_2 atom. When the unpaired electron is located at C_2 , there are two important hyperconjugations that significantly contribute to stabilizing the IB1 radical: $\pi(C_5-C_6) \rightarrow \pi^*(C_1-C_2)$ with an $E_{i-j}^{(2)}$ value of ≈ 0.569 eV, and $\eta_2(O_2) \rightarrow \pi^*(C_1-C_2)$ with an $E_{i-j}^{(2)}$ value of ≈ 0.734 eV. In contrast, for the IB2 radical, only one hyperconjugation strongly aids in its stabilization: $\eta_2(O_2) \rightarrow \pi^*(C_1-C_2)$, with an $E_{i-j}^{(2)}$ value of ≈ 1.15 eV. Finally, in the IB3 radical, the hyperconjugation that contributes most to its stabilization is $\eta_1(O_2) \rightarrow \sigma^*(C_2-C_3)$. However, the $E_{i-j}^{(2)}$ value for this interaction is lower, indicating relatively poor stabilization of the radical in this region of the molecule. When the unpaired electron is located on the C_3 atom, there are three significant hyperconjugations involving donor orbitals $\pi(C_1-C_2)$, $\pi(C_5-C_6)$, and $\eta_3(Br_1)$ of IB1 with the acceptor orbital $\pi^*(C_3-C_4)$ contribute to its stabilization, with $E_{i-j}^{(2)}$ values of ≈ 0.525 , ≈ 0.703 , and ≈ 0.390 eV, respectively. In the case of IB2 and IB3, only one crucial hyperconjugation each was observed in the stabilization of their radicals: $\eta_2(O_2) \rightarrow \pi^*(C_1-C_2)$ with an $E_{i-j}^{(2)}$ value of ≈ 1.15 eV for IB2, and $\eta_1(O_2) \rightarrow \sigma^*(C_2-C_3)$ with an $E_{i-j}^{(2)}$ value of ≈ 0.241 eV for IB3.

Collectively, the NBO results underscore the decisive role of substitution geometry in dictating radical stability. IB1 achieves

stabilization through a distributed network of hyperconjugations, IB2 depends on one dominant interaction, and IB3 is structurally penalized by steric congestion, which suppresses orbital overlap. These findings reconcile the paradox observed in global descriptors: although IB3 exhibits the lowest ionization potential and narrowest HOMO–LUMO gap, its radical intermediates lack sufficient hyperconjugative support, reducing its efficacy as an antioxidant. The duality of bromination—enhancing electronic softness while constraining delocalization—emerges here as a fundamental trade-off that limits the utility of this class in biodiesel stabilization.

The antioxidant potential of the dibrominated derivatives was evaluated employing site-specific reactivity indices, radical stability parameters, and ionization potential metrics. Fukui's f^0 function (Figure 4a) consistently identified bromine substituents and the phenolic oxygen as the most electrophilic sites for potential radical attack, with the electronic polarization induced by bromination rendering these sites particularly susceptible to electron abstraction. Notably, the absence of labile hydrogen atoms in DMB molecules indicates HAT is not their operative scavenging pathway; instead, their antioxidant mechanism is primarily governed by electron transfer processes. This mechanism is supported by the computed electronic descriptors and is further illustrated in

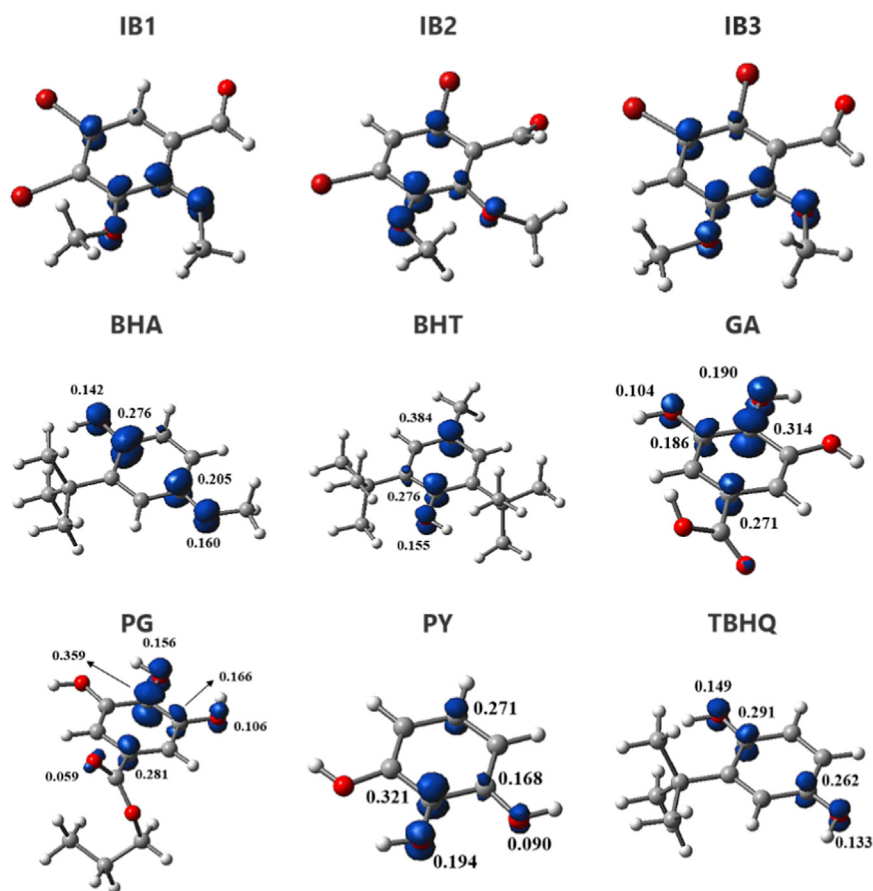
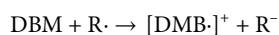


