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Review Article

The Potential of Underutilized Plant Resources and Agricultural Wastes for Enhancing Biodiesel Stability: The Role of Phenolic-Rich Natural Antioxidants

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Growing concerns about energy security and environmental sustainability have fueled demand for sustainable and renewable energy sources in recent years. Biodiesel, a renewable alternative to conventional fuels, has gained significant attention as a potential source of energy. However, the stability of biodiesel during storage and its susceptibility to oxidation remain major challenges. To address these issues, researchers have turned their focus to the utilization of natural antioxidants. Studies on sources of natural antioxidants, particularly those made from waste, such as food, have been extensively conducted. However, there are still some restrictions, such as inconsistency in quality, the development of microbes, and difficulties with regulations, all of which have an impact on sustainability and the phenolic contents. Phenolic compounds are known for their excellent antioxidant properties and ability to inhibit the oxidation process. The review provides an overview of various underutilized plant resources and agricultural wastes that are rich in phenolic contents and demonstrate higher antioxidant activities, such as *Vitex doniana*, *Uapaca kirkiana*, *Parinari curatellifolia*, *Tamarindus indica* L, fruit peels, and crop residues. It discusses the extraction methods employed to obtain phenolic antioxidants from these sources and highlights their antioxidant activities. Additionally, the review examines the effects of phenolic antioxidants on key parameters, including induction period, peroxide value, acid value, and viscosity. The review concluded by highlighting the potential of underutilized plant resources and agricultural wastes as sustainable sources of phenolic-rich natural antioxidants for enhancing biodiesel stability. According to the literatures, phenolic antioxidants present in underutilized plant resources and agricultural wastes can chelate metal ions, scavenge free radicals, and break oxidation chain reactions, thereby preventing the degradation of biodiesel. Moreover, the limitation of the use of natural antioxidants in the stabilization of biodiesel like instability at high temperatures has been highlighted.

1. Introduction

Energy consumption is increasing globally on a daily basis as a result of population growth and technological advancements [1, 2]. The International Energy Agency (IEA) estimates that the demand for energy increased globally by 40% in 2019 compared to growth rates of 2018 [3]. Fossil fuels, which are currently being exhausted and have a severe influence on the environment as well as being the primary sources of

greenhouse gases, are the main source of energy that is globally consumed [4, 5]. As a result of the aforementioned drawbacks of fossil fuels, researchers have been driven to find a substitute for conventional fossil fuel [6, 7]. Biodiesel, as one of the liquid fuels produced from renewable sources, is a promising alternative to petro diesel; it can be locally produced, and it has a number of benefits, including renewability [8], reduced greenhouse gas (GHG) emissions [4], and minimized the “carbon footprint” [9]. Biodiesel is greatly preferred as a substitute

for petroleum diesel because it has comparable physical and chemical properties [10]. Utilizing biodiesel as an alternative fuel increases energy security, improves the environment and air quality, and has safety benefits [11].

Despite its benefits, the biggest challenge with biodiesel is the presence of unsaturated fatty acids, which severely undergo oxidative degradation and render it unfit for use in engines [12]. The result of biodiesel oxidation is increased viscosity, acidity, and solid deposits in the fuel. Various studies, for example, by Suraj et al. [13], reported the increase in peroxide and acid values of the biodiesel after one year of storage. The surface tension, kinematic viscosity, and density of the biodiesel all increased during the same period. Moreover, Acharya et al. [14] observed the same trend of increasing kinematic viscosity and acid number with changes in flashpoint and density for *Jatropha* and *Mahua* biodiesel in comparison with mineral diesel. Tables 1 and 2 show the changes in physical and chemical parameters as reported by Suraj et al. and Acharya et al., respectively. From a chemistry perspective, the increase in viscosity begins when the oxidation of methyl ester starts with the formation of peroxides [15]. The production of more polar, oxygen-containing molecules and oxidized polymeric compounds during storage enhances the viscosity of the methyl esters, which can cause the development of gums and sediments that clog filters [16]. Free fatty acids, double-bond isomerization, and the formation of higher molecular weight molecules are all results of the oxidation process [17]. Hydroperoxide produced by oxidative degradation can undergo complicated secondary reactions, such as breaking into more reactive aldehydes, which subsequently oxidize into acids to increase acid value [18]. These changes cause the quality of biodiesel to decline, which makes marketing more difficult and thus demonstrates the need for additional research on the oxidative stability of biodiesel during storage for long periods, thus adding antioxidants [19].

Some synthetic antioxidants, such as butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), butylated hydroxytoluene (BHT), and propyl gallate (PG), have been used as additives to overcome the oxidative instability of biodiesel, but they frequently have drawbacks, such as the fact that they are derived from fossil sources, which raises the cost of production of biodiesel and is carcinogenic [20]. Finding a natural alternative antioxidant that is inexpensive, renewable, and nontoxic in nature is necessary to get around the drawbacks of synthetic antioxidants [21]. Natural antioxidants have proven to be effective in controlling the lipid oxidation of biodiesel [22]. These compounds work by giving a hydrogen atom to free radicals or reactive oxygen species, which stops the biodiesel from oxidizing even at very low concentrations [23]. Despite their excellent role, the sustainability of feedstocks is a critical issue in the production of natural antioxidants [24]. To ensure the sustainability of natural antioxidant production, feedstocks should be free from socioeconomic conflicts. Numerous studies including review paper have looked into sustainable sources of natural antioxidants, particularly those derived from food waste (Table 3). However, there are still limitations such as inconsistent quality, growth of microorgan-

TABLE 1: Measured properties of fresh, aged Karanja biodiesel and mineral diesel [13].

| Physical chemical parameter | Fresh Karanja biodiesel | Aged Karanja biodiesel | Mineral diesel |
|-------------------------------|-------------------------|------------------------|----------------|
| Viscosity (cSt) | 5.10 | 5.75 | 2.90 |
| Density (kg/m ³) | 889.9 | 893.3 | 825.5 |
| Surface tension (mN/m) | 27.8 | 28.9 | 26.01 |
| Acid value (mg KOH/g oil) | 0.35 | 1.45 | — |
| Peroxide value (meq/kg) | 12.30 | 152.5 | — |
| Rancimat induction period (h) | 4.14 | 0.33 | — |

isms, regulatory challenges, presence of heavy metals, plastic fragments, and waste tableware which affect even the level of phenolic contents and its sustainability [25]. Thus, there is a need to examine new (alternative) sustainable sources of natural antioxidants. According to the literature that has been examined, currently there is no review study on the potential of natural antioxidants from underutilized plants and agricultural waste for improving biodiesel stability, therefore justifying this review paper.

As a result, the focus of this review paper is on the investigation of the potential of natural antioxidants produced from underutilized plant resources and agricultural waste to be utilized in improving biodiesel stability. Underutilized plants and agricultural wastes pose less of a threat to food production, have higher phenolic contents with consistent quality, and are produced in large quantities, making them readily accessible sources for the production of natural antioxidants [26]. This is supported by the recently published work (Table 4) on the use of natural antioxidants extracted from noncompetitive resources such as agricultural wastes and neglected species. The flow chart of the article selections in this work has been depicted in Scheme 1. The review starts with background information on biodiesel and its stability issues, reaction mechanisms, and structural composition. Antioxidants and their categories, extraction techniques, and working mechanisms have been covered. Practical implications, technoeconomics, and future perspectives have also been pointed out.

2. Methodology

A thorough and comprehensive search of the literature was carried out to identify studies associated with the oxidative stability of biodiesel. A keyword in combination with the Boolean operators “OR” and “AND” was used to retrieve all relevant information. The keywords used was “Antioxidant” AND “Phenolic compound” AND “Underutilized Plant” AND “Biodiesel” OR “bio-oil” OR “biofuels” OR “Biodiesels” were set for Scopus, Google Scholar, PubMed, HINARI, African Journals Online (reached via Research4Life using Nelson Mandela African Institutions of Science and Technology (NM-AIST) library account) databases, University repositories,

TABLE 2: Physical-chemical properties of Mahua biodiesel and Jatropha biodiesel in comparison with mineral diesel [14].

| Parameter | Mahua biodiesel | Jatropha biodiesel | Mineral diesel |
|---|-----------------|--------------------|----------------|
| Density at 15°C (kg/m ³) | 882 | 870 | 824 |
| Kinematic viscosity (mm ² /sec) at 40 °C | 4.2 | 4.1 | 2.30 |
| Flash point (°C) | 170 | 180 | 53 |
| Acid value (mg KOH/gm) | 0.45 | 0.38 | 0.25 |
| Calorific value (MJ/kg) | 38.5 | 39.9 | 42 |
| Oxidation stability (h) | 8.2 | 3.75 | 23.70 |

TABLE 3: Antioxidants from various food waste materials.

