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A Sustainable Approach to Enhancing Biodiesel Oxidation Stability Using a Natural Antioxidant

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Abstract: Biodiesel, an alternative to fossil diesel fuel, has low oxidation stability due to the presence of unsaturated fatty acid methyl esters (FAMEs) in its composition. Oxidation of biodiesel reduces fuel quality, shortens storage life, and causes pollution and clogging in the engine fuel system. Adding synthetic antioxidants to biodiesel improves its oxidation stability. However, because synthetic antioxidants are petroleum-based products with toxic and environmental impacts, sustainable natural antioxidant additives are needed to improve the oxidation stability of biodiesel. Natural plant and other-source antioxidants offer an environmentally friendly, sustainable approach to enhancing the oxidative stability of biodiesel. This study investigated the effect of sage essential oil (SEO), rich in phenols, on the oxidation stability of biodiesel. In this study, 2500 ppm of SEO was added to biodiesel fuel for analysis. To measure the effectiveness of sage oil, a natural resource, comparative tests were conducted with samples containing the same concentration of the synthetic commercial antioxidant butylated hydroxytoluene (BHT). During the process, the chemical structures of fuels with and without the antioxidant were analyzed using spectroscopic and thermal analysis methods. Furthermore, the changes in the basic thermophysical fuel properties resulting from the antioxidant addition were determined. The data obtained revealed the potential of SEO to improve the oxidative resistance of biodiesel.
Keywords: Antioxidant, Biodiesel, Fuel properties, Oxidation, Sage essential oil

INTRODUCTION

The continuously growing global energy demand, combined with limited fossil fuel reserves and concerns about the environment and energy security, has intensified the search for sustainable, renewable energy alternatives [1]. In this context, renewable fuels have emerged as a critical option for future energy systems, with the potential to reduce environmental degradation and support energy security [2]. Among these fuels, biodiesel has attracted considerable attention as a promising alternative to petroleum-derived diesel fuel, particularly for compression-ignition engines, owing to its biodegradability, renewability, and compatibility with existing diesel engine infrastructure [3].
Biodiesel is produced by transesterifying vegetable oils, animal fats, or waste biooils, yielding fatty acid methyl esters (FAMEs). Biodiesel serves as a sustainable alternative to petroleum diesel, offering enhanced engine longevity through superior lubricity and a high cetane number for smoother combustion. Environmentally, it significantly reduces lifecycle carbon emissions and exhaust pollutants, such as particulate matter and sulfur oxides, while its biodegradability minimizes the impact of spills. Furthermore, its high flash point ensures safer handling and storage, providing a domestically sourced

energy solution that integrates easily into existing diesel infrastructure. Despite its advantages, biodiesel suffers from a major drawback: poor oxidative stability. This limitation is primarily due to the presence of unsaturated FAMEs, which are chemically susceptible to oxidation during storage and use [4]. Oxidative degradation is one of the most critical challenges for biodiesel, as it directly affects fuel quality and engine performance.

The oxidation of biodiesel is a free-radical-mediated chain reaction that proceeds through initiation, propagation, and termination stages [5]. During initiation, hydrogen atoms at allylic positions adjacent to carbon–carbon double bonds are abstracted, forming lipid radicals. In the propagation stage, these radicals rapidly react with oxygen to form peroxyl radicals, which further generate hydroperoxides. These primary oxidation products are unstable and decompose into a variety of secondary oxidation products, including aldehydes, ketones, carboxylic acids, low-molecular-weight hydrocarbons, and polymeric species [6]. The accumulation of these degradation products leads to a series of severe operational and physicochemical problems.

