

The Role of Chalcone Derivatives as Potential Antioxidant Additive for Biofuel Applications: A Critical Review

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Abstract

The world's energy demands have been rising to unprecedented levels due to the depletion of fossil resources and concerns about global warming. A potential remedy to these challenges is to investigate alternative bioenergy sources while also increasing the efficiency of existing biofuels. Biofuels are renewable energy sources since they are biodegradable fuels made from biomass. Notwithstanding the positive aspects of biofuels, their use can lead to issues such as poor oxidation, inherent stability, and limited energy supply, significantly impacting biofuel consumption, emissions, and energy efficiency. Small molecules, such as chalcone analogs, are good options for additive applications because they are versatile, easy to synthesize, inexpensive, integral materials across various applications, and provide energy for critical chemical reactions. Compounds with potential characteristics such as antioxidant activity and considerable energy availability are eligible to be used as fuel additives. The abundance of antioxidant properties of chalcone molecules is the most significant consideration in their use as additives for biofuels. Antioxidant additives offer numerous benefits, including the reduction of NO_x emissions. The current review delves into the synthesis methods and performance of the chalcone molecule as an additive, including comprehensive information on antioxidant mechanisms, oxidation stability studies, antioxidant additives, and energy availability.

Keywords: Chalcone, Biofuels, Antioxidant property, Calorific value, Additive Application.

Received 31 January 2025; First Review 03 March 2025; Accepted 19 March 2025.

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How to cite this article

Sankaran Nampoothiri V, Sunil Raj R, Saji Chandran, Lynnette Joseph, The Role of Chalcone Derivatives as Potential Antioxidant Additive for Biofuel Applications: A Critical Review, J. Cond. Matt. 2025; 03 (02): 27-38.

Available from:
<https://doi.org/10.61343/jcm.v3i02.139>



Introduction

The Energy Institute (EI) published the 72nd edition of the statistical assessment of the global energy study, which found that the world continues to rely on fossil fuel usage, with coal, oil, and natural gas accounting for 80% of the total. In comparison, renewable sources contribute only 8.2% [1]. A few studies have reported on the production statistics of these fossil fuels with oils, coal, natural gas, nuclear energy, hydroelectricity, and others. According to the BP Statistical Review of World Energy, published in June 2009, it is found that 88% of primary energy production comes from fossil fuels, with oil (35%), coal (29%), and natural gas (24%). Nuclear energy accounts for 5% of total primary energy consumption, followed by hydroelectricity at 6% [2].

Fossil fuels are detrimental to the environment and are a major threat to the terrestrial ecosystem. Fuel combustion emits significant amounts of pollutants, including carbon

dioxide and carbon monoxide, causing considerable environmental issues and compromising living conditions.

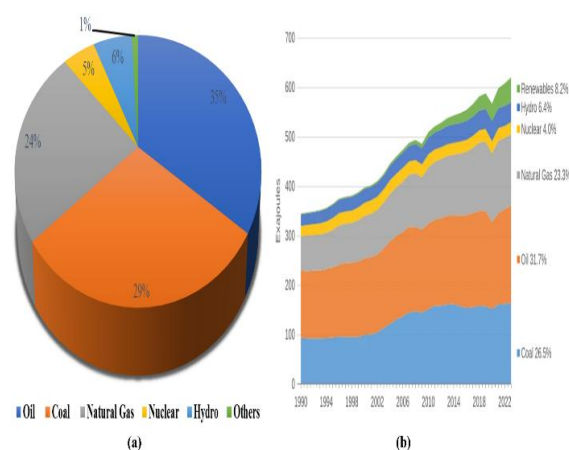


Figure 1: (a) Production of world primary energy [2] from different sources in 2009 (b) Global primary energy consumption, 1990-2023 (reported by the 72nd edition of Statistical Review of World Energy).

Another important consideration is the finite supply of these non-renewable energy sources. This raises a crucial question of how long we will be able to acquire petroleum goods [3], as their availability is a significant global concern. The nearly entire fatigue state of fossil fuels has boosted the scientific community's interest in alternative bioenergy sources with enhanced fuel efficiency [4]. Study findings and evaluations periodically warn of the declining availability of conventional energy sources, like petroleum, natural gas, coal, and massive volumes of environmentally innocuous biomass, which are recommended as viable options to meet energy needs [5].

Biofuels are considered renewable energy sources because they are biodegradable fuels made from biomass [6]. Though the method of producing biofuel from enduring biomass is complicated, extensive research in the area is going on constantly, as they are an excellent alternative to nonrenewable fuels [7]. Renewable fuel will reach 4.6 million barrels of equivalent oil per day in 2040, up from 1.3 million barrels of equivalent oil per day today. This will raise the percentage of biofuels in the global energy matrix [8,9]. The concern is that oxidation, intrinsic stability, and energy availability constraints affect the energetic performance of currently employed biofuels [10]. Furthermore, according to a 2010 study by Lelieveld *et al.*, [11] air pollution causes approximately 3 million premature deaths globally. Hence, the need for other options in the case of bioenergy sources is critical, considering the increasing percentage of air pollution caused by motor vehicles, gases from industry, and other factors.