| Source of food waste | Type of antioxidant/chemical | Extraction technique | Ref. |
|------------------------------|--|--|------|
| Grape skin | Flavonoid | High-pressure/high-temperature | [27] |
| Peanut roots | Resveratrol | Deep eutectic solvent | [28] |
| Dry tomato peel | Lycopene and β -carotene | Supercritical CO ₂ solvent extraction | [29] |
| Spent coffee | Carotenoid | Soxhlet extraction | [30] |
| Potato peel | <i>p</i> -coumaric acid, salicylic acid, and vanillic acid | Solvent extraction | [31] |
| Apple industry waste biomass | Fumaric acid | Fermentation | [32] |
| Ginger | Gingerol and shogaol | Solvent extraction | [33] |

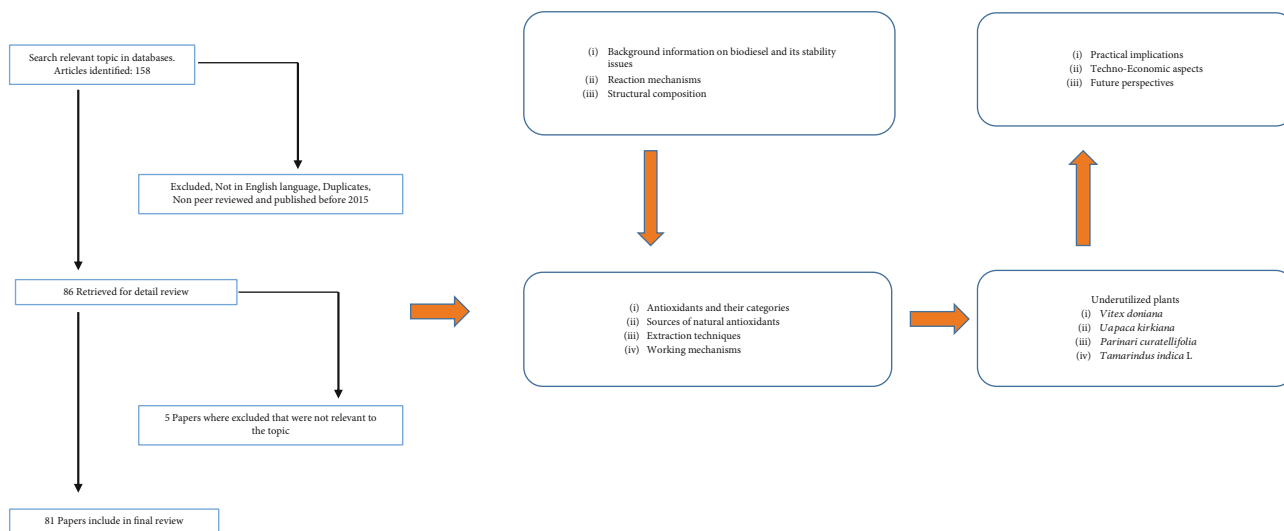
TABLE 4: Literatures on related works.

| Source of biodiesel | Source of antioxidants | Experiment conducted | Finding | Ref. |
|---------------------|---------------------------------|---|---|------|
| Fish biodiesel | Orange peel | Kinematic viscosity, acid value, and oxidation stability | Natural antioxidants signifying a protective influence and preventing the initiation step of oxidation | [34] |
| Soybean | Bael leaf | Oxidation stability | The extract could scavenge over 73% of DPPH radicals The extract contained 74.66 mg GAE/g of phenolics and showed greater protection to soybean biodiesel than most of the natural antioxidants reported protection factor of 3.03 | [35] |
| Tallow | Jabuticaba peels | Oxidation stability Kinetics Thermodynamics | Increased the biodiesel induction period compared to the control to 14.31 h Decreased the rate constants at each evaluated temperature | [36] |
| Palm oil | Ripe mango peel extract | Oxidation stability | The oxidation process was nonspontaneous and endothermic in all assays IP of biodiesel blends with petro-diesel (B10) with antioxidants was greater than 24.00 h | [37] |
| Colza | Clove waste thyme essential oil | Engine performance test Emissions test | Antioxidants provided substantial improvements in smoke opacity and CO ₂ emission | [38] |
| Soybean | Pomegranate peel | Oxidation stability | Increment of the induction time of pure biodiesel by up to 1.83 The extract is a promising natural antioxidant for biodiesel | [39] |
| Waste cooking oil | <i>Camellia assamica</i> | Thermal stability Storage stability Oxidation stability | Addition of antioxidants has shown a significant improvement in thermal stability and reduced residual formation Induction period of the B20 improved up to 9.2 h. | [40] |

and conference books of abstracts were used to retrieve published papers, peer-reviewed articles, case reports, and conference presentations as presented in Figures 1–3. In addition, article references were cross-checked and saved as the source of studies included in this review.

Citations were managed using the Mendeley software. Mendeley is a referential system that has been used by a

number of national and international journals, including Scopus, DOAJ, Google Scholar, and Thomson Reuters [41]. The author, the year of publication, the article's title, as well as the volume, issue, and page numbers of the sources, were used to spot duplicate entries. The following criteria were used to screen articles on oxidation stability of biodiesel, oxidation mechanism, extraction of natural antioxidants, and



SCHEME 1: Flow chart of the review's article selection

selection of antioxidants, solvent selection, and diagnostic challenges in the storage of biodiesel:

(1) Published in English between 2015 and 2023, unless there was limited information; (2) antioxidant feedstock that is sustainable and economically feasible; and (3) some information relating to oxidative stability tests and biodiesel degradation mechanisms. Articles that had not been peer-reviewed were expressly excluded. After using the aforementioned screening procedures, validity was evaluated, and the complete text of each chosen article was retrieved for in-depth examination.

3. Basics of Biodiesel Oxidation Mechanism

The ability of biodiesel to resist degradation is referred to as “oxidation stability,” and it is crucial for determining how long a biodiesel will last and how long it should be stored [42]. The oxidation stability of biodiesel has a direct influence on its performance in engines and its storage time, which is why it is important to monitor its stability over a certain period of storage [43, 44]. The oxidation of hydrocarbons present in biodiesel occurs through three general stages: initiation, propagation, and termination [45]. As with all chain reactions, the mechanism can be described in terms of the formation of free radicals during the initiation reaction, their transformation into additional radicals during the propagation reaction, and their combining to produce stable products during the termination reaction [46]. Allylic hydroperoxides are the main products of double bond oxidation and undergo a variety of reactions, such as rearrangement to produce products with a similar molecular weight, fission to produce shorter-chain molecules (aldehydes and acids), and dimerization to produce compounds with a greater molecular weight, like dimer acids [47, 48]. As a result, the physical chemical properties of the fuel, such as kinetic viscosity, acid number, flash point, and flow characteristics, are affected by the molecules formed. Moreover, the corrosion impact in the engine is brought on by

molecules formed with higher acidic values, like organic acids [49].

Initiation stage: this is formed when hydrogen atoms from either the allylic or bisallylic carbon are lost when biodiesel comes into contact with an initiator during processing or storage [50], creating a free radical carbon that is extremely reactive, as is shown in



In the *propagation stages* here, the fatty acid free radical (R) quickly interacts with an oxygen molecule to produce peroxy radicals (ROO), as in equation (2). This peroxide radical is extremely unstable and can interact with the fatty acid substrate (RH) to produce both fatty acid hydroperoxide ($ROOH$) and free fatty acid radicals, which leads to a self-sustaining chain reaction as in [51]



During this stage, antioxidants can be visualized playing their role by scavenging the free radicals formed and stopping the propagation process. By doing that, antioxidants help maintain the stability of biodiesel.

In the *termination stages* here, two free radicals that are similar to one another fuse to produce nonradical species, as in [46]



or



These recombination reactions create monomers, which turn them into stable and nonradical products, as seen in Figure 4.