FIGURE 3 Spin density distributions of radical intermediates for dibrominated DMBs derivatives (IB1–IB3) and reference phenolic antioxidants, calculated at the M06-2X/6-311++G (d,p) level (isovalue = 0.015). Blue lobes represent unpaired electron density with Mulliken spin populations indicated. DMB derivatives show spin localization influenced by methoxy and bromine substitution, whereas phenolic antioxidants display delocalization centered on hydroxyl groups and adjacent carbons, reflecting distinct stabilization mechanisms.

Scheme 1, where the free radical ($R\cdot$) captures an electron from the additive, leading to the formation of a radical cation and a neutralized radical species.

In this process, $R\cdot$ captures an electron from the additive (DMB), generating a radical cation ($[DMB\cdot]^+$) and a neutralized radical (R^-) as schematically illustrated in Scheme:



The relative stability of the radical intermediates, expressed as enthalpy differences (ΔH , **Figure 4b**), follows the order $IB3 > IB2 > IB1$. These values are comparable to those of commercial antioxidants such as GA and PG, suggesting that despite structural distortions introduced by bromination, the DMBs can form radicals of competitive stability. In these radicals, the unpaired electron preferentially localizes on C2, C3, and C5 in IB1, C3 and C6 in IB2, and C3 and C5 in IB3 before undergoing free radical scavenging. The IP calculations further refine this mechanistic framework. Gas-phase values are ≈ 8.48 , ≈ 8.43 , and ≈ 8.17 eV for IB1, IB2, and IB3, respectively, which situate them within the reference range of phenol (Xue et al., 2013a) (≈ 8.31 eV), glutathione (Aguir et al., 2022b) (≈ 7.55 eV), phenolic chalcones (Xue et al., 2013b) (mean: ≈ 7.55 eV), and other chalcones (Aguir et al., 2023) (≈ 8.02 eV).

Solvent effects significantly modulate these values, with reductions of $\approx 12\%$ in nonpolar solvents and up to $\approx 20\%$ in polar solvents. This trend enhances reactivity in the presence of water an inevitable biodiesel contaminant due to its hygroscopic nature thereby ensuring antioxidative activity under practical conditions (Christensen and McCormick, 2023; Fregolente et al., 2012; Rodriguez et al., 2018).

Commercial antioxidants display similar solvent-dependent behavior (Schober and Mittelbach, 2004; Serqueira et al., 2015; de Sousa et al., 2014; Kreivaitis et al., 2013; Hazrat et al., 2021). BHA and BHT exhibit pronounced reductions, from ≈ 7.46 – 7.55 eV in the gas phase to ≈ 5.68 – 5.94 eV in water (**Figure 4c**), rationalizing their widespread efficiency in biodiesel applications. GA, PG, and PY, by contrast, maintain consistently high IPs with limited solvent sensitivity, conferring robustness but reduced reactivity (Hosseinzadeh-Bandbafha et al., 2022; Lau et al., 2024; Erdemir et al., 2005). TBHQ represents an intermediate case, with reactivity enhanced in nonpolar solvents, consistent with its efficiency in biodiesel-like matrices. While IB1 emerges as the most thermodynamically stable, IB3 is the most reactive but least stabilized, and IB2 exhibits intermediate behavior. These mechanistic insights confirm that dibromination can produce