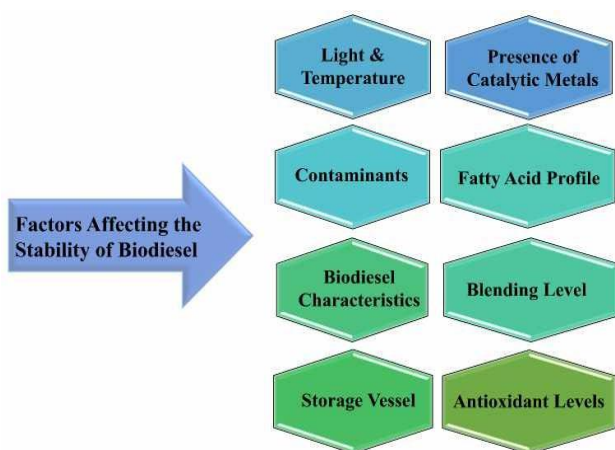


Figure 2: Primary Reasons that affect the efficiency of Biodiesel.

An early-generation biofuel that can be produced from plant or animal sources is biodiesel [12,13]. Biodiesel has caught experts' interest compared to other potential alternative resources due to its numerous benefits [14]. The essential truth is that biodiesel has a lower impact on global warming than fossil-based alternatives due to climate-friendly biogenic carbon dioxide in animal fat and vegetable oil. Biodiesel has more excellent biodegradability, intrinsic

lubricity, combustion efficiency, lower aromatic and sulfur content, more remarkable flash point, and higher cetane number than petroleum diesel, which are significant technical and environmental benefits. According to a 2014 study by Oliveira and Coelho [15], ethanol and biodiesel are the primary renewable fuels utilized in land transportation worldwide. The global energy matrix [3] gets increased contribution from biodiesel and ethanol.

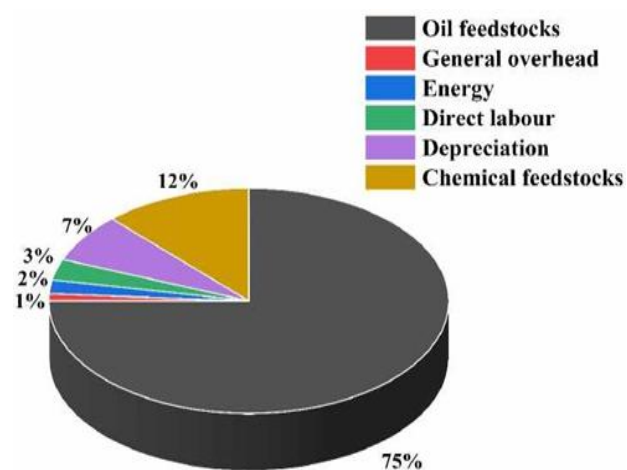


Figure 3: Average cost estimate for producing biodiesel [16–18].

However, a matter of concern lies in the fact that biodiesel's calorific value is 5% lower than that of mineral diesel, and biodiesel engines lose 1-8% of their power [19]. Furthermore, various factors influence biodiesel manufacturing costs, such as chemicals and catalysts, feedstock, etc. The feedstock is the most significant factor, accounting for over 75 percent of the entire production cost of biodiesel. Feedstock selection differs among countries based on agricultural techniques and geography. Type selection and cost-effective feedstock are crucial to reducing the total expense of biodiesel. Aside from the high cost of producing biodiesel fuel, other significant drawbacks exist.

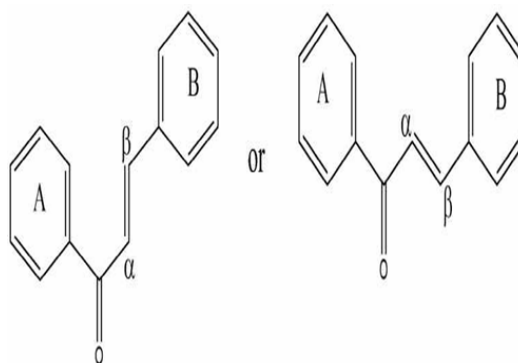


Figure 4: The general structure of chalcones [19].

Having one or more hydroxyl groups is regarded as a significant element in the antioxidant action of chalcones

[20]. It is critical to boost the efficiency of existing fuels while also seeking potential alternative bioenergy sources to meet the world's needs. Here, we emphasize the key elements of the chalcone molecule as a biofuel additive, revealing its potential as the next generation of efficient additives. Three key areas are addressed in the following:

- 1) Profile of the Chalcone molecule
- 2) Effects of Antioxidant additives on biofuels
- 3) Impact of chalcone as an antioxidant additive on biofuel

Basics of Chalcone Derivative

Chalcone's significant role in the synthesis of therapeutic substances, owing to its massive number of replaceable hydrogen atoms that allow for many derivatives, especially into the two aromatic rings, is a key attraction in the twenty-first century. Therapeutic substances such as deoxybenzoin and hydantoin, crucial in pharmacology, are derived from chalcone molecules. Chalcone molecules, also known as alpha beta-unsaturated ketones, contain reactive keto ethylene and are referred to as benzylidene acetophenones or benzalacetophenones. Kostanecki and Tambor deduced that these compounds are members of the chalcone family [21].

The nomenclature of chalcone compounds changes over time. The prime numbers are ascribed to the phenyl ring that wraps around the carbonyl system in the chemical abstract pattern, whereas the British Chemical Abstract pattern and the Journal of the Chemical Society assigned prime numbers to the phenyl ring that is situated away from the carbonyl system [22].

Antioxidant Additives

Several additives are used in biofuels, particularly biodiesel. These include Metal-based additives, Oxygenated additives, Antioxidant additives, Cold flow improver additives, Lubricity improver additives, and Cetane number improver additives [23].