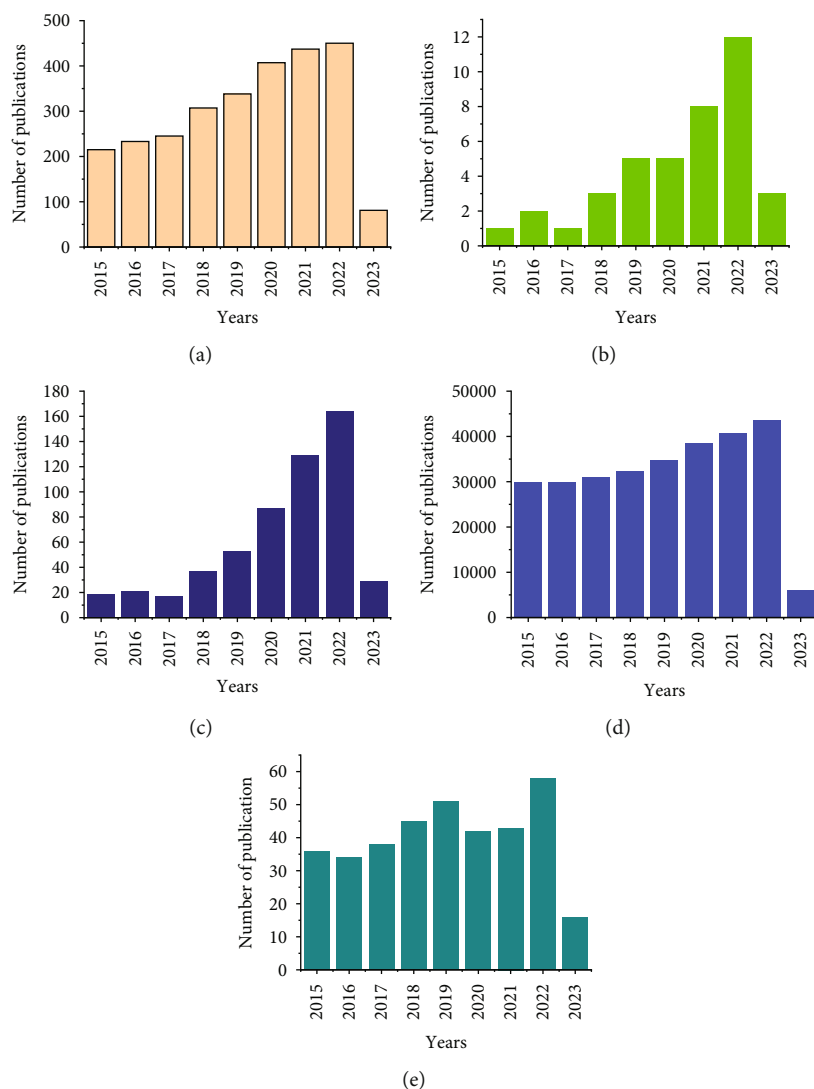


FIGURE 1: Number of publications with the word (a) “phenolic compounds,” (b) “Underutilized Plants,” (c) “Agricultural wastes,” (d) “Antioxidant” OR “Antioxidants” OR “Natural antioxidants,” and (e) “Biodiesel” OR “bio-oil” OR “biofuels” OR “Biodiesels” in the PubMed data base from 2015 to 2023.

3.1. Operation Principle of Biodiesel Oxidation Mechanisms.

Transesterifying an oil or fat with an alcohol, usually methanol, leads to the corresponding alkyl esters, which are defined as biodiesel, as represented in Figure 5. Biodiesel has the same fatty acid profile as the parent oil or fat. Due to the fact that many vegetable oils, including nonedible and edible ones such as jatropha, rapeseed, and soybean, possess a significant amount of fatty acids with double bonds, oxidative stability is of concern, especially when storing biodiesel over an extended period of time [52]. The presence of double bonds that are highly chemically reactive in the fatty acid chain is the source of the primary oxidation products, allylic hydroperoxides [53]. The formed hydroperoxide species, the original double bond, may have undergone cis- or transisomerization [54, 55]. Hydroperoxides are unstable and easily form a variety of secondary oxidation products, which include fission to give shorter-chain compounds (aldehydes and organic acids), rearrangement to

give products of similar molecular weight, and dimerization to give products of higher molecular weight that affect the quality of biodiesel, such as higher acid value and viscosity [56].

3.1.1. Methylene Group (-CH₂-) as a Site of Attack during Autooxidation. The methylene group (-CH₂-) carbons between the olefinic carbons are the primary targets of attack in biodiesel’s oxidative degradation [57]. During this reaction, free radicals and reactive oxygen species detach a methylene hydrogen atom from polyunsaturated fatty acids to form a carbon-centered lipid radical [58]. A conjugated diene is produced by the spontaneous rearrangement of 1,4-pentadiene. This conjugated diene interacts with molecular oxygen to produce a lipid peroxy radical, as seen in Figure 6. The radical reaction is propagated by the removal of a proton from nearby polyunsaturated fatty acids, which results in the formation of a lipid hydroperoxide and the

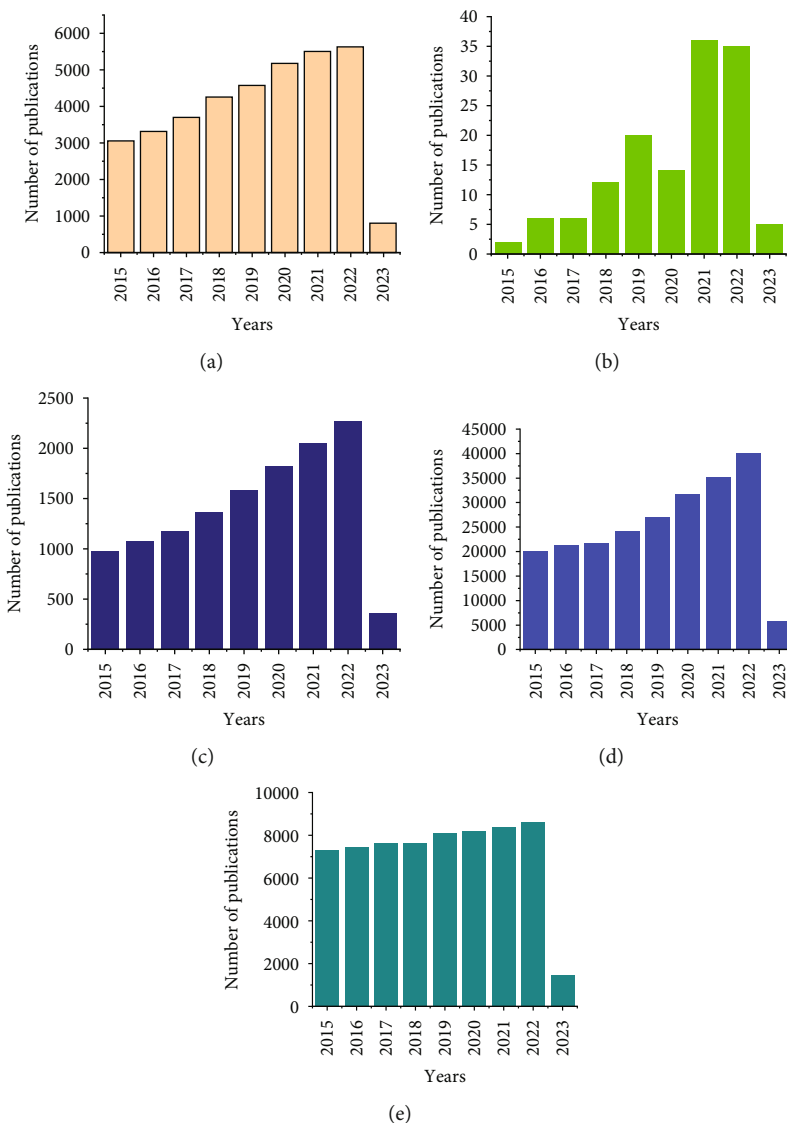


FIGURE 2: Number of publications with the word (a) “*phenolic compounds*,” (b) “*Underutilized Plants*,” (c) “*Agricultural wastes*,” (d) “*Antioxidant*” OR “*Antioxidants*” OR “*Natural antioxidants*,” and (e) “*Biodiesel*” OR “*bio-oil*” OR “*biofuels*” OR “*Biodiesels*” in the Scopus data base from 2015 to 2023.

regeneration of a carbon-centered lipid radical [59]. After an initial induction period, this reaction can move very quickly since it is a chain reaction. As a result, the quality of biodiesel is compromised [60]. The likelihood of autoxidation increases with the amount of unsaturation in the oil used to produce biodiesel. For example, Table 5 shows different feedstocks for biodiesel production with their types of fatty acids. As shown in Table 5, the higher degree of unsaturation of the fatty acid present in biodiesel feedstock such as *Croton megalocarpus* oil (90.30%), lin seeds (91.50%), and castor seeds (97.64%) is the reason for it to be highly prone to autoxidation upon exposure to factors that trigger an oxidation reaction. Moreover, it has been reported that the rates of degradation for methyl linolenate (C18:3) and methyl linoleate (C18:2) are higher than those of methyl oleate (C18:1) [61].