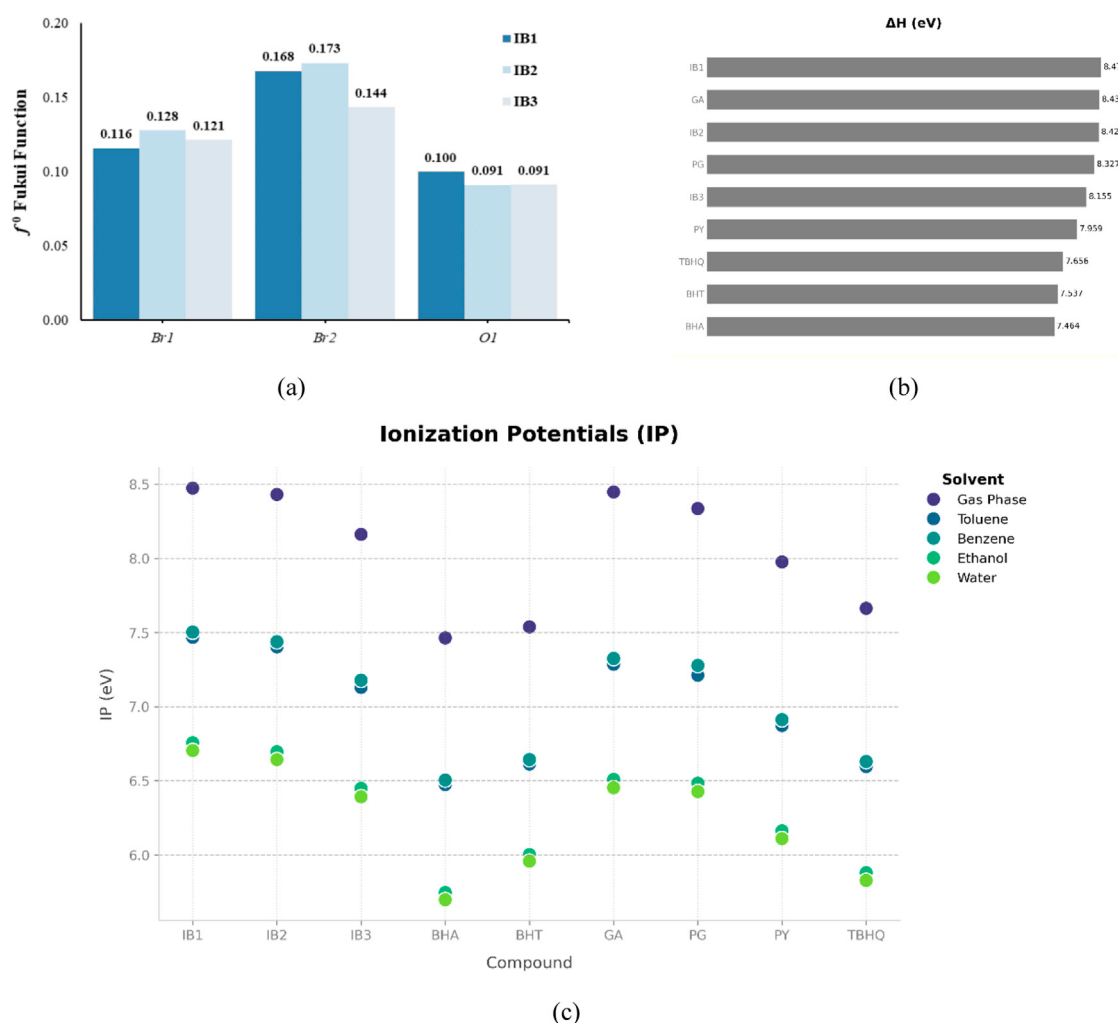


FIGURE 4
(a) The f^0 for radical attacks on DMBs, **(b)** graph of ΔH of DMB compounds and their respective radicals and **(c)** a graph of the ionization potentials of DMBs and commercial biodiesel additives. All values computed at the M06-2X/6-311++G (d,p) level. Solvent effects are indicated where applicable.

competitive descriptors relative to established phenolic antioxidants, although the dual influence of bromine facilitating ET but constraining delocalization—remains a fundamental computationally observed limitation of these structures.

The machine learning-derived reaction rate constants provide predictive (Table 1) insights into the radical-trapping potential of DMB derivatives relative to established commercial antioxidants. The three DMB derivatives exhibit k_{OH} values that situate them within the same theoretical reactivity regime as BHT and GA, but below the highly reactive benchmarks TBHQ, BHA, and particularly PG, which was identified as the most reactive antioxidant among those assessed. This computational ranking aligns qualitatively with literature trends for antioxidant efficiency in biodiesel, where PG, TBHQ, and BHA typically suppress oxidation and extend induction periods more effectively than BHT and GA under Rancimat conditions (Varatharajan and Pushparani, 2018; Hosseinzadeh-Bandbafha et al., 2022; Schober and Mittelbach, 2004; Mittelbach and Schober, 2003; Yamauchi et al., 2024; Singh et al., 2022; hao Ni et al., 2020; Chen et al., 2019). Consequently, the moderate (k_{OH})

values predicted for the DMBs suggest radical scavenging capabilities comparable to BHT, indicating suitability for scenarios requiring controlled stabilization.

Furthermore, the similarity between IB1 and IB3 suggests that their structural differences have minimal impact on hydroxyl radical trapping, whereas the lower reactivity of IB2 implies specific electronic or steric constraints. While the present work is strictly theoretical, the derived descriptor–kinetics hierarchy establishes a concrete framework for future validation, serving as a bridge to practical observations. To confirm the predicted performance, the rank ordering established herein—based on IP, softness, NBO hyperconjugation, and ML-derived (k_{OH}) should be directly confronted with a targeted experimental protocol. This validation would necessitate DPPH and ABTS radical-scavenging assays to determine (IC_{50}) values, correlating kinetic rates with computed electronic descriptors, alongside DSC and TGA measurements on treated biodiesel to determine oxidation onset temperatures and mass-loss profiles. Thus, this

study provides the theoretical foundation and a concise roadmap for subsequent experimental verification of DMB derivatives as effective biodiesel stabilizers.

4 Final considerations

This study integrated computational descriptors frontier molecular orbitals, Fukui indices, ionization energies, spin density distributions, and NBO hyperconjugation analyses to elucidate the antioxidant mechanisms of dibrominated DMBs derivatives compared to commercial phenolic benchmarks. Our calculations suggest that bromination enhances electronic softness and facilitates electron transfer, positioning DMB additives as computationally promising for radical scavenging in biodiesel stabilization. However, increased softness and planarity deviation, particularly in ortho-substituted derivatives, may restrict conjugation and reduce the persistence of radical intermediates.

Within the DMB series, IB1 is predicted to combine a favorable electron-donating profile with distributed stabilization potential, while IB3 displayed high reactivity but limited radical stability due to local electronic effects. IB2 exhibits intermediate behavior based on our analyses. When benchmarked against commercial antioxidants, distinct mechanistic contrasts are indicated by our computational results. BHA and BHT are characterized in our study as achieve efficiency through low ionization potentials and hydroxyl-centered resonance stabilization; GA and PG rely on wide HOMO–LUMO gaps and extended delocalization across multiple hydroxyl groups; TBHQ benefits from solvent-dependent reactivity optimized for nonpolar biodiesel matrices. The dibrominated derivatives, by contrast, operate through halogen-induced polarization and ET pathways, situating them in a mechanistically distinct class. These results demonstrate that the antioxidant potential of DMB derivatives depends on achieving the right balance between reactivity and radical stability. Optimization of substitution patterns can be guided by computational descriptors established in this study, and may inform the design of future fuel additives, once validated experimentally.