Understanding the roles of these additives is crucial as they can prevent fuel instability and its subsequent outcomes, such as deterioration of appearance, darkening, and accumulation of gums and sediments, and they also affect combustion attributes [24–27]. The outcomes of Ashok et al. [28] Palash et al. [29] showed that adding an antioxidant additive to biodiesel effectively reduced NO_x emissions. Mechanically, these additives primarily block the formation of free radicals (hydroperoxyl (OOH), peroxy (ROO), and alkoxy (RO) in readily degradable fuels such as biodiesel, reducing the chances of these free radicals reacting with N_2 or N_2O during fuel storage or combustion and thus reducing

NO_x emissions. Various factors, including the composition of the biodiesel, the unsaturation concentration, and the biodiesel blends, determine the additive's concentration. A combination of antioxidant additives can improve fuel stability to the standard specification.

Antioxidant Property of Chalcone Derivatives

The literature shows that numerous chalcone derivatives exhibit significant antioxidant activity. Many chalcones have been synthesized and found to have antioxidant properties due to their versatility in receiving a range of functional groups in their rings. Studies also found that hybrid derivatives had antioxidant characteristics. Yasukazu Ohkatsu et al. investigated chalcone derivatives' antioxidant and photo-antioxidant characteristics and the impacts of hydroxyl groups connected to the molecule's aromatic rings [30]. They synthesized the chalcone molecule using a 1:3 ratio of malonyl-coenzyme A and p-coumaroyl-coenzyme A molecules. The radical-scavenging activity of all chalcone molecules was assessed regarding the number (n) of peroxy radicals caught by a phenolic moiety and the radical-trapping rate constant. The study found that the examined chalcones have good antioxidation properties acquired from the precursor, p-coumaric acid.

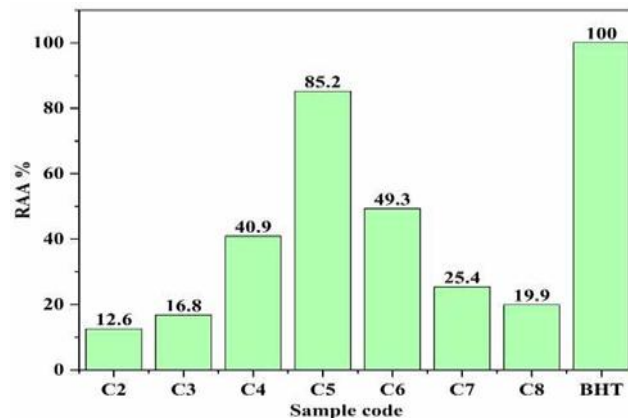


Figure 5: Relative antioxidant activity percentage (RAA %) employing β -carotene-linoleic acid assay.

Munevver Sokmen et al. [31] conducted antioxidant investigations on seven synthetic curcuminoids and one chalcone molecule. DPPH & β -carotene/linoleic acid tests evaluated the compound's antioxidant properties. In the β -carotene-linoleic acid assay, 2,4,6-trihydroxyphenolic chalcone (C5) inhibited the synthesis of conjugated dienes more effectively than all other curcuminoids (C1-7). The chalcone (C5) inhibited the production of conjugated dienes by 85.2%, indicating that the molecule has an increased antioxidant ability. While the synthetic curcuminoids C6 and C4 had the most significant values (49.3% and 40.9%, respectively), the rest had relatively low values, with all of them having a value of less than 30%. So, according to this antioxidant activity assay, the chalcone molecule has higher

antioxidant activity than all other curcuminoid samples, with a comparable value of 85.2% to that of the synthetic antioxidant butylated hydroxytoluene (BHT), which inhibits the formation of conjugated dienes by 100 %. The chalcone (C5) has a higher antioxidant value due to its polyphenolic nature, which improves its water solubility and reaction with linoleic acid in the emulsion. This also protects it from oxidation and yields conjugated dienes [31].

The primary explanation for the potent antioxidant nature of chalcone derivatives is associated with the presence of functional groups of various kinds. Arene rings and conjugated double bond systems increase the possibility of electron transfer processes; low redox potentials and various intramolecular interactions contribute to chalcone's high antioxidant activity. The type and position of the substituents connected to a chalcone molecule determine its level of antioxidant capability. Shaifali Singh et al. [32] investigated the antioxidant properties of a series of chalcone derivatives by changing the substituents and measuring all samples using the DPPH method.

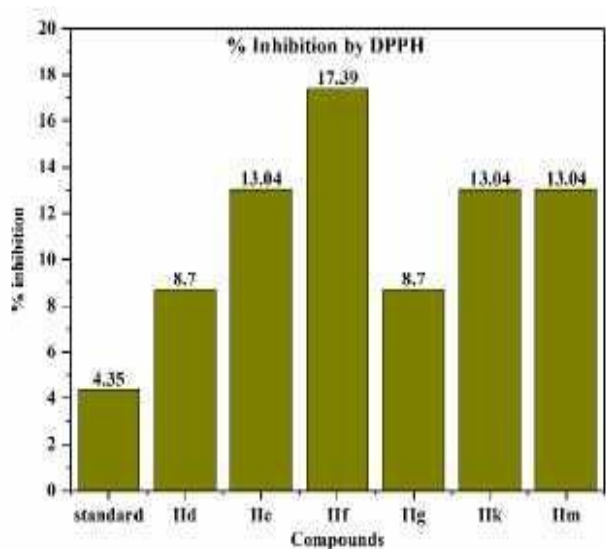


Figure 6: Results of Antioxidant Activity Study with the DPPH Method.

According to the findings, all chalcone derivatives displayed good antioxidant properties. Sample IIf displayed the most robust activity, whereas the IId, IIf, IIg, IIk, and IIIm samples showed average antioxidant potential.