3.2. Physics behind Biodiesel Oxidation Mechanisms. The physics behind biodiesel oxidation mechanisms can be explained by considering the chemical reactions and physical properties involved. As it has been explained, in terms of molecular structure, biodiesel is composed of fatty acid methyl esters, which are typically derived from their feedstock such as edible and nonedible seeds [62], as shown in Table 5. Unsaturated bonds that are found in fatty acid methyl esters, including carbon-carbon double bonds, make biodiesel vulnerable to oxidation reaction [63]. Furthermore, the oxidation of biodiesel requires a certain amount of energy to initiate the chemical reactions. This energy is known as the activation energy. Light and heat can provide the necessary activation energy to start the oxidation process [64]. Once the reactions have started, they may go through a number of stages, releasing energy and producing reactive

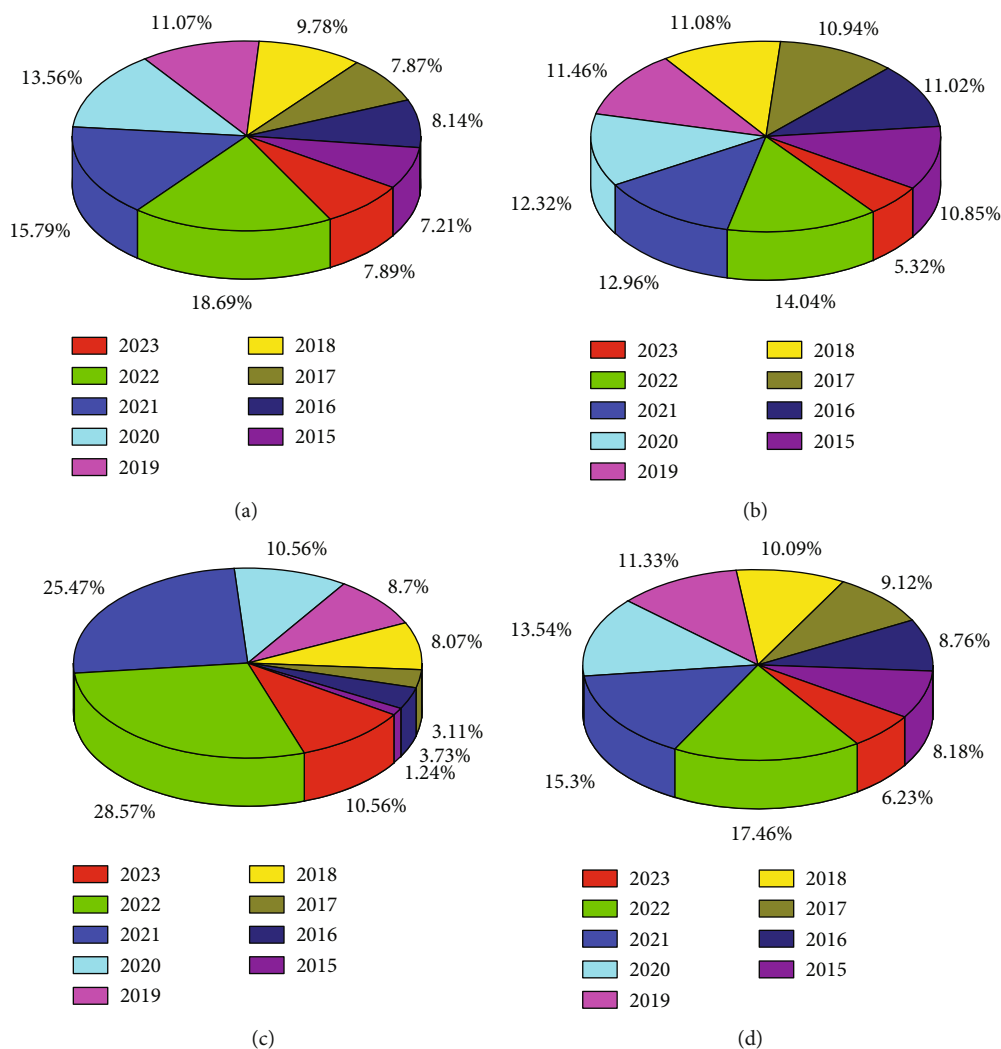


FIGURE 3: Number of publications in percentage as selected from the Google Scholar from 2015 to 2023. (a) "Agricultural waste," (b) "Biodiesel" OR "bio-oil" OR "biofuels" OR "Biodiesels," (c) "Underutilized Plants," and (d) "Natural antioxidants".

species that compromise the quality of the biodiesel [65]. Moreover, the kinetics of biodiesel oxidation describe how the oxidation reactions occur over time. The rate at which the reactions take place is influenced by factors such as temperature, oxygen concentration, and the presence of catalysts [66]. Higher temperatures generally increase the reaction rate, while the availability of oxygen and catalysts can enhance the oxidation process [67]. Therefore, it is advised that developing ways to prevent or minimize the oxidation process requires an understanding of the mechanics or physics of biodiesel oxidation. By controlling factors such as exposure to oxygen, temperature, and the use of antioxidants, it is possible to slow down the oxidation process and preserve the quality of biodiesel.

4. Antioxidants

Antioxidants are substances that slow down the production of oxidants or stop the reproduction of free radicals through a variety of mechanisms, including scavenging the species

that initiate peroxidation [76], chelation by metal ions to delay propagation [77], terminating singlet oxygen to prevent the production of peroxides [78], and stopping an autoxidation chain reaction. Chain-breaking antioxidants and hydroperoxide decomposers are two types of antioxidants in terms of mechanism; the former are referred to as primary antioxidants and the latter as secondary antioxidants. Antioxidants interrupt the propagation process of free radicals (such as radical ROO) by providing them with a hydrogen atom from their major active group, OH or NH [79]. As represented in Figure 7, the produced phenoxy radicals are stable because they can take on a variety of mesomeric configurations. Consequently, the phenoxy radical produced does not initiate additional reactions [80]. Currently, the use of antioxidants in the stabilization of biodiesel has been increasing (Figure 8) [62]. The most widely used primary antioxidants are substituted phenolic compounds, secondary aromatic amines, and thiophenols such as 2,6-di-tert-butyl-4-methylphenol, pyrocatechol, N-methylaniline, and benzenethiol, as shown in Figures 9(a)–9(d) [81].

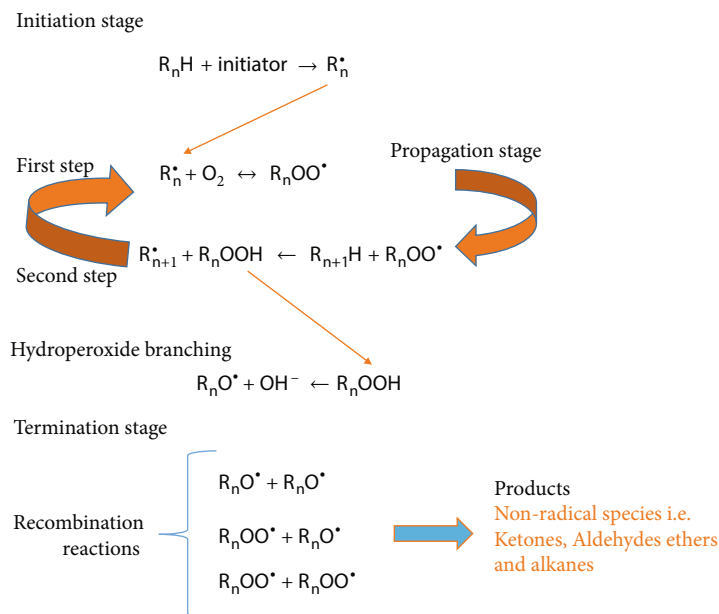


FIGURE 4: Detailed mechanism of biodiesel oxidation as modified from [49].

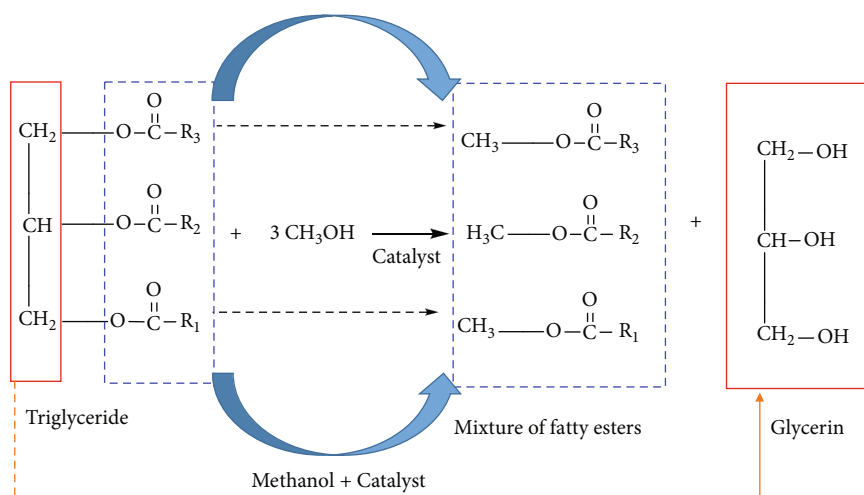


FIGURE 5: Transesterification for biodiesel production.

Other typical examples include naturally occurring antioxidants, like tocopherols and flavonoids (3-hydroxy-2-phenylchroman-4-one), as seen in Figures 8(f) and 9(e).