Data availability statement

The original contributions presented in the study are included in the article/[Supplementary Material](#), further inquiries can be directed to the corresponding authors.

Author contributions

IB: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review and editing, Writing – original draft. AA: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft. AC: Conceptualization, Data curation,

Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review and editing. HN: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review and editing.

Funding

The author(s) declared that financial support was not received for this work and/or its publication.

Acknowledgements

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Conselho Nacional de Desenvolvimento Científico e Tecnológico and Fundação de Amparo à Pesquisa de Goiás. Theoretical calculations were performed in the High-Performance Computing Center of the Universidade Estadual de Goiás.

Conflict of interest

The author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fceng.2025.1716732/full#supplementary-material>

References

- Aguiar, A. S. N., Dos Santos, V. D., Borges, I. D., Navarrete, A., Aguirre, G., Valverde, C., et al. (2022a). Bromine substitution effect on structure, reactivity, and linear and third-order nonlinear optical properties of 2,3-Dimethoxybenzaldehyde. *J. Phys. Chem. A* 126, 7852–7863. doi:10.1021/acs.jpca.2c04658
- Aguiar, A. S. N., Borges, I. D., Borges, L. L., Dias, L. D., Camargo, A. J., Perjesi, P., et al. (2022b). New insights on glutathione's supramolecular arrangement and its *in silico* analysis as an angiotensin-converting enzyme inhibitor. *Molecules* 27, 7958. doi:10.3390/molecules2727958
- Aguiar, A. S. N., Dias, P. G. M., Queiroz, J. E., Firmino, P. P., Custódio, J. M. F., Dias, L. D., et al. (2023). Insights on potential photoprotective activity of two butylchalcone derivatives: synthesis, spectroscopic characterization and molecular modeling. *Photonics* 10, 228. doi:10.3390/photonics10030228
- Alabugin, I. V., Gilmore, K. M., and Peterson, P. W. H. (2011). Wiley Interdisciplinary Reviews: Computational Molecular Science 1, 109–141. doi:10.1002/wcms.6
- Almeida, E. S., Portela, F. M., Sousa, R. M., Daniel, D., Terrones, M. G., Richter, E. M., et al. (2011). Behaviour of the antioxidant tert-butylhydroquinone on the storage stability and corrosive character of biodiesel. *Fuel* 90, 3480–3484. doi:10.1016/j.fuel.2011.06.056
- Alvares, C. A., Stape, J. L., Sentelhas, P. C., Gonçalves, J. L. de M., and Sparovek, G. (2013). Köppen's climate classification map for Brazil. *Meteorol. Zeitschrift* 22, 711–728. doi:10.1127/0941-2948/2013/0507
- Amran, N. A., Bello, U., and Hazwan Ruslan, M. S. (2022). The role of antioxidants in improving biodiesel's oxidative stability, poor cold flow properties, and the effects of the duo on engine performance: a review. *Heliyon* 8, e09846. doi:10.1016/j.heliyon.2022.e09846
- Arumugam, S., Muthaiyan, R., and Rajendran, S. (2023). Assessment of oxidative stability of biodiesel and biodiesel blends. *Energy sources*. 45, 6371–6387. doi:10.1080/15567036.2023.2217089
- Barrera, N. F., Cabezas-Escare, J., Muñoz, F., Muriel, W. A., Gómez, T., Calatayud, M., et al. (2025). Fukui function and Fukui potential for solid-state chemistry: application to surface reactivity. *J. Chem. Theory Comput.* 21, 3187–3203. doi:10.1021/acs.jctc.5c00086
- Borges, I., Navarrete, A., Aguirre, G., Aguiar, A., Oliveira, S., Camargo, A., et al. (2022). Synthesis and molecular modeling study of two bromo-dimethoxybenzaldehydes. *J. Braz. Chem. Soc.* doi:10.21577/0103-5053.20220023
- Borges, I. D., Faria, E. C. M., Custódio, J. F. M., Duarte, V. S., Fernandes, F. S., Alonso, C. G., et al. (2022). Insights into chalcone analogues with potential as antioxidant additives in diesel–biodiesel blends. *RSC Adv.* 12, 34746–34759. doi:10.1039/d2ra07300e