Free radical damage generates oxidative stress in the system, which the antioxidants help to regulate. In addition to the phenyl and hydroxyl groups, the presence of vinylene and reactive keto groups in chalcones and their derivatives shows good antioxidative potential. The research findings are given in table 1 [32]. The high degree of variability in the structure of chalcone and aurone molecules can be utilized to evolve novel antioxidants with improved efficacy and lower toxicity. Tamanna Narsinghani et al. [33]

executed a comparison analysis to determine the antioxidant potential of chalcone and aurone derivatives.

Table 1: Name and Sample code of the chalcone molecules [32].

Chalcone	Sample Code
1-(2-hydroxyphenyl)-3-(2-methoxyphenyl) prop-2-en-1-one	IId
1-(2-hydroxyphenyl)-3-(4-methoxyphenyl) prop-2-en-1-one	IIf
1-(2-hydroxyphenyl)-3-(2,4-dimethoxyphenyl) prop-2-en-1-one	IIf
3-(2-chlorophenyl)-1-(2-hydroxyphenyl) prop-2-en-1-one	IIg
3-(2,6-dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one	IIk
1-(2-hydroxyphenyl)-3-(4-nitrophenyl) prop-2-en-1-one	IIIm

All the chalcone compounds were synthesized following the Claisen- Schmidt condensation approach, and aurone was synthesized through oxidative cyclization. Four distinct in vitro investigations were used to assess the antioxidant activity of each sample. Among the chalcone molecules, SB7 (2',5'-dihydroxy-4'- dimethylamino chalcone) showed the most favorable antioxidative properties, especially in the DPPH free radical scavenging assay, iron chelating assay, and reducing power assay.

Similarly, the aurone sample SB8 (5-hydroxy-4'- dimethylamino aurone) demonstrated good antioxidant properties, particularly in iron chelating, hydrogen peroxide scavenging, and reduced power assays. The chalcone sample SB2 (2',4'-dihydroxy-4-dimethylamino chalcone) and aurone sample SB8 (5-hydroxy-4'- dimethylamino aurone) demonstrated strong antioxidant properties in iron chelation and reducing power tests.

Table 2: Sample code and compound name of all the samples.

Sample Code	Compound
SB1	2',5' - Dihydroxy-3,4-dimethoxy chalcone
SB2	2',4' - Dihydroxy-4-dimethylamino chalcone
SB3	6 - Hydroxy-4'- dimethylamino aurone
SB4	6- Hydroxy-4'- chloro aurone
SB5	2',4'- Dihydroxy- 4- chloro chalcone
SB6	5- Hydroxy-3',4'-dimethoxy aurone
SB7	2',5'- Dihydroxy-4-dimethylamino chalcone
SB8	5- Hydroxy-4'-dimethylamino aurone
SB9	6- Hydroxy-3',4'-dimethoxy aurone
SB10	2',4'- Dihydroxy-3,4-dimethoxy chalcone

The study ultimately found that a specific functional group in the molecule can increase or decrease the antioxidant mechanism. Adding a dimethylamino group to samples SB7

(chalcone) and SB8 (aurone) significantly increases antioxidant activity. Still, including a chloro group reduces activity for chalcone and aurone, specifically SB4 and SB5. The group's attachment to the A-ring (ideally at position 5/5') gave higher antioxidant properties in the samples [33]. Lucas M. Berneira et al. studied the effect of functional groups in chalcone structures as substituents on antioxidant activity [34]. They synthesized a Chalcone analog using Claisen-Schmidt condensation with moderate to good yields.

Table 3: Antioxidant activity of all the samples using different assays [33].

Sample No.	DPPH scavenging ability IC ₅₀ µg/ml ± SD	H ₂ O ₂ scavenging ability IC ₅₀ µg/ml ± SD	Iron chelating activity assay IC ₅₀ µg/ml ± SD	Reducing power IC ₅₀ µg/ml ± SD
SB1	132.22 ± 0.7	89.59 ± 1.8	159.22 ± 1.02	111.79 ± 0.69
SB2	65.8 ± 0.7	135.88 ± 0.53	140.16 ± 1.08	53.6 ± 1.1
SB3	109.92 ± 1.02	193.91 ± 0.36	179.33 ± 0.31	70.1 ± 2.2
SB4	266.12 ± 0.49	178.13 ± 0.36	179.18 ± 0.74	188.31 ± 0.31
SB5	264.95 ± 1.6	129.02 ± 0.85	159.97 ± 0.29	155.87 ± 0.68
SB6	222.19 ± 0.7	206.57 ± 0.19	185.05 ± 1.2	151.43 ± 0.25
SB7	24.32 ± 0.87	153.85 ± 2.1	90.81 ± 0.86	47.79 ± 1.3
SB8	243 ± 0.13	174.07 ± 1.9	149.98 ± 0.51	64.16 ± 1.2
SB9	173.29 ± 0.94	248.16 ± 0.76	213.83 ± 0.68	168.23 ± 0.83
SB10	35.2 ± 1.5	70.1 ± 0.92	166.73 ± 2.5	134.45 ± 0.34
Ascorbic acid	98.77 ± 0.53	445.92 ± 1.4	126.12 ± 0.5	53.24 ± 0.72

The presence of hydroxyl groups mainly contributes to an increase in the effect of compounds because these active hydroxyl substituents can delay the formation of hydroperoxides through the transfer of protons that stabilize free radicals in the oil. In contrast, A decreased antioxidant property was observed in chalcone molecules with methoxy groups, which restricts electron capture from the radical. Differential scanning calorimetry noted that hydroxychalcone molecules had antioxidant activity in biodiesel at concentrations of 1250 ppm or higher [34]. Visakh Prabhakar et al. [35] showed that the antioxidant capabilities of chalcones are affected by substituents. The Claisen-Schmidt reaction was used to generate nine monosubstituted chalcone derivatives. The percentage inhibition of the ten target chalcones, including the unsubstituted parent chalcone, was estimated, revealing that ortho derivatives are the most appropriate for antioxidant activity.