4.1. Categories of Primary and Secondary of Antioxidants

4.1.1. Synthetic Antioxidants. Synthetic antioxidants are synthesized in a laboratory or industry by combining chemical compounds; they are chemically made substances since they do not occur naturally, and they are added to biodiesel as additives to help reduce fatty acid oxidation [82]. Chain-breaking synthetic antioxidants such as phenolics and amines have been most often used in biodiesel storage technology [83]. Examples of synthetic antioxidants are shown in Figure 10, which include butylated hydroxytoluene, butylated hydroxyanisole, tertiary butylhydroquinone, pyrogallol,

and propyl gallate [82]. Synthetic antioxidants are often used to protect biodiesel fuel from oxidation and degradation, but the toxicity of these additives is a major concern [84]. It has been found that some synthetic antioxidants can be toxic to aquatic organisms and can accumulate in the environment [78]. Furthermore, the overuse of these additives can cause adverse effects on the quality of biodiesel, such as discoloration and the formation of sludge.

To reduce the risk of toxicity, biodiesel producers are increasingly turning to natural antioxidants such as rosemary extract, potato peel extract, and other plant extracts [85]. These natural antioxidants provide an effective way to protect biodiesel without introducing additional toxins into the environment [86]. Furthermore, natural antioxidants are typically more cost-effective and easier to source than their synthetic counterparts [87]. In cases where natural

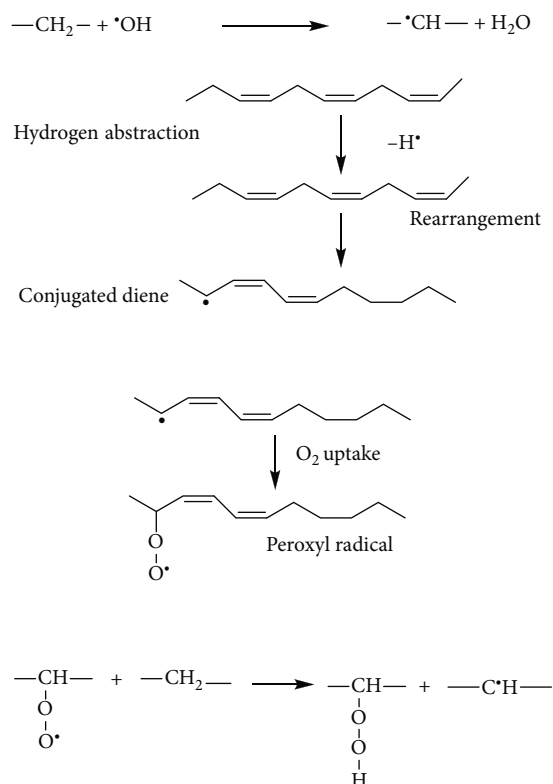


FIGURE 6: Peroxy radical formation mechanism on methylene group [60].

antioxidants are not sufficient and perform poorly, synthetic antioxidants can be applied in very small amounts so as to enhance the efficiency of natural antioxidants [80]. For example, Waweru et al. [88] made a blend of natural antioxidants with the synthetic antioxidant 1,2,3-trihydroxybenzene for the purpose of enhancing the performance of natural antioxidants. The study reported that the performance of natural antioxidants extracted from clove waste blended with 1,2,3-trihydroxybenzene showed higher improvements in oxidation stability by 398% at 800 ppm compared to unblended natural ones, as seen in Table 6. The higher performance was triggered by the synergetic effect of both natural and synthetic antioxidants and the higher phenolic contents of clove waste extract. However, while synthetic antioxidants can still be used in some cases, it is important to take measures to reduce the risk of toxicity and ensure that they are properly incorporated into the biodiesel fuel [89].

4.1.2. Natural Antioxidants. Natural antioxidants are compounds that occur in nature and attempt to keep a product's conditions ideal for a longer period of time by delaying oxidative degradation [90]. They are compounds that can be purposefully added to biodiesel in order to alter their physical chemical properties, especially in improving oxidative stability, or to increase their suitability for the purpose for which they were designed [91]. Some of the most popular natural antioxidants include tocopherols [92], polyphenols [93], ascorbates [94], tocotrienols [90], lignin [95], chlorophylls [96], and carotenoids [97]. Natural antioxidants

contain one or more unstable hydrogens (from OH groups) that can react with peroxide radicals generated during the oxidative degradation of free fatty acid methyl esters (Figure 11) [98].

Some of these naturally occurring antioxidants, such as sterols, tocopherols, and tocotrienols, are present in feedstock for the production of biodiesel [99]. These antioxidants remain in the biodiesel throughout the production process, but during the distillation and purification processes, these built-in antioxidants are destroyed, making the product more vulnerable to oxidation. As a result, it shows that the addition of additional antioxidants is necessary. Numerous studies have demonstrated that when natural antioxidants are properly extracted and added to biodiesel in the right proportions, they outperform synthetic antioxidants. For example, Rodrigues et al. [100] compared the performance of synthetic antioxidants with that of natural turmeric ethanolic extract on the oxidation stability of biodiesel. The study revealed that, when compared to synthetic antioxidants, natural antioxidants (ECE) had the best reaction in slowing the oxidation process at a reaction temperature of 110°C, as seen in Table 7. The higher performance was related to the presence of phenolic compounds named curcuminoids, with a total phenolic content of 7.95 mg EAG/g. Furthermore, Li et al. [101] made a comparison between natural antioxidants produced from rosemary and synthetic antioxidant TBHQ in soybean oils used for deep-frying French fries. The results showed that when compared to TBHQ in terms of oxidation characteristics, rosmarinic acid (RA), rosemary extracts (RE), and carnosic acid (CA) were the three antioxidants that performed the best in terms of quality and stability, as seen in Table 8. The performance of natural antioxidants is attributed to their structures; for example, rosmarinic acid antioxidant is a phenolic acid consisting of four phenolic hydroxyl groups. The phenolic hydroxyl groups are the ones that determine the higher performance of phenolic antioxidants [102]. Narayanasamy et al. [103] evaluated the effect of star anise as a natural antioxidant on the oxidation stability of lemongrass oil. The study revealed that the addition of antioxidant increased the induction period from 2.50 to 19.79 h at 1500 ppm. Therefore, it was concluded that the addition of natural antioxidant with higher phenolic contents enhanced the storage stability of biodiesel and thereby improving its market value.

All of those studies suggest that natural antioxidants may be used instead of synthetic ones because they are effective and can completely replace them. However, some concerns with natural antioxidants are the sustainability of their sources, extraction techniques, and the type of solvent that will be utilized throughout the extraction process [104]. These factors, as well as others, have an impact on how well natural antioxidants work. For example, the sustainability of antioxidant sources can have a significant impact on the sustainability of biodiesel in the market [84]. Consumers and stakeholders are increasingly concerned about sustainability and are willing to pay a premium for more sustainable products [105]. Therefore, using sustainable sources of antioxidants can help biodiesel producers differentiate themselves in the market, gain a competitive advantage, and meet the growing demand for more sustainable products. However,

TABLE 5: Fatty acid profiles of the selected biodiesel's feedstocks.

| Biodiesel's feedstock | Type of fatty acids | | | | | | | Total unsaturated (%) | Ref. |
|------------------------------|---------------------|-------|-------|-------|-------|-------|-------|-----------------------|------|
| | C14:0 | C16:0 | C16:1 | C18:0 | C18:1 | C18:2 | C18:3 | | |
| Jatropha seeds | 0.0 | 14.22 | 1.01 | 8.39 | 44.59 | 31.42 | 0.0 | 77.02 | [68] |
| Soy bean | 0.0 | 11.00 | 0.70 | 4.10 | 22.00 | 53.90 | 7.60 | 87.60 | [69] |
| Neem seeds | 0.2-0.26 | 14.90 | 0.10 | 20.60 | 43.90 | 17.9 | 0.4 | 62.30 | [70] |
| Cotton seeds | 0.53 | 10.33 | 0.37 | 3.64 | 32.82 | 39.29 | 0.0 | 72.48 | [71] |
| Pongamia | 0.99 | 39.97 | 0.0 | 14.10 | 34.13 | 10.16 | 0.0 | 44.73 | [72] |
| Rape seeds | 0.0 | 4.90 | 0.0 | 2.10 | 73.30 | 14.20 | 0.0 | 87.50 | [73] |
| Croton megallo Carpus oil | 0.0 | 5.70 | 0.0 | 3.90 | 11.80 | 71.60 | 6.90 | 90.30 | [74] |
| Sunflower seeds | 0.0 | 7.29 | 0.0 | 13.55 | 18.79 | 58.98 | 0.12 | 77.89 | [72] |
| Lin seeds | 0.0 | 4.40 | 0.30 | 3.80 | 20.70 | 15.90 | 54.60 | 91.50 | [70] |
| Castor seeds | 0.0 | 1.96 | 0.0 | 0.40 | 4.70 | 89.74 | 3.20 | 97.64 | [75] |