- Chen, P., Wang, Z., Wu, J., Xia, H., Tai, C., and Li, R. (2019). Effects of phenolic antioxidants on biodiesel oxidative stability and emission. *Environ. Prog. Sustain Energy* 38, 13203. doi:10.1002/ep.13203
- Christensen, E. D., and McCormick, R. L. (2023). Water contamination impacts on biodiesel antioxidants and storage stability. *Energy & Fuels* 37, 5179–5188. doi:10.1021/acs.energyfuels.2c03911
- Cui, M., Hou, X., Han, Y., Zhang, Y., Liu, Z., Li, J., et al. (2025). Real-world emissions and formation mechanism of IVOs from biodiesel-fueled agricultural machinery. *Environ. Sci. Technol.* 59, 9017–9026. doi:10.1021/acs.est.4c11004
- Davis, M., Ahiduzzaman, Md., and Kumar, A. (2018). How will Canada's greenhouse gas emissions change by 2050? A disaggregated analysis of past and future greenhouse gas emissions using bottom-up energy modelling and sankey diagrams. *Appl. Energy* 220, 754–786. doi:10.1016/j.apenergy.2018.03.064
- de Aguiar, A. S. N., de Carvalho, L. B. R., Gomes, C. M., Castro, M. M., Martins, F. S., and Borges, L. L. (2025). Computational insights into the antioxidant activity of luteolin: density functional theory analysis and docking in cytochrome P450 17A1. *Pharmaceuticals* 18, 410. doi:10.3390/ph18030410
- de Sousa, L. S., de Moura, C. V. R., de Oliveira, J. E., and de Moura, E. M. (2014). Use of natural antioxidants in soybean biodiesel. *Fuel* 134, 420–428. doi:10.1016/j.fuel.2014.06.007
- Duarte, V. S., D. Borges, I., d'Oliveira, G. D. C., Faria, E. C. M., de Almeida, L. R., Carvalho-Silva, V. H., et al. (2023). Arylsulfonamide chalcones as alternatives for fuel additives: antioxidant activity and machine learning protocol studies. *New J. Chem.* 47, 10003–10015. doi:10.1039/d3nj00255a
- Duarte, V. S., de Paula, R. L. G., Almeida, L. R., D'Oliveira, G. D. C., Pérez, C. N., Custódio, J. M. F., et al. (2025). Exploring quinolinone–chalcones: synthesis, antioxidant potential and industrial applications in biofuels. *Biofuels, Bioprod. Biorefining* 19, 1765–1783. doi:10.1002/bbb.2774
- Erdemir, A., Li, S., and Jin, Y. (2005). Relation of certain quantum chemical parameters to lubrication behavior of solid oxides. *Int. J. Mol. Sci.* 6, 203–218. doi:10.3390/i6060203
- Etim, A. O., Jisieike, C. F., Ibrahim, T. H., and Betiku, E. (2022). “Biodiesel and its properties,” in *Production of biodiesel from non-edible sources* (Elsevier), 39–79. doi:10.1016/B978-0-12-824295-7.00004-8
- Fernandes, D. M., Serqueira, D. S., Portela, F. M., Assunção, R. M., Munoz, R. A., and Terrones, M. G. (2012). Preparation and characterization of methylic and ethylic biodiesel from cottonseed oil and effect of tert-butylhydroquinone on its oxidative stability. *Fuel* 97, 658–661. doi:10.1016/j.fuel.2012.01.067
- França, F. R. M., dos Santos Freitas, L., Ramos, A. L. D., da Silva, G. F., and Brandão, S. T. (2017). Storage and oxidation stability of commercial biodiesel using Moringa oleifera lam as an antioxidant additive. *Fuel* 203, 627–632. doi:10.1016/j.fuel.2017.03.020
- Fregolente, P. B. L., Fregolente, L. V., and Wolf Maciel, M. R. (2012). Water content in biodiesel, diesel, and biodiesel–diesel blends. *J. Chem. Eng. Data* 57, 1817–1821. doi:10.1021/je300279c
- Freitas, A. V., Alves, G. G. B., Paschoal, G. M. A., Lafargue-dit-Hauret, W., Hiorns, R. C., Bégué, D., et al. (2024). A DFT bottom-up approach on non-fullerene acceptors: what makes highly efficient acceptors. *J. Mater. Sci.* 59, 10888–10903. doi:10.1007/s10853-024-09811-1
- Fukui, K. (1982). Role of frontier orbitals in chemical reactions. *Science* 218, 747–754. doi:10.1126/science.218.4574.747