Impact of Chalcone as an Antioxidant Additive for Biofuel Applications

Compared to mineral diesel, the most significant difficulty for biodiesel is its higher oxidation tendency, and the risks of microorganism's proliferation are very substantial in diesel-biodiesel blends [36]. The oxidation of biodiesel triggers a series of reactions in the system. It starts with developing hydroperoxides, which may generate impermeable gums and sediments, causing obstructions on fuel injector nozzles and fuel filters. The mere presence of germs exacerbates the condition by catalyzing the reaction. As a result of oxidation and bacterial products, the process results in increased fuel viscosity. Chalcone's prominent antioxidant properties can be used to mix with biodiesel to improve its oxidative stability. Since it is rarely recorded in the literature, chalcones are versatile compounds because of the aromatic rings in the structure, which allow for substituting numerous functional groups.

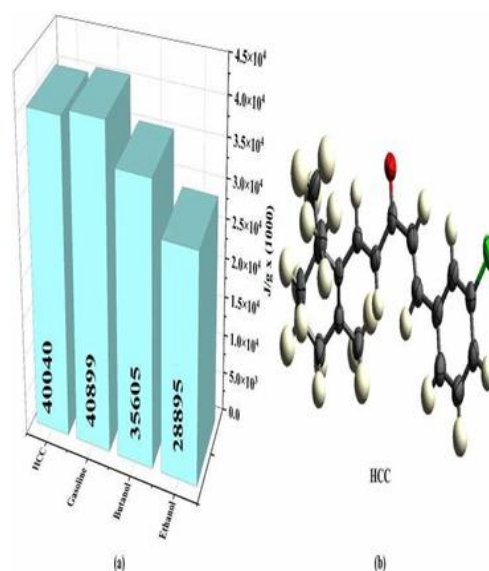


Figure 7: A comparison of the calorific powers of ethanol, butanol, petrol, and HCC. The fuels used were n-butanol, hydrated ethanol, and ordinary type C gasoline [37].

Eduardo Coelho da M. Faria et al. [37] reported the performance of a trimethoxy-chalcone (C₁₈H₁₈O₄) utilized as an antioxidant addition for diesel and biodiesel blends. They studied the efficacy of C₁₈H₁₈O₄ chalcone as a potential antioxidant additive, for which it was blended with S10 B20 diesel. They conducted a 140-day storage stability test on S10 B20 diesel blended with C₁₈H₁₈O₄ chalcone. The oxidation stability before and after the test was assessed using the accelerated oxidation method (modified Rancimat Method). According to the findings, the accelerated oxidation stability time is enhanced by 50% for chalcone concentrations of 0.05 mg/mL, which is lower than 0.03 mg/mL chalcone concentration. Hence, the chalcone concentration directly influences the fuel's

oxidation stability. The HOMO and LUMO energy also reveal the GAP value (241.7 kJ/mol), which shows the high reactional stability for $C_{18}H_{18}O_4$. Because of its remarkable antioxidant activity in diesel S10 B20, the study concluded that chalcone $C_{18}H_{18}O_4$ is a promising option for additive development. They also explored the possible additive application of a chalcone 4-(4-chlorophenyl)-1-[4-(2-oxo-2-phenylethoxy) phenyl]- butan-2-one (HCC), $C_{23}H_{17}ClO_3$. An adequate energy availability and antioxidant effect define a potential additive's performance. Eduardo Coelho da M. Faria et al. [37] compared the calorific energy availability of gasoline, butanol, ethanol, and HCC. The chalcone compound (HCC) showed a significant calorific power value of 40040 j/g, higher than butanol (35605 j/g) and ethanol (28895 j/h) [8], indicating a value comparable to gasoline fuel. There is just a 2.14% distinction between chalcone HCC and gasoline fuel. They found that for biofuels, chalcone HCC is a practical addition and also has a variety of uses, including chemical susceptibility, energy enhancement, and potential biological applications [8]. The calorific power measurement indicates a compound's ability to liberate energy during oxidation, and for fuels, higher calorific power values are related to more remarkable performance, perhaps allowing it to be used as a fuel additive.

Another chalcone compound, namely 1-[3-(2-oxo-2-phenyl-ethoxy)-phenyl]-3-phenyl-propenone (chalcone I) [38], had a calorific value of 12783 kcal/kg when compared to HCC chalcone (chalcone II) [8] molecules and some fuels. The experimental values for fuels such as gasoline, butanol, and ethanol are comparable to those found in the literature [39–41]. The calorific power of chalcone II was found to be 85% larger than that of ethanol (6906 kcal/kg) and around 30% more than that of gasoline (9775 kcal/kg). The value of E_{GAP} was calculated theoretically, showing similar kinetic stability for chalcones I and II, as reported by Eduardo Coelho da M. Faria et al [38]. The E_{GAP} values of chalcone I and chalcone II (599.51 kJ/mol and 602.34 kJ/mol, respectively) were compared to BHT (E_{GAP} = 546.1 kJ/mol) [42], toluene derivatives (E_{GAP} = 477.8 kJ/mol) [43], and thiazolidinone (E_{GAP} = 481.8 kJ/mol) [44]. From the comparison, these chalcones revealed comparable kinetic stability to other additives utilized. The comparison study suggests additional research on the use of chalcones as additives.