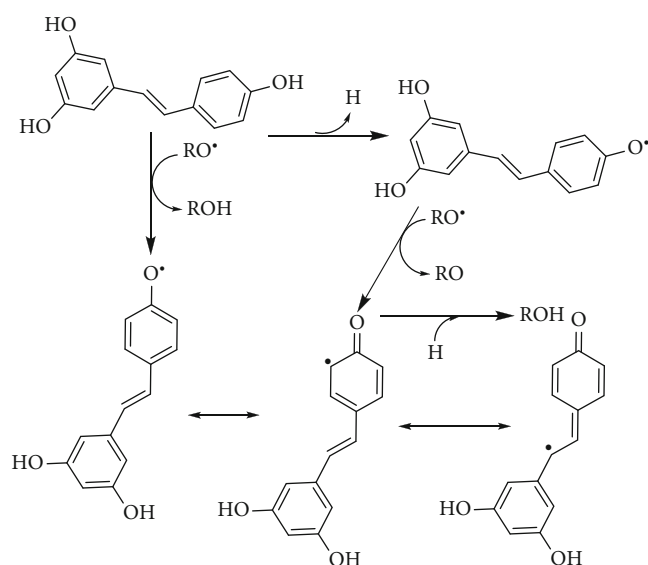


FIGURE 7: Mesomeric resonance of phenoxy radicals from resveratrol natural antioxidants.

natural antioxidant composition can change depending on a number of variables, including plant species, growing conditions, and harvest period.

4.1.3. Sources of Natural Antioxidants. In order to ensure sustainability and lower production costs, choosing the right feedstock is crucial when generating natural antioxidants for biodiesel storage. Waste materials, weeds, and nonedible sources can be used as antioxidant feedstock. Currently, vegetables [106], fruits [107], cereals [108], and beverages [109] are among the edible feedstocks used to extract antioxidants. However, the named sources of natural antioxidants that are most frequently used are connected to immediate food sources, raising the possibility of socioeconomic concerns about food insecurity and contributing to the product's unsustainability [110]. The utilization of nonedible feedstock such as weeds, agricultural wastes [111], and less competi-

tive, underutilized plant species for the manufacture of natural antioxidants is thus unavoidable.

It is crucial to adopt a comprehensive interdisciplinary strategy that considers both phytochemistry and the practical application of those phenolic compounds in order to further evaluate and compile the potential of the underutilized plant species, for instance, its use in biodiesel storage technology [112]. Utilizing underutilized species and agricultural waste with higher phenolic contents, such as clove waste, as reported in our previous work [88], will assure sustainability and reduce the overall cost of manufacturing antioxidants because they are less competitive with other social uses and thus make it easier to commercialize biodiesel. Moreover, a stable cropping system can be built with more possibilities if today's underutilized plants are used more widely [113]. This will also increase their tolerance to abiotic and biotic stresses. Through their products and uses, these plants significantly contribute to providing raw materials for secondary production, such as natural antioxidants [112].

Africa, for example, is plentiful in biodiversity resources, which is not surprising given the continent's tropical and subtropical climates [114]. There are a huge number of phenolic compounds that are naturally produced by plants, and the abundance of the plants themselves can be a driving factor in utilizing these potential resources in different fields like biofuel technology. Here, more emphasis is placed on the utilization of underutilized plants and agricultural wastes in biodiesel storage. A summary of some underutilized African plants and their potential antioxidants can be found in Table 9.

5. Underutilized Plants

The word "underutilized plant" has been used to describe plant species that have potential but have gone out of favor for a variety of reasons, along with other terms like "orphan," "minor," "new plants," and "neglected" [112]. These plants have been found to be high in polyphenols and flavonoids, which may explain why many researchers recommend investigating them [124, 125]. Moreover, they have been shown to be a good source of natural antioxidants

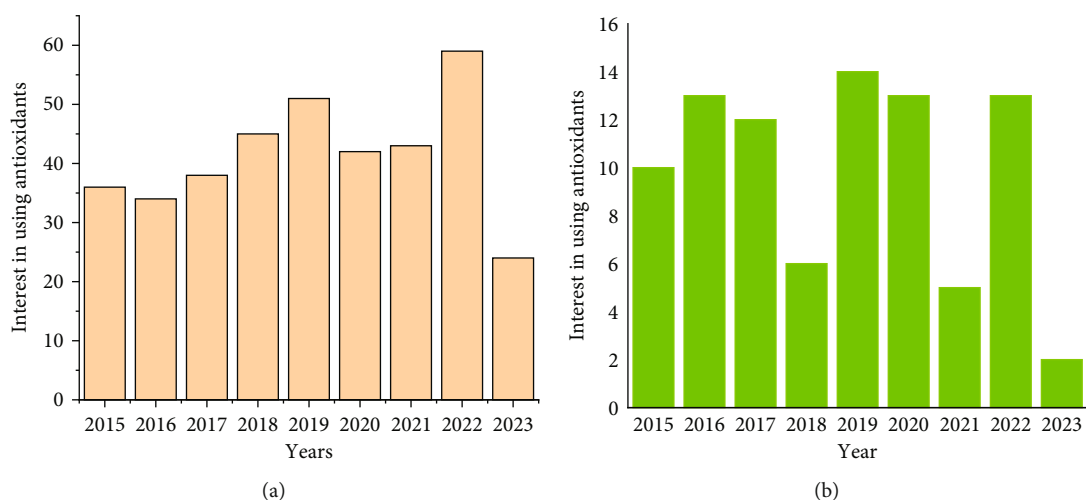


FIGURE 8: Application of antioxidants in the stabilization of biodiesel as depicted in PubMed (a) and Scopus (b).

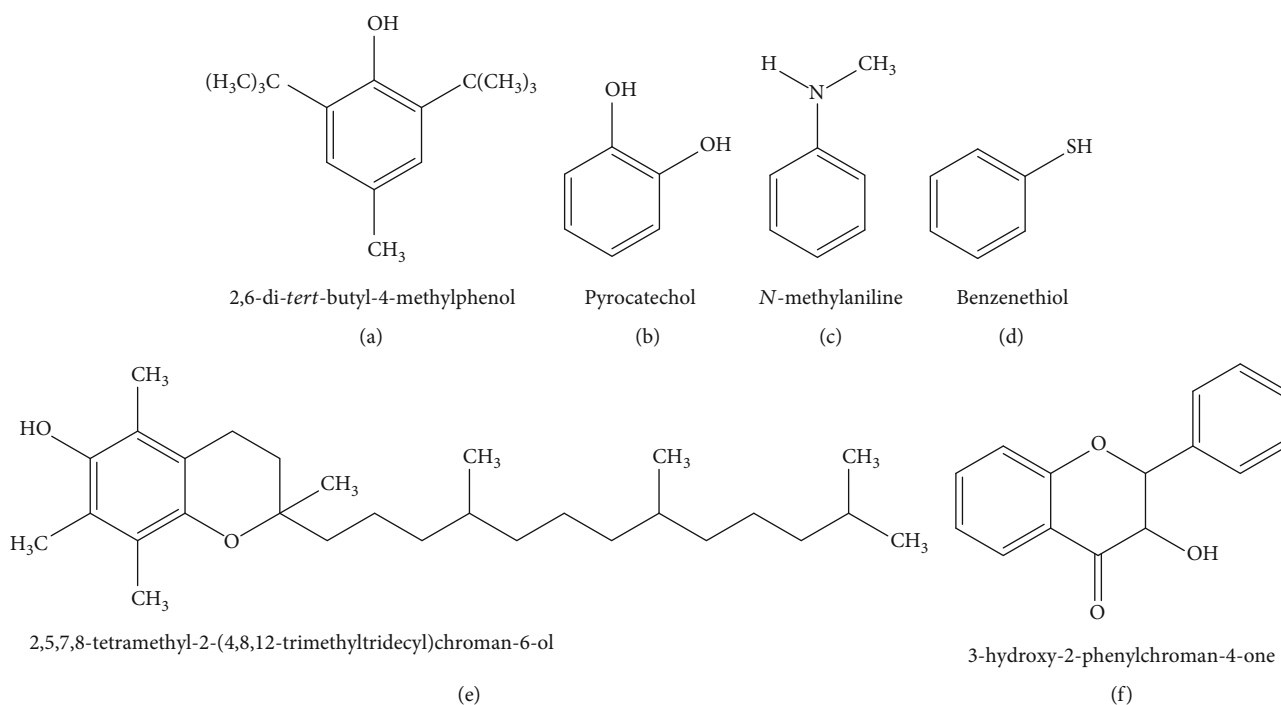


FIGURE 9: Some representatives of primary antioxidants.

for storage technologies such as food and biofuel [126]. Underutilized plants can also adapt to various environmental conditions, ranging from drought areas to wet land. This ensures their sustainability and increases the likelihood that they could be used as a sustainable source of natural antioxidants. Figures 1(b) and 2(b) show how interest in applying underused plants has been growing. Moreover, as depicted in Figure 3, utilization of underutilized plants has been increasing; for example, there was an increase from 1.24% in 2015 to 28.57% in 2022. The rise in demand rates demonstrates the promise of these species. The high phenolic content of this plant species, which has been proven, will help scavenge free radicals when applied as a stabilizing agent

in biodiesel. The following are examples of some underutilized plant species that have the potential to be used as alternative sources of natural antioxidants in biodiesel.