- Ganiev, B., Mardonov, U., and Kholikova, G. (2023). Molecular structure, HOMO–LUMO, MEP – analysis of triazine compounds using DFT (B3LYP) calculations. *Mater. Today Proc.* doi:10.1016/j.matpr.2023.09.191
- Gawai, K. R., Lokhande, P. D., Kodam, K. M., and Soojhawon, I. (2005). Oxidation of carbonyl compounds by whole-cell biocatalyst. *World J. Microbiol. Biotechnol.* 21, 457–461. doi:10.1007/s11274-004-2467-y
- Giakoumis, E. G., Rakopoulos, C. D., Dimaratos, A. M., and Rakopoulos, D. C. (2012). Exhaust emissions of diesel engines operating under transient conditions with biodiesel fuel blends. *Prog. Energy Combust. Sci.* 38, 691–715. doi:10.1016/j.pecs.2012.05.002
- hao Ni, Z., Li, F. s., Wang, H., Wang, S., Gao, S. y., and Zhou, L. (2020). Antioxidative performance and oil-soluble properties of conventional antioxidants in rubber seed oil biodiesel. *Renew. Energy* 145, 93–98. doi:10.1016/j.renene.2019.04.045
- Hazrat, M. A., Rasul, M. G., Khan, M. M. K., Mofijur, M., Ahmed, S. F., Ong, H. C., et al. (2021). Techniques to improve the stability of biodiesel: a review. *Environ. Chem. Lett.* 19, 2209–2236. doi:10.1007/s10311-020-01166-8
- He, B. B., Thompson, J. C., Routt, D. W., and Van Gerpen, J. H. (2007). Moisture absorption in biodiesel and its petro-diesel blends. *Appl. Eng. Agric.* 23, 71–76. doi:10.13031/2013.22320
- Hohenberg, P., and Kohn, W. (1964). Inhomogeneous electron gas. *Phys. Rev.* 136, B864–B871. doi:10.1103/physrev.136.b864
- Hosseinzadeh-Bandbafha, H., Kumar, D., Singh, B., Shahbeig, H., Lam, S. S., Aghbashlo, M., et al. (2022). Biodiesel antioxidants and their impact on the behavior of diesel engines: a comprehensive review. *Fuel Process. Technol.* 232, 107264. doi:10.1016/j.fuproc.2022.107264
- Ileri, E., and Koçar, G. (2014). Experimental investigation of the effect of antioxidant additives on NOx emissions of a diesel engine using biodiesel. *Fuel* 125, 44–49. doi:10.1016/j.fuel.2014.02.007
- Jenkin, M. E., and Hayman, G. D. (1999). Photochemical ozone creation potentials for oxygenated volatile organic compounds: sensitivity to variations in kinetic and mechanistic parameters. *Atmos. Environ.* 33, 1275–1293. doi:10.1016/s1352-2310(98)00261-1
- Kebiroglu, H., and Ak, F. (2023). Molecular structure, geometry properties, HOMO–LUMO, and MEP analysis of acrylic acid based on DFT calculations. *J. Phys. Chem. Fundam. Mater.* 6, 92–100. doi:10.54565/jphcfum.1343235
- Kim, J. H., Chan, K. L., Mahoney, N., and Campbell, B. C. (2011). Antifungal activity of redox-active benzaldehydes that target cellular antioxidation. *Ann. Clin. Microbiol. Antimicrob.* 10, 23. doi:10.1186/1476-0711-10-23
- Kim, B., Ma, X., Chen, C., Ie, Y., Coir, E. W., Hashemi, H., et al. (2013). Energy level modulation of HOMO, LUMO, and band-gap in conjugated polymers for organic photovoltaic applications. *Adv. Funct. Mater.* 23, 439–445. doi:10.1002/adfm.201201385
- Knothe, G. (2007). Some aspects of biodiesel oxidative stability. *Fuel Process. Technol.* 88, 669–677. doi:10.1016/j.fuproc.2007.01.005
- Kohn, W., and Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Phys. Rev.* 140, A1133–A1138. doi:10.1103/physrev.140.a1133
- Kreivaitis, R., Gumbyte, M., Kazancev, K., Padgurskas, J., and Makarevičienė, V. (2013). A comparison of pure and natural antioxidant modified rapeseed oil storage properties. *Ind. Crops Prod.* 43, 511–516. doi:10.1016/j.indcrop.2012.07.071
- Lapuerta, M., Rodríguez-Fernández, J., Ramos, A., and Álvarez, B. (2012). Effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels. *Fuel* 93, 391–396. doi:10.1016/j.fuel.2011.09.011
- Lau, C. H., Lau, H. L. N., Ng, H. K., Thangalazhy-Gopakumar, S., Lee, L. Y., and Gan, S. (2024). Evaluation of synthetic and bio-based additives on the oxidation stability of palm biodiesel: parametric, kinetics and thermodynamics studies. *Sustain. Energy Technol. Assessments* 64, 103738. doi:10.1016/j.seta.2024.103738