Igor D. Borges et al. [45] Performed structural alterations on chalcone molecules abbreviated as BCH and NCH, where the changes are associated with the third aromatic ring of both chalcones. Observations on oxidation stability results via the modified Rancimat method reveal that NCH chalcone performs better than BCH chalcone and S10 B15 without additives samples. Furthermore, the NCH functioned efficiently at lesser concentrations (109.0 ppm

(BCH) & 100.7 ppm (NCH)). Both compounds delayed biofuel degradation and retained biofuel characteristics for 90 days without further processing.

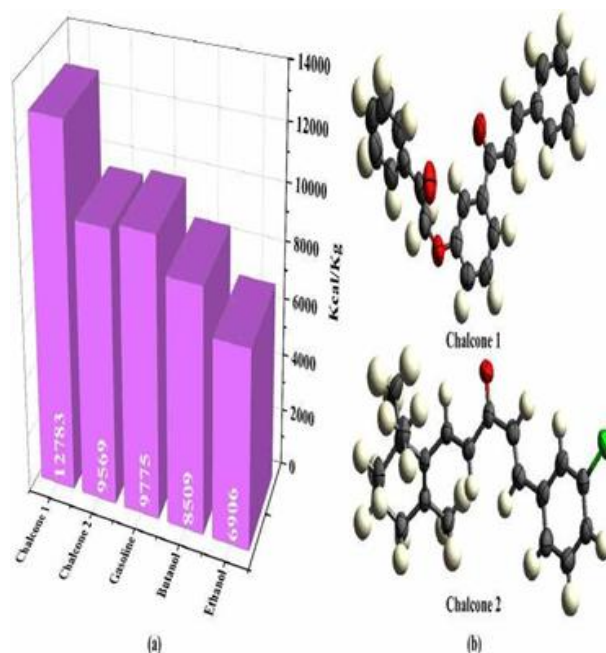


Figure 8: A comparison of the calorific power of chalcones I and II, familiar type C petrol, n-butanol, and hydrated ethanol [38].

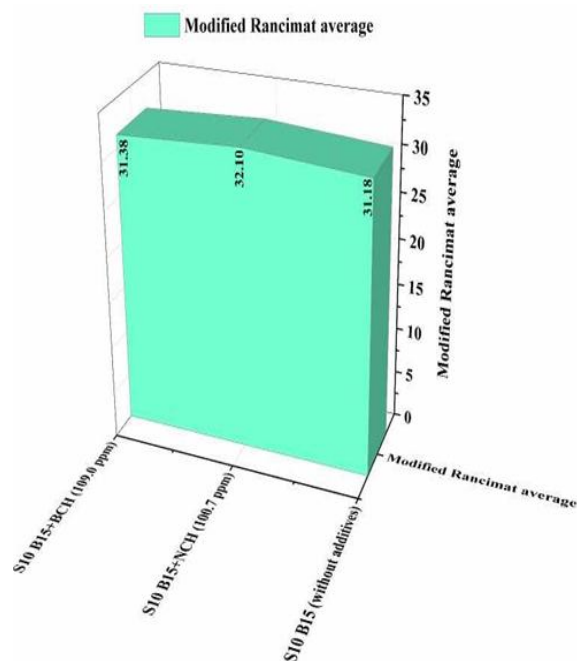


Figure 9: The modified Rancimat approach yields the measurement of oxidation stability of all the samples [45].

The amount of energy freed during the oxidation of a fuel commune to the heat of combustion. The total amount of energy delivered during fuel oxidation is often referred to as the heat of combustion[46]. Its higher value indicates more extraordinary fuel performance. It is best to use additives with considerable energy availability.

Arylsulfonamide chalcones had outstanding heat of combustion values comparable to conventional fuels with high energy availability. The oxidative stability results from the Rancimat method showed a stability of roughly 27 hours in a diesel-biodiesel mix (B20) following 140 days of storage. It is superior to certain commercial additives, as reported by Duarte et al. in 2023 [47].

BCH and NCH chalcones have higher kinetic stability and are comparable to other additives. These findings unambiguously showed the practicality of the compounds stated previously (BCH, NCH) as antioxidant additives to diesel-biodiesel mixtures to maintain fuel properties' A. Moreira et al. [48] conducted an oxidative stability comparison study that included a synthetic chalcone TMC20 and a commercial additive after 140 days of stability, utilizing the Rancimat test.

Table 4: Sample identification [48].

Sample	Description (fuel + additive)	Additive concentration	Bottle filling percent
S1	S10 B11 diesel	Free	25 (± 0.27) % v/v
S2	S10 B11 diesel	Free	100 (± 0.07) % v/v
S3	S10 B11 diesel + TMC20	0.03 (± 0.002) mg/mL	25 (± 0.27) % v/v
S4	S10 B11 diesel + TMC20	0.03 (± 0.002) mg/mL	50 (± 0.14) % v/v
S5	S10 B11 diesel + TMC20	0.03 (± 0.002) mg/mL	100 (± 0.07) % v/v
S6	S10 B11 diesel + commercial additive	0.5 (± 0.08) % v/v	25 (± 0.27) % v/v
S7	S10 B11 diesel + commercial additive	0.5 (± 0.08) % v/v	100 (± 0.07) % v/v
S8	S10 B11 diesel + commercial additive	0.8 (± 0.08) % v/v	25 (± 0.27) % v/v
S9	S10 B11 diesel + commercial additive	0.8 (± 0.08) % v/v	100 (± 0.07) % v/v
S10	S10 B11 diesel + commercial additive	1.0 (± 0.08) % v/v	25 (± 0.27) % v/v
S11	S10 B11 diesel + commercial additive	1.0 (± 0.08) % v/v	100 (± 0.07) % v/v

It was completed following the regulations provided in standard EN 1575168. The theoretical calculations reveal that the TMC20 has more kinetic stability than other additive compounds. Compared to commercial additives, the performance of TMC20 is inferior since chalcone molecules are used naturally at a relatively low concentration of 0.03 mg/mL without any other type of processing. The chalcone in the fuel+TMC2 mixture preserved the fuel's qualities over 140 days of preservation while postponing the fuel's degradation [48].