5.1. *Uapaca kirkiana* (Wild Loquat). *Uapaca kirkiana* is an underutilized indigenous fruit tree that is well adapted to the Miombo ecological zone in sub-Saharan Africa [127]. Fruits from the tree have an oval form, are yellow-brown in color, have a fleshy skin, and have luscious pulp inside, as shown in Figure 12. The fruit is commonly called “Mikusu” or “Makusu” in Swahili and Miguhu in Hehe. The plant is abundantly available in Tanzania, Malawi, Zimbabwe, Zambia, Angola, and Mozambique, as depicted

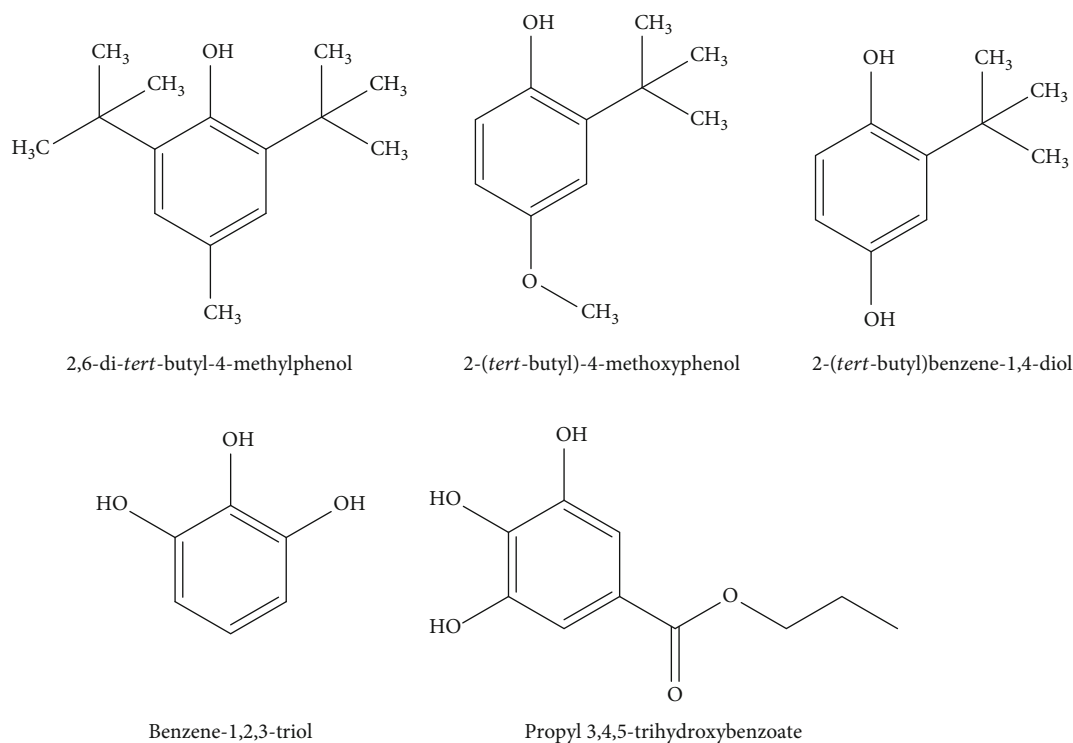


FIGURE 10: Chemical structures of synthetic antioxidants.

TABLE 6: Performance of natural antioxidants blended with synthetic antioxidants [88].

| Source and type of antioxidants | Concentration | Phenolic contents (mg GAE/g) | Induction period improvement (%) |
|---------------------------------|---------------|------------------------------|----------------------------------|
| Clove waste (eugenol) | 1000 | 220.0 ± 0.1 | 153 |
| Babul barks (catechin) | 800 | 48.0 ± 0.2 | 236 |
| Blends of clove with PY | 800 | — | 398 |
| Babul with pyrogallol | 800 | — | 46 decreased |

in Figure 13. This natural plant, like other species, has a wide range of phytochemical and functional properties because of variations in soil quality and environmental conditions [128].

For instance, Muchuweti et al. [128] analyzed the phenolic compounds found in *U. kirkiana* of ripe and unripe fruits; the results showed that both ripe and unripe fruit contained amounts of tannins, including phenolic acids, that could work as antioxidants for scavenging free radicals that could degrade lipids or biodiesel, hence performing a protective role. Moreover, Ndhala et al. [129] investigated the antioxidant effects of four wild fruits, including *U. kirkiana*, and the results showed that the peels of *U. kirkiana* had higher DPPH radical-scavenging effects, reducing power, and superoxide-scavenging effects. The reason for the results is related to the presence of higher total phenolic contents in the extract. Chawafambirra et al. [130] investigated the relationship between the functional and chemical properties of *U. kirkiana* fruit pulp, and the findings revealed that the fruit extract exhibits a higher antioxidant activity as a result of the presence of a higher phenolic content of 82.5 ± 0.01 g GAE/g.

Unfortunately, despite prior efforts to describe applicability, knowledge on the full utilization of the plant is still insufficiently documented, particularly on its use as a source of natural antioxidants for biofuel technology. Based on the aforementioned findings, this plant's extract can therefore be employed as a source of natural antioxidants for biodiesel storage technology.

5.2. *Vitex doniana*. *Vitex doniana* is a wild plant that belongs to the family *Lamiaceae*, and there are about 250 species in this family [130, 131]. Fruit from the plant is commonly called “mfudu” or “mfulu” in Swahili and Hehe [132]. It is green when immature and purplish-black on ripening, with a starchy black pulp, as seen in Figure 14. Each fruit contains one hard conical seed, which is about 1.5–2.0 cm long and 1–1.2 cm wide. Among these wild plant resources, *Vitex doniana* is an abundant and widespread species in African countries, including West African countries [133], East African countries [134], and Central Africa [135]. In Tanzania, for example, it is abundantly available in coastal regions, southern regions, and northern regions [136].

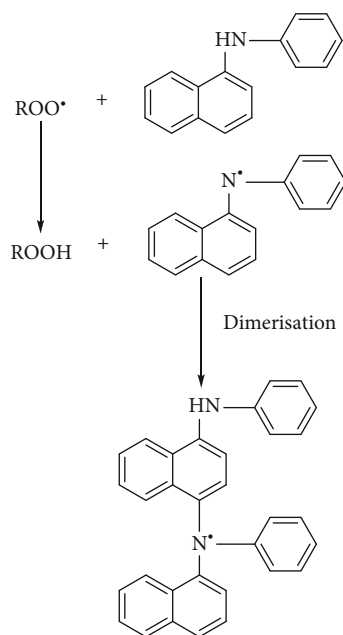


FIGURE 11: N-phenyl-naphthalen-1-amine natural antioxidant scavenging a free radical.

TABLE 7: Comparative study of synthetic and natural antioxidants [100].

| Samples | Induction period (hours) | | | |
|---------|--------------------------|-------------|-------------|-------------|
| | 110°C | 115°C | 120°C | 125°C |
| BHA | 6.44 ± 0.01 | 5.02 ± 0.06 | 3.32 ± 0.01 | 2.28 ± 0.01 |
| BHT | 3.12 ± 0.05 | 2.20 ± 0.01 | 1.54 ± 0.03 | 0.96 ± 0.02 |
| PG | 10.18 ± 0.04 | 7.60 ± 0.03 | 4.84 ± 0.03 | 3.26 ± 0.02 |
| ECE | 10.9 ± 0.03 | 7.54 ± 0.01 | 4.14 ± 0.01 | 2.88 ± 0.01 |
| Control | 1.98 ± 0.01 | 1.56 ± 0.01 | 1.08 ± 0.01 | 0.64 ± 0.01 |

TABLE 8: Comparison of natural antioxidants and synthetic antioxidant TBHQ [101].

| Antioxidants | Days of frying | Induction period (hours) | | | | | |
|------------------------|----------------|--------------------------|-----|-----|------|-----|-----|
| | | 0 | 1 | 2 | 3 | 4 | 5 |
| Control | | 3.8 | 2.6 | 2.6 | 2.1 | 1.8 | 1.8 |
| TBHQ | | 8.1 | 2.7 | 2.7 | 2.2 | 1.9 | 1.6 |
| Carnosic acid (CA) | | 5.9 | 3.0 | 2.6 | 2.5 | 2.5 | 2.8 |
| Rosmarinic acid (RA) | | 4.1 | 3.9 | 3.4 | 2.4 | 2.4 | 2.7 |
| Rosemary extracts (RE) | | 3.8 | 3.1 | 2.6 | 2.15 | 2.0 | 1.9 |