- Lee, C. Y., Sharma, A., Semenya, J., Anamoah, C., Chapman, K. N., and Barone, V. (2020). Computational study of ortho-substituent effects on antioxidant activities of phenolic dendritic antioxidants. *Antioxidants* 9, 189. doi:10.3390/antiox9030189
- Li, Y., and Evans, J. N. S. (1995). The Fukui function: a key concept linking frontier molecular orbital theory and the hard-soft-acid-base principle. *J. Am. Chem. Soc.* 117, 7756–7759. doi:10.1021/ja00134a021
- Luque, R., Lovett, J. C., Datta, B., Clancy, J., Campelo, J. M., and Romero, A. A. (2010). Biodiesel as feasible petrol fuel replacement: a multidisciplinary overview. *Energy Environ. Sci.* 3, 1706–1721. doi:10.1039/c0ee00085j
- Mendes, R. A., da Mata, V. A. S., Brown, A., and de Souza, G. L. C. (2024). A density functional theory benchmark on antioxidant-related properties of polyphenols. *Phys. Chem. Chem. Phys.* 26, 8613–8622. doi:10.1039/d3cp04412b
- Mittelbach, M., and Schober, S. (2003). The influence of antioxidants on the oxidation stability of biodiesel. *J. Am. Oil Chem. Soc.* 80, 817–823. doi:10.1007/s11746-003-0778-x
- Nc, P., K. V., Kg, S., Mn, R., R. A. R., J. T., et al. (2023). Quantum computations of non-steroidal anti-inflammatory drug molecules using density functional theory. *Chem. Phys. Impact* 7, 100317. doi:10.1016/j.chphi.2023.100317
- Pantoja, S. S., Conceição, L. R. V. Da, Costa, C. E. F. Da, Zamian, J. R., and Filho, G. N. D. R. (2013). Oxidative stability of biodiesels produced from vegetable oils having different degrees of unsaturation. *Energy Convers. Manag.* 74, 293–298. doi:10.1016/j.enconman.2013.05.025
- Parr, R. G., Szentpály, L. V., and Liu, S. (1999). Electrophilicity index. *J. Am. Chem. Soc.* 121, 1922–1924. doi:10.1021/ja983494x
- Patino-Camino, R., Cova-Bonillo, A., Rodríguez-Fernández, J., Iglesias, T. P., and Lapuerta, M. (2021). Relaxation dynamics of ethanol and N-Butanol in diesel fuel blends from terahertz spectroscopy. *J. Infrared Millim. Terahertz Waves* 42, 772–792. doi:10.1007/s10762-021-00807-5
- Pearson, R. G. (1992). The electronic chemical potential and chemical hardness. *J. Mol. Struct. (Theochem)* 255, 261–270. doi:10.1016/0166-1280(92)85014-c
- Pearson, R. G. (2005). Chemical hardness and density functional theory. *J. Chem. Sci.* 117, 369–377. doi:10.1007/bf02708340
- Plácido, J., and Capareda, S. (2016). Conversion of residues and by-products from the biodiesel industry into value-added products. *Bioresour. Bioprocess* 3, 23. doi:10.1186/s40643-016-0100-1
- Pullen, J., and Saeed, K. (2012). An overview of biodiesel oxidation stability. *Renew. Sustain. Energy Rev.* 16, 5924–5950. doi:10.1016/j.rser.2012.06.024
- Pullen, J., and Saeed, K. (2014). Experimental study of the factors affecting the oxidation stability of biodiesel FAME fuels. *Fuel Process. Technol.* 125, 223–235. doi:10.1016/j.fuproc.2014.03.032
- Rajamohan, S., Hari Gopal, A., Muralidharan, K. R., Huang, Z., Paramasivam, B., Ayyasamy, T., et al. (2022). Evaluation of oxidation stability and engine behaviors operated by Prosopis juliflora biodiesel/diesel fuel blends with presence of synthetic antioxidant. *Sustain. Energy Technol. Assessments* 52, 102086. doi:10.1016/j.seta.2022.102086
- Reed, A. E., Weinstock, R. B., and Weinhold, F. (1985). Natural population analysis. *J. Chem. Phys.* 83, 735–746. doi:10.1063/1.449486
- Rizwanul Fattah, I. M., Masjuki, H. H., Kalam, M. A., Mofijur, M., and Abedin, M. J. (2014). Effect of antioxidant on the performance and emission characteristics of a diesel engine fueled with palm biodiesel blends. *Energy Convers. Manag.* 79, 265–272. doi:10.1016/j.enconman.2013.12.024
- Rocha, M., Di Santo, A., Arias, J. M., Gil, D. M., and Altabef, A. B. (2015). *Ab-initio* and DFT calculations on molecular structure, NBO, HOMO–LUMO study and a new vibrational analysis of 4-(Dimethylamino) benzaldehyde. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 136, 635–643. doi:10.1016/j.saa.2014.09.077
- Rodrigues, J. S., do Valle, C. P., Uchoa, A. F. J., Ramos, D. M., da Ponte, F. A. F., Rios, M. A. d. S., et al. (2020). Comparative study of synthetic and natural antioxidants on the oxidative stability of biodiesel from tilapia oil. *Renew. Energy* 156, 1100–1106. doi:10.1016/j.renene.2020.04.153
- Rodriguez, R. del G., Scanlon, B. R., King, C. W., Scarpore, F. V., Xavier, A. C., and Pruski, F. F. (2018). Biofuel-water-land nexus in the last agricultural frontier region of the Brazilian cerrado. *Appl. Energy* 231, 1330–1345. doi:10.1016/j.apenergy.2018.09.121
- Ryu, K. (2009). Effect of antioxidants on the oxidative stability and combustion characteristics of biodiesel fuels in an indirect-injection (IDI) diesel engine. *J. Mech. Sci. Technol.* 23, 3105–3113. doi:10.1007/s12206-009-0902-6
- Saluja, R. K., Kumar, V., and Sham, R. (2016). Stability of biodiesel – a review. *Renew. Sustain. Energy Rev.* 62, 866–881. doi:10.1016/j.rser.2016.05.001
- Sanches-Neto, F. O., Dias-Silva, J. R., Keng Queiroz Junior, L. H., and Carvalho-Silva, V. H. (2021). Py SiRC: machine learning combined with molecular fingerprints to predict the reaction rate constant of the radical-based oxidation processes of aqueous organic contaminants. *Environ. Sci. Technol.* 55, 12437–12448. doi:10.1021/acs.est.1c04326