One of the most significant consequences of biodiesel oxidation is the deterioration of fuel properties. Oxidative degradation increases acid value, viscosity, and density while reducing calorific value and overall fuel quality. In addition, polymerization of oxidation intermediates forms high-molecular-weight, insoluble compounds, commonly referred to as gums and sediments. These deposits can accumulate in fuel storage tanks, fuel injectors, and combustion chambers, leading to injector fouling, poor atomization, and incomplete combustion. Furthermore, oxidation products such as organic acids accelerate corrosion of fuel system components, particularly metallic parts, thereby reducing engine durability and reliability. Another critical issue with biodiesel oxidation is fuel filter plugging. Insoluble degradation products and polymerized compounds can clog fuel filters, leading to restricted fuel flow, pressure drops, and potential engine stalling. This is particularly problematic during long-term storage or under high-temperature operating conditions, where oxidation reactions are significantly accelerated. Collectively, these effects not only compromise engine performance but also increase maintenance costs and reduce biodiesel's overall sustainability as a fuel [7]. Given these challenges, oxidation stability is considered one of the most important quality parameters for biodiesel, as it directly affects its storage stability, transportability, and engine applicability. Therefore, improving biodiesel's oxidative resistance has become a key research priority in fuel science. Various approaches have been explored to enhance oxidation stability, including selecting low-unsaturation feedstocks, hydrogenation, blending with petroleum diesel, and incorporating antioxidant additives [8].

Among these methods, antioxidant use is the most practical and widely adopted strategy. Antioxidants inhibit oxidation and are well established for controlling biodiesel oxidation. They do so by interrupting the free radical chain reaction (breaking the chain), either by donating hydrogen atoms, scavenging reactive radical species, or decomposing hydroperoxides, thereby preventing their formation and propagation [9]. Synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tert-butylhydroquinone (TBHQ) are highly effective in improving biodiesel stability. However, their petroleum-based origin, potential toxicity, and environmental concerns limit their sustainability and large-scale applicability [10].

In recent years, attention has increasingly turned to natural plant-based antioxidants as sustainable alternatives. These bio-based compounds, including phenolics, flavonoids, and essential oils, exhibit strong radical-scavenging activity and are non-toxic, biodegradable, renewable, and environmentally benign [4]. Their use aligns with the principles of green chemistry and sustainable fuel development.

In this study, sage essential oil (SEO), a natural antioxidant rich in phenolic compounds [11], is investigated for its ability to enhance the oxidation stability of biodiesel. The performance of SEO is evaluated against the commercial synthetic antioxidant butylated hydroxytoluene (BHT) at the same concentration. The effects of antioxidant addition on the chemical structure and thermophysical properties of biodiesel are analyzed using spectroscopic and thermal characterization techniques. The

study aims to demonstrate the potential of natural sage essential oils as sustainable and effective alternatives to synthetic antioxidants for improving biodiesel oxidation stability.

MATERIALS and METHOD

In this study, biodiesel produced from waste frying oil via transesterification and conforming to EN 14214 specifications was used. The biodiesel was blended with petroleum diesel at a 50% volumetric ratio to prepare a diesel-biodiesel fuel blend (B50). SEO, used as a natural antioxidant in the study, was obtained from a certified producer. This oil, obtained by distillation for use in health and cosmetic applications, is highly pure. The antioxidant activity of sage stems from its high phenol content [12]. To compare the performance of SEO and BHT (Brand: Tekkim, purity: ≥99.5%), a commercial antioxidant was also supplied. Both the natural antioxidant, SEO, and the synthetic antioxidant, BHT, were separately added to the B50 fuel at a concentration of 2500 ppm each. The prepared samples were coded as B50+SEO and B50+BHT, respectively. A precision balance with a resolution of 0.001 g was used to weigh the fuels and the antioxidants. To ensure homogeneity of the mixture, the samples were first stirred for 15 minutes on a magnetic stirrer, then for 5 minutes in an ultrasonic bath. After preparation, the samples were transferred to appropriate glass storage containers. The oxidation stability of the base fuel (B50) and the samples containing SEO and BHT were investigated using Fourier Transform Infrared Spectroscopy (FTIR) (Brand: Bruker Tensor 27 and Spectral Range: 400–4000 cm^{-1} with the resolution of 1 cm^{-1}) and Differential Scanning Calorimetry (DSC) (Brand/Model: TA/Q 2000). The DSC method details are presented in Table 1. FTIR analysis provided detailed insight into the effect of antioxidants on oxidation resistance and the changes in the chemical structures (bond structures and functional groups) of the samples. DSC analysis was used to determine the crystallization temperature, a critical indicator of the cold-flow behavior of the fuels. Furthermore, basic fuel properties, including density, flash point, water content, distillation temperatures, and sulfur content, were measured for the fuel samples. The equipment and test methods used for fuel analysis are given in Table 2.