From figure 10, samples S3, S4, and S5 correspond to a fuel+ mixture of chalcone TMC20 with the same additive

concentration and varying bottle filling percent. The additive does not stop fuel oxidation; rather, it simply postpones it.

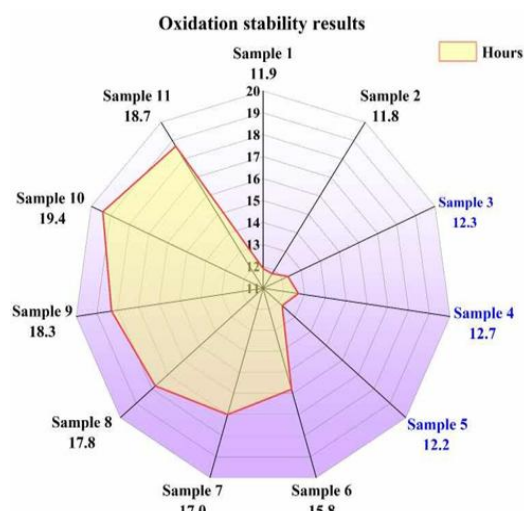


Figure 10: Results of the Rancimat test show oxidation stability following 140 days of stability. According to procedure EN 15751:2014, repeatability $r = 0.22027 + 0.0434$ (here x is the average of the two measurements that were made) was used to compute the measurement uncertainty represented by error bars [48,49].

The study recommends implementing additives to maintain the fuel's physical and chemical properties while enhancing its stability during storage and using chalcones as a comparable biofuel additive. Loide O Sallum et al. [45,50] reported that cyclohexanone-based chalcones are good alternatives in the field of fuel additives with the chalcones $C_{24}H_{26}O$, $C_{20}H_{14}OCl_4$, and $C_{20}H_{16}OCl_2$ with the sample codes BH I, BH II and, BH III respectively, showing good calorific value.

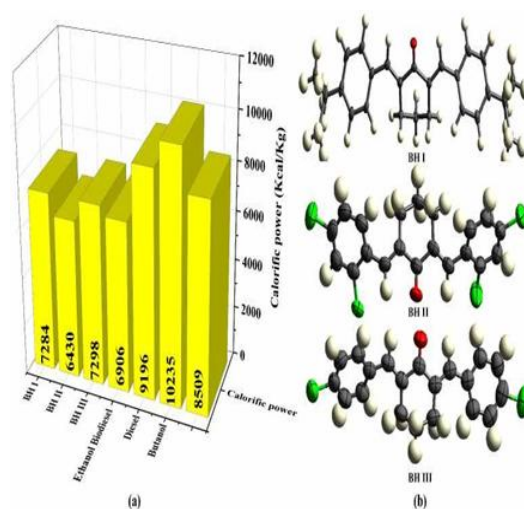


Figure 11: Values of calorific power for chalcone BH I, II, and III and n-butanol, diesel, biodiesel, and hydrated ethanol. The calorific value of biodiesel depends on its composition. (Performed with an average value) [50].

All three chalcones had a calorific value higher than ethanol and slightly lower than biodiesel. The study strongly recommends the additive application of chalcones with fuels.

Discussion

The current research world primarily focuses on methods to strengthen the oxidative stability of biodiesel, such as adding antioxidants to its composition [51]. The capacity of these compounds to prevent or reduce fuel oxidation makes them more widely accepted [52]. The antioxidant activity of chalcone has been noted, where its α , β -unsaturation aryl structure provides an advantage and might have substituents called hydroxyls, which are usually associated with its antioxidant activities. Despite its significant antioxidant properties, adding chalcones as a biodiesel blend has yet to be frequently reported in the literature. The literature characterized the chalcone compounds based on prospective features such as solid energy availability and antioxidant activity. The capacity of chalcones to interact in many different kinds of chemical and biological interactions suggests the usage of biofuels [8]. The compounds' antioxidant activity was assessed using different radical scavenging methods and antioxidant additive analysis, such as rancimat and modified raincoat tests, to analyze oxidation stability. Looking through the literature, it is recognizable that substitutions play a significant role in antioxidant activity in chalcones. Among the replacements, substituting specific functional groups contributes to higher antioxidant activity, with the substitution site being crucial. Diverse functional groups play diverse roles and contribute to antioxidant activity. The presence of double bonds also contributes significantly to the antioxidant properties of chalcones. The synthesis technique, environmental factors, fuel management and storage, and biodiesel components all have an impact on the antioxidant effect.