- Saxena, V., Kumar, N., and Saxena, V. K. (2017). A comprehensive review on combustion and stability aspects of metal nanoparticles and its additive effect on diesel and biodiesel fuelled C.I. engine. *Renew. Sustain. Energy Rev.* 70, 563–588. doi:10.1016/j.rser.2016.11.067
- Schober, S., and Mittelbach, M. (2004). The impact of antioxidants on biodiesel oxidation stability. *Eur. J. Lipid Sci. Technol.* 106, 382–389. doi:10.1002/ejlt.200400954
- Serqueira, D. S., Dornellas, R. M., Silva, L. G., de Melo, P. G., Castellan, A., Ruggiero, R., et al. (2015). Tetrahydrocurcuminoids as potential antioxidants for biodiesels. *Fuel* 160, 490–494. doi:10.1016/j.fuel.2015.07.104
- Serqueira, D. S., Pereira, J. F., Squizzato, A. L., Rodrigues, M. A., Lima, R. C., Faria, A. M., et al. (2021). Oxidative stability and corrosivity of biodiesel produced from residual cooking oil exposed to copper and carbon steel under simulated storage conditions: dual effect of antioxidants. *Renew. Energy* 164, 1485–1495. doi:10.1016/j.renene.2020.10.097
- Silva, F. R. da, Baumgardt da Silva, F. J. L., Vandresen, F., da Silva Lisboa, F., and Sequinel, R. (2025). Oxidative stability of biodiesel: challenges and perspectives for the sustainability of a large-scale program in Brazil. *Biofuels* 16, 545–552. doi:10.1080/17597269.2024.2432154
- Singh, A., Prajapati, P., Vyas, S., Gaur, V. K., Sindhu, R., Binod, P., et al. (2022). A comprehensive review of feedstocks as sustainable substrates for next-generation biofuels. *Bioenergy Res.* 16, 105–122. doi:10.1007/s12155-022-10440-2
- Sterpu, A. E., Simeadrea, B. G., Chis, T. V., and Săpunaru, O. V. (2024). Corrosion effect of biodiesel-diesel blend on different metals/alloy as automotive components materials. *Fuels* 5, 17–32. doi:10.3390/fuels5010002
- Sui, M., Chen, Y., Li, F., Wang, W., and Shen, J. (2021). Study on the mechanism of auto-oxidation of jatropha biodiesel and the oxidative cleavage of C–C bond. *Fuel* 291. doi:10.1016/j.fuel.2020.120052
- Sundus, F., Fazal, M. A., and Masjuki, H. H. (2017). Tribology with biodiesel: a study on enhancing biodiesel stability and its fuel properties. *Renew. Sustain. Energy Rev.* 70, 399–412. doi:10.1016/j.rser.2016.11.217
- Takano, Y., and Houk, K. N. (2005). Benchmarking the Conductor-like polarizable continuum model (CPCM) for aqueous solvation free energies of neutral and ionic organic molecules. *J. Chem. Theory Comput.* 1, 70–77. doi:10.1021/ct049977a
- Thuy, P. T., and Son, N. T. (2022). Thermodynamic and kinetic studies on antioxidant capacity of amentoflavone: a DFT (density functional theory) computational approach. *Free Radic. Res.* 56, 526–535. doi:10.1080/10715762.2022.2146584
- Usmani, R. A., Mohammad, A. S., and Ansari, S. S. (2023). Comprehensive biofuel policy analysis framework: a novel approach evaluating the policy influences. *Renew. Sustain. Energy Rev.* 183, 113403. doi:10.1016/j.rser.2023.113403
- Varatharajan, K., and Pushparani, D. S. (2018). Screening of antioxidant additives for biodiesel fuels. *Renew. Sustain. Energy Rev.* 82, 2017–2028. doi:10.1016/j.rser.2017.07.020
- Weinhold, F., and Landis, C. R. (2001). Natural bond orbitals and extensions of localized bonding concepts. *Chem. Educ. Res. Pract.* 2, 91–104. doi:10.1039/b1rp90011k
- Weinhold, F., and Landis, C. R. (2012). *Discovering chemistry with natural bond orbitals*. USA: John Wiley & Sons, Inc.
- Weinhold, F., Landis, C. R., and Glendening, E. D. (2016). What is NBO analysis and how is it useful? *Int. Rev. Phys. Chem.* 35, 399–440. doi:10.1080/0144235x.2016.1192262
- Wenceslau, P. R. S., Aguiar, A. S. N., Duarte, V. S., de Almeida, L. R., Franco, C. H. J., de Aquino, G. L. B., et al. (2025). Comprehensive analysis of pyrazoline analogs: exploring their antioxidant potential as biofuel additives. *ACS Omega* 10, 40843–40856. doi:10.1021/acsomega.5c00398
- Xue, Y., Zhang, L., Li, Y., Yu, D., Zheng, Y., An, L., et al. (2013a). A DFT study on the structure and radical scavenging activity of newly synthesized hydroxychalcones. *J. Phys. Org. Chem.* 26, 240–248. doi:10.1002/poc.3074
- Xue, Y., Zheng, Y., Zhang, L., Wu, W., Yu, D., and Liu, Y. (2013b). Theoretical study on the antioxidant properties of 2'-hydroxychalcones: H-Atom vs. electron transfer mechanism. *J. Mol. Model* 19, 3851–3862. doi:10.1007/s00894-013-1921-x
- Yaakob, Z., Narayanan, B. N., Padikkaparambil, S., K, S. U., and P, M. A. (2014). A review on the oxidation stability of biodiesel. *Renew. Sustain. Energy Rev.* 35, 136–153. doi:10.1016/j.rser.2014.03.055
- Yamauchi, M., Kitamura, Y., Nagano, H., Kawatsu, J., and Gotoh, H. (2024). DPPH measurements and structure–activity relationship studies on the antioxidant capacity of phenols. *Antioxidants* 13, 309. doi:10.3390/antiox13030309
- Yang, Z., Hollebone, B. P., Wang, Z., Yang, C., and Landriault, M. (2013). Factors affecting oxidation stability of commercially available biodiesel products. *Fuel Process. Technol.* 106, 366–375. doi:10.1016/j.fuproc.2012.09.001
- Yusuf, N. N. A. N., Kamarudin, S. K., and Yaakub, Z. (2011). Overview on the current trends in biodiesel production. *Energy Convers. Manag.* 52, 2741–2751. doi:10.1016/j.enconman.2010.12.004
- Zhang, G., and Musgrave, C. B. (2007). Comparison of DFT methods for molecular orbital eigenvalue calculations. *J. Phys. Chem. A* 111, 1554–1561. doi:10.1021/jp061633o
- Zhao, Y., and Truhlar, D. G. (2008). The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* 120, 215–241. doi:10.1007/s00214-007-0310-x