Table 1. The DSC analysis details

Characteristics	Value
Sample mass [mg]	5
N_2 flow rate [mL/min]	50
Ramp rate [℃/min]	10
Temperature range [℃]	-90 to +25

Table 2. The equipment and test method used for fuel analysis

Analysis	Equipment	Test Method	Accuracy
Density [g/cm^3]	Mettler Toledo D4	EN ISO 12185	∓ 0.0001 g/cm^3
Water content [%, m/m]	Koehler Karl Fischer Titrator	EN ISO 12937	∓ 1 ppm
Cold Filter Plugging Point [℃]	ISL OptiFPP CFPP analyzer	EN ISO 116	∓ 1℃
Flash point [℃]	Pensky-Martens flash point testers	EN ISO 2719	∓ 0.5 ℃
Distillation [℃]	Herzog automatic distillation analyzer	EN ISO 3924	∓ 0.1 ℃
Sulfur content [mg/kg]	Analytik Jena Multi EA 3100	EN ISO 20846	∓ 1 ppm

DISCUSSION

FTIR spectra are plotted as wavenumber (cm^{-1}) versus transmittance (%T) in Figure 1, showing the spectral regions where specific molecular vibrations occur in the samples. Wavenumber and transmittance were determined for the following vibrations: $_v$(O-H) (3000-3700 cm^{-1}), $_v$(C-H) (2700-3000 cm^{-1}), $_v$(C=O) (1500-1800 cm^{-1}), and $_v$(C-O) (600-1400 cm^{-1}). Oxidation stability is primarily governed by the $_v$(O-H) and $_v$(C-H) vibrations of the samples. In the FTIR spectrum, $_v$(C-O) and $_v$(C=O) vibrations indicate the presence of ether or ester functional groups in a sample [13]. These vibrations

are characteristic of biodiesel products. The carbonyl group $_{v}$(C=O) from the ester was observed at 1744 cm^{-1}; the $_{v}$C-O stretching vibration from the ester was observed at 1245, 1120, and 1019 cm^{-1}. The spectra also exhibited other functional group peaks, such as the stretching vibration of biodiesel, as shown in Figure 1. Antioxidant effects were observed in the fuel samples at 2500 ppm concentration. The valence-strain vibration of an unbonded hydroxyl group $_{v}$(O–H) is generally reported as 3700–3500 cm^{-1}.

Furthermore, FTIR analysis showed that the vibrational movements (2700-3000 cm^{-1}) in the $_{v}$C-H bonds were weakened. This is because the fuel became more saturated (stable), making it more difficult for the fuel to degrade and form sediment upon contact with air [7]. The effects of SEO and synthetic BHT antioxidants are clearly evident in the area shown in Figure 1. Thanks to the structural changes that occur when these antioxidant substances are added to the fuel, harmful substances formed by fuel degradation are reduced, thereby weakening the signals at 600–800 cm^{-1} and 1300–1500 cm^{-1}. In most analyses, the characteristic signal above 1720 cm^{-1}, corresponding to the main structure of biodiesel, was observed. The absence of another signal immediately next to this signal indicates that there are no undesirable acids (carboxylic acids) in the fuel [10]. This confirms that the fuel's oxidation resistance has increased. In general, it can be concluded that SEO may exhibit antioxidant effects similar to those of BHT.