The energy GAP (E_{GAP}), the theoretically determined absolute difference between HOMO and LUMO applying the Density Functional Method (DFT) of chalcone compounds, exhibits significant antioxidant potential [53]. The antioxidant potential is directly correlated with the energy GAP value [37]. The comparison study of E_{GAP} performance of different chalcone molecules and commercial additives is shown in table 5. The E_{GAP} or GAP parameter determines molecular reactivity and chemical stability. GAP values in the high ranges signify substantial excitation energy, low chemical reactivity, and outstanding chemical stability. According to the results of the comparative study, the chalcone molecules have excellent or comparable E_{GAP} values to commercial additives such as BHT, thiazolidinone, toluene derivatives, which are widely employed to preclude or cut down oxidation processes in biodiesel. Thermodynamics of a compound depends on

various factors. Accessibility of energy is directly proportional to molecular shape. As a result, characteristics such as chemical bonding structure, carbon content, and oxygenated compound content have a significant impact on the thermodynamic property of the compound [8].

Table 5: Comparison study of E_{GAP} performance of different chalcone molecules and commercial additives.

Chalcone & Sample Code	E_{GAP} Value (Kj/mol)	Ref	Commercial Additive	E_{GAP} Value (Kj/mol)	Ref
C ₂₃ H ₁₈ O ₃ (I)	599.51	[38]	BHT	546.1	[42]
C ₂₃ H ₁₇ BrO ₃ (BCH)	598.11	[45]	Toluene Derivative	477.8	[43]
C ₂₃ H ₁₇ NO ₅ (NCH)	586.38		Thiazolidinone	481.8	[44]
C ₁₈ H ₁₈ O ₄ (TMC20)	565.38	[37]	Ether Molecule	273.8 - 404.6	[54]
C ₂₃ H ₁₇ ClO ₃ (HCC)	602.34	[8]	P-Phenylene Diamine	56.8 - 114.5	[55,56]

The calorific ability of the chalcone molecule as an additive has been assessed in terms of energy. The calorific value (CV) provides fuel characteristics such as intrinsic energy and is the quantity of heat transmitted into the burning chamber during the period of combustion [57].

Table 6: Calorific value of chalcones.

Chalcone Compound & Sample Code	Calorific Value (Kcal/kg)	Ref
C ₂₃ H ₁₈ O ₃ (I)	12783	[38]
C ₂₃ H ₁₇ ClO ₃ (HCC)	9569	[58]
C ₂₄ H ₂₆ O (BH I)	7284	[50]
C ₂₀ H ₁₄ OCl ₄ (BH II)	6430.2	
C ₂₀ H ₁₆ OCl ₂ (BH III)	7298.7	

Table 7: Calorific values of fuels.

Fuels	Calorific Value (Kcal/kg)	Ref
Gasoline	9775	[50]
Butanol	8509	
Ethanol	6906	
BD-B100 (methyl palm)	8525.7	[59]
BD-B100 (Cynara cardunculus)	8885.0	[50,60]
BD-B25 (Pomace Olive)	10399.3	

This pertains primarily to the compound's ability to release energy during the oxidation process, whereas high calorific power values are correlated with more outstanding performance in fuels [38]. Tables 6 and 7 show the calorific value of some chalcones and fuels, respectively. According

to the comparison, chalcone molecules have a performance similar to or comparable to that of fuels. Some chalcone molecules show higher calorific values than some of the fuels reported here. The high calorific value of fuels is related to improved performance. As a result, the excellent energy availability and susceptibility of chalcone molecules strongly suggest that chalcones can be associated with fuels. Eventually, it will increase the stability and efficiency of the compound.

Conclusion and Future Prospective

In recent studies, scientists and researchers have expressed a strong interest in chalcones and their analogs. These molecules are versatile and suited for an extensive list of applications. The capability to make substitutions on aromatic rings results in notable features that can be employed in various fields. Chalcone analogs as fuel additives are a far superior answer to the current energy availability problem, despite their synthesis being less expensive and faster; also, the absence of chlorinated reagents makes them more environmentally friendly. This review examined the potential application of chalcone analogs as biofuel additives based on their antioxidation properties, factors influencing antioxidation properties, oxidation stability, and additive potential capabilities using experimental and theoretical methodologies. Based on the results;

- Most of the research showed that among all the different properties of chalcone, the antioxidative property is the most essential, favoring additive application. Several variables contribute to the improved antioxidative properties of chalcone analogs, including their structure, substitutions, substitution positions, and effects such as resonances.
- Chalcone analogs are highly effective materials for preserving biofuel characteristics. They have good oxidation stability properties comparable to some commercial additives.
- The more significant part of the studies has addressed the significance of additive compounds. These chemicals can improve the qualities of fuels, including diesel, biodiesel, petrol, and aviation oil, by combining them, resulting in increased fuel economy and efficiency.
- Particularly in biodiesel because NO_x emissions are high due to higher oxygen content, higher in-cylinder gas temperature, fluctuations in fuel injection parameters, lower compressibility, and higher cetane numbers.
- Most of the studies recommended future studies on the additive application side of the chalcone molecule due to its beneficial blending capabilities compared to various fuels

in terms of experimental studies (calorific) and theoretical studies (kinetic stability).

- Aside from its outstanding antioxidant properties and oxidation stability, chalcone's susceptibility and superior energy availability make it a suitable fuel additive.

Small molecules like chalcones are less expensive and easier to synthesize and have already received widespread acceptance in many technological fields. Yet, this review discovered that the potential of chalcones as a cheaper, more efficient alternative additive still needs to be fully explored. The results from the literature validate that chalcone molecules can be used as a possible candidate for additive application in the perspectives of antioxidant effectiveness, oxidative stability, and energy availability in the future. The lack of literature on this topic necessitates thoroughly examining this potential additive application of chalcone analogs, which has yet to receive the attention it deserves. This review suggests additional research on this topic. As a result, scientists can generate more energy-efficient biofuels while developing new, highly efficient fuel additives that will significantly solve the energy availability constraint of currently used biofuels.

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