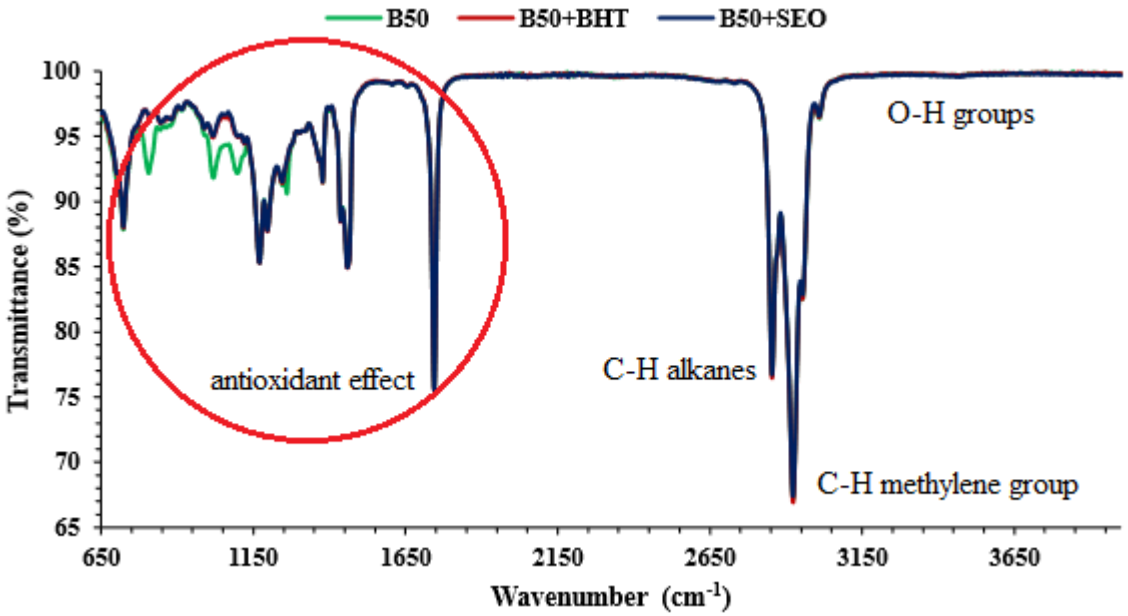

Figure 1. FTIR spectra for fuel samples

Figure 2 shows the DSC measurement results of fuel samples under an N_2 atmosphere. The graph clearly shows how the crystallization behavior of the B50 blend changes with the addition of antioxidants. While BHT, a synthetic antioxidant, provides the expected protective effect, SEO, a natural alternative, likewise stabilizes the fuel's thermal profile. Examining the dominant peak in the graph, it is evident that the B50 fuel begins to crystallize at higher temperatures than the other samples. This indicates that the fatty acid methyl esters in the biodiesel phase transition to the solid phase at higher temperatures. In addition, the lower-intensity peak observed for B50 indicates that the heat released during crystallization (the enthalpy) is lower. The fact that the fuel begins to crystallize at higher temperatures means it oxidizes faster or that its oxidation resistance is weakened [14]. The crystallisation onset temperatures (T_{onset}) for B50, B50+SEO, and B50+BHT fuel samples were determined to be -5.34 °C, -5.61 °C, and -5.47 °C, respectively. The lower T_{onset} values for B50+SEO and B50+BHT samples compared to B50 indicate that these antioxidants not only increase oxidative stability but also improve the low-temperature flow properties of the fuel. The results show that the

SEO additive outperforms BHT. It is thought that SEO causes a slight shift or broadening of the crystallization peak by altering the intermolecular interactions within B50.

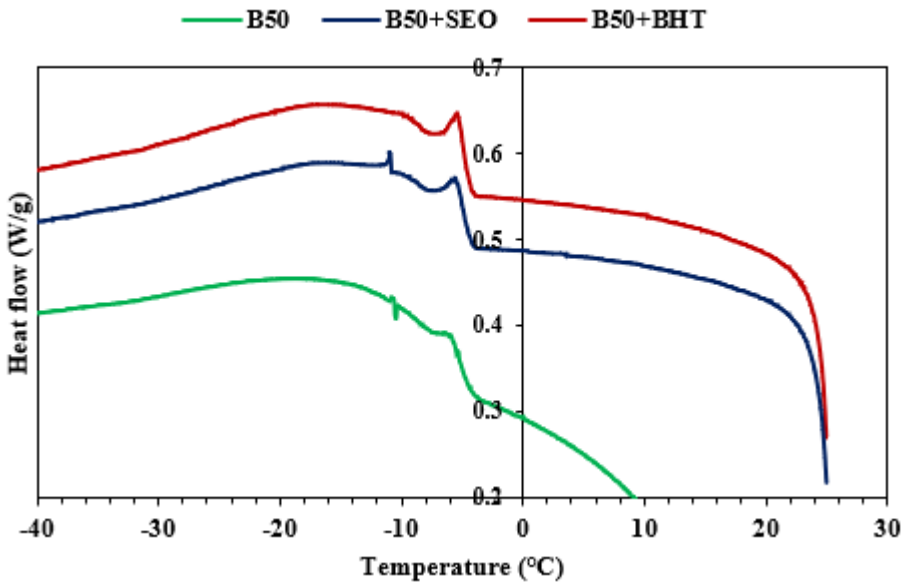

Figure 2. DSC thermograms of fuel samples under N_2 atmosphere

Some key thermophysical properties measured for reference fuel, natural antioxidant, and synthetic antioxidant-added fuel samples are given in Table 3. As shown in the table, adding the identified antioxidant did not significantly alter fuel properties. This result is expected because the amount of antioxidant additive added to the fuel was at the ppm level (2.5 g/kg), which is quite low. Since the densities of SEO and BHT are higher than those of both diesel and biodiesel, the densities of B50+AEY and B50+BHT mixtures also increased slightly compared to B50. The addition of antioxidants also increased the flash point by 1 °C. According to the DSC analysis results, although SEO and BHT lowered the fuel's crystallization temperature, this effect was not clearly reflected in the cold-filter clogging-point measurements. It is thought to be due to the low resolution of the measuring instrument (ISL OptiFPP CFPP analyzer). In addition, antioxidants primarily protect the chemical structure of the bonds rather than affect the fuel's freezing point.

Table 3. Fuel analysis results

Property		**B50**	**B50+SEO**	**B50+BHT**
Density [kg/m^3]		861.3	861.5	861.5
Water content [%, m/m]		0.042	0.042	0.042
Cold Filter Plugging Point [°C]		-11	-11	-11
Flash point [°C]		77.5	78.5	78.5
Sulfur content [mg/kg]		3.8	4.1	3.8
Distillation [°C]	Initial boiling point	189.9	188.9	191.2
	T10	257.5	269.3	270.9
	T50	311.9	311.9	313.2
	T90	343.1	338.4	341.9
	Final boiling point	358.5	356.5	359.7
	250 °C, %(v/v)	7.9	5.5	7.1
	350 °C, %(v/v)	96.6	97.5	96.5
	%95 (v/v), °C	348.7	345.5	349.2

Due to the high purity of the antioxidants and their addition to the fuel at very low proportions, no change in the fuel's water content was observed. However, adding SEO resulted in a slight increase in the fuel's sulfur content. This indicates that sulfur-containing compounds may be present in the SEO composition.

No significant difference in specific distillation temperatures was observed either. As illustrated in Figure 3, the incorporation of antioxidants produced a distinct change to the fuel's initial distillation profile. Across the 5%-40% distilled volume fractions, both the B50+BHT and B50+SEO blends exhibited noticeably higher distillation temperatures than the neat B50 base fuel, indicating suppressed initial volatility. Beyond the 40% threshold, the three curves converged and remained nearly identical until the end of the process. This initial distillation lag is primarily due to the higher chemical purity and higher boiling points of the antioxidant compounds compared with the lighter hydrocarbon fractions in the baseline fuel.

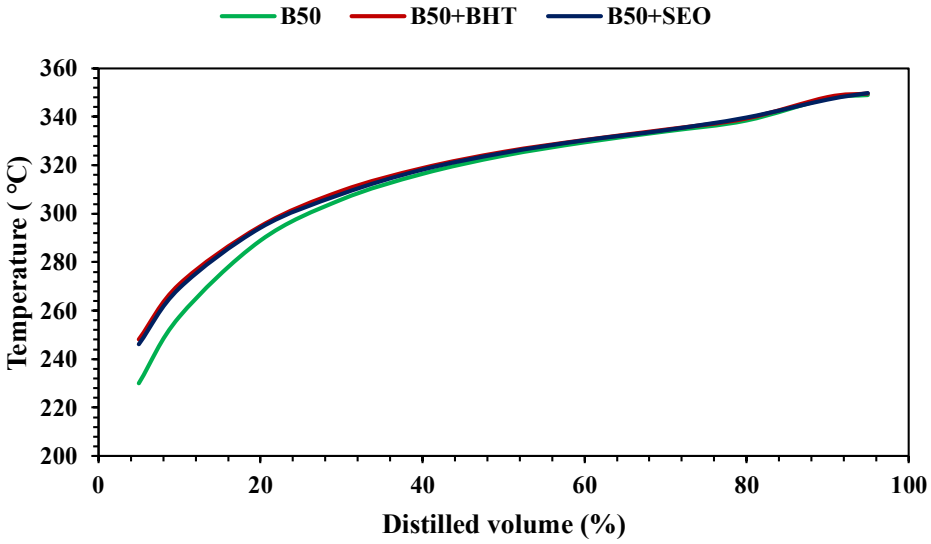

Figure 3. Distillation curves for fuel samples

Overall, based on the fuel analysis results, it is concluded that both SEO and BHT, at the concentrations used, had only a limited effect on the base fuel's thermophysical properties. While B50 is an experimental or localized mandate (such as in Indonesia) [15], it is governed by adjustments to standard diesel and biodiesel guidelines. Therefore, there is no specific international fuel specification for B50. However, minor changes in measured fuel properties support its suitability for practical use and compatibility with existing diesel engines and fuel infrastructure [16].

CONCLUSIONS

This study investigated the antioxidant effect of sage essential oil (SEO) in biodiesel. To assess its effectiveness, the commercial synthetic antioxidant BHT was also used. Both antioxidants were added to a diesel-biodiesel blend (B50) at a concentration of 2500 mg/kg. The FTIR spectrum showed the effect of these additives on the fuel's molecular chemical bonds, confirming their antioxidant performance. DSC results showed improved oxidative resistance and cold-flow performance with the addition of antioxidants. The crystallisation temperatures for B50, B50+SEO, and B50+BHT fuel samples were determined to be -5.34 °C, -5.61 °C, and -5.47 °C, respectively. The results show that the SEO additive outperforms BHT.

Adding antioxidants to B50 did not significantly change fuel properties, supporting their compatibility with engine technology and fuel infrastructure. However, the increase in sulfur content with SEO would limit the amount of natural antioxidants that can be added to the fuel. The results of this study support the use of SEO as a natural antioxidant to enhance the oxidation stability of biodiesel in a sustainable manner.

Future studies can directly measure the oxidation stability of fuel samples using an accelerated oxidation test to determine the induction period with the Rancimat method or the PetroOxy test. Furthermore, engine operation can be studied with the added SEO B50.

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