The fruits are rich in phytochemicals, such as polyphenols, making the extract of this underutilized plant work as an antioxidant source in various storage technologies such as food and biodiesel. For example, [136] investigated the antioxidant activities of *Vitex doniana* fruits from coastal forests in Tanzania. The finding showed that the antioxidant activities in (mg GAE/g) of wild fruits *Vitex doniana* from two coastal regions (Tanga and Coastal) determined using diphenyl-1-picrylhydrazyl (DPPH) ranged between

71.0 ± 0.4 and 49.11 ± 0.04 in fruit samples from Tanga and 65.6 ± 0.1 and 48.3 ± 0.1 in fruit samples from Coast region, as seen in Table 10. In addition, Traore et al. [137] analyzed the phenolic contents and antioxidant activities of *Vitex doniana* fruit pulp and peel. The results revealed the presence of a higher amount of phenolic compounds in peel than pulp, and peel extract also showed the strongest antioxidant capacities, as seen in Table 11. Thus, the considerable antioxidant activity depicted by *V. doniana* indicated its potential as a source of natural antioxidants. However, despite the potential of *V. doniana* extract to show higher antioxidant activities, it is still not applied in practical applications such as food storage or biofuel storage technology. Given their abundance, underutilized status, lack of social or economic conflicts, and most significantly, their abundance of phytochemicals with antioxidant potential, they constitute a sustainable source.

5.3. *Parinari curatellifolia*. *Parinari curatellifolia*, which belongs to the *Magnoliopsida* class and is in the family *Chrysobalanaceae*, is quite diverse in terms of size and shape, growing from a small shrub up to 3 meters tall to a huge tree up to 15-20 meters tall. It is an evergreen with spreading pale-green foliage that forms a dense, mushroom-like crown [137, 138]. The tree has a single bare stem with bark that is deeply gray in color. *P. curatellifolia* produces an ovoid drupe fruit that is initially russet-yellow to gray before turning orange-yellow when ripe (Figure 15). It contains an edible kernel and a pale yellow-to-reddish mealy pulp. The plant flourishes in environments with annual mean temperatures of 10 to 30°C and rainfall ranging from 100 to 2700 mm at altitudes of 0 to 1900 m. *P. curatellifolia* plant parts are used in traditional medicine [139, 140].

One of the most potent and therapeutically effective bioactive molecules found in this plant is the family of aromatic hydroxylated compounds known as polyphenols, which includes flavonoids [141]. Because of the presence of those polyphenol compounds, *P. curatellifolia* seed extract has historically been used as medication to treat a number of degenerative diseases of the central nervous system [142]. Additionally, it has been demonstrated that the plant extract has stronger antioxidant properties [143]. For example, [114] studied the lipid composition and antioxidant properties of 12 underutilized wild plant seeds from Burundi, including *Parinari curatellifolia*. Results showed that *P. curatellifolia* has the highest total phenolic content and has significant antioxidant activity. Based on the study results, it was suggested that this extract be employed in a variety of practical applications, including those that deal with food, cosmetics, pharmaceuticals, and lipochemistry, as well as other storage technologies like biodiesel storage.

5.4. *Tamarindus indica* L. (*Tamarind*). The tamarind (*Tamarindus indica* L.), which naturally grows in many tropical and subtropical locations, is a member of the *Leguminosae* family [144]. The plant is abundantly available in African countries such as Tanzania, Sudan, Sierra Leone, Ivory Coast, Liberia, Ghana, Kenya, Cameroon, the Republic of Congo, and others [145]. Its fruits are generally used as

TABLE 9: Some of underutilized plants of Africa.

| Name of plant (scientific name) | Common name | Bioactive compounds | Ref. |
|---------------------------------|-------------|--|-------|
| <i>Punica granatum</i> L. | Pomegranate | Punicalagin, anthocyanins, cyanidin, and pelargonidin 3-glucosides and 3,5-glucosides as well as flavonols | [115] |
| <i>Garcinia kola</i> | Bitter kola | Anthocyanins, flavonoids, glycosides, phenols, tannins, triterpenoids, and steroids | [116] |
| <i>Bixa orellena</i> | Achiote | Phenols, flavonoids and tannins | [117] |
| <i>Uapaca kirkiana</i> | Wild loquat | Tannins, flavonoids, and phenolic acid | [118] |
| <i>Vitex doniana</i> | Black plum | Polyphenols, flavonoids, and anthocyanin | [119] |
| <i>Parinari curatellifolia</i> | Mobola plum | Flavonoids, anthocyanins, tannins, alkaloids, saponosides, glycosides, anthraquinones, and free quinones | [120] |
| <i>Capsicum annum</i> | Paprika | Capsaicinoids, carotenoids, and phenolic compounds | [121] |
| <i>Allium sativum</i> | Ginger | Phenolic compounds and thiosulfinate | [122] |
| <i>Nicotiana rustica</i> | Tobacco | Flavonoid and phenolic compounds | [123] |
| <i>Tamarindus indica</i> L. | Tamarind | Phenolic compounds and flavonoid | [124] |

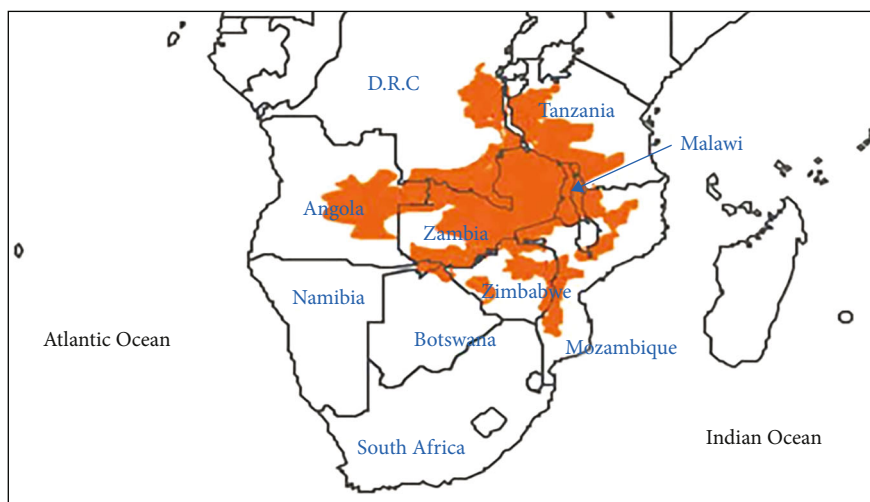
FIGURE 12: *Uapaca kirkiana* (wild loquat) plant and fruits.

FIGURE 13: The wild loquat distribution in some African countries [130].

a seasoning, spice, and beverage for medicinal purposes [146]. The fruit has a little curvature and is composed of 55% pulp, 34% seeds, 11% shell, and a pod of fiber [147], as seen in Figure 16. Due to their ability to tolerate extended droughts, tamarind trees are excellent low-input, high-

yielding trees since they can flourish in poor soils and semi-arid climates [148].

Traditionally, dried or boiled tamarind leaves and flowers have been applied as poultices to boils, sprains, and inflamed joints. Moreover, they used to make extracts that

FIGURE 14: *Vitex doniana* plant with ripe and unripe fruits.TABLE 10: The percentage antioxidant activity of *V. doniana* fruits from Tanga and Coast forests of Tanzania [136].

| Concentration ($\mu\text{g/ml}$) | Antioxidant activity | |
|------------------------------------|----------------------|------------------|
| | Tanga | Coastal |
| 1000 | 71.01 ± 0.39 | 65.61 ± 0.05 |
| 500 | 65.43 ± 0.04 | 55.34 ± 0.25 |
| 250 | 61.10 ± 0.01 | 54.27 ± 0.01 |
| 125 | 57.83 ± 0.04 | 51.03 ± 0.00 |
| 62.5 | 49.11 ± 0.04 | 48.27 ± 0.06 |

were used to treat a variety of conditions, including conjunctivitis, jaundice, erysipelas, hemorrhoids, and dysentery [148]. The phenolic antioxidants present in tamarind (*Tamarindus indica*) seeds, such as epicatechin, 2-hydroxy-3,4-dihydroxyacetophenone, methyl 3,4-dihydroxybenzoate, and 3,4-dihydroxyphenyl acetate, are the reasons for the role they play [149]. For example, according to Leng et al. [150], dried tamarind leaves have a high antioxidant capacity, suggesting that tamarind can provide a natural alternative supply of antioxidants. Not only the fresh parts of tamarind but also the byproducts from tamarind processing have been used to extract antioxidants [151]. For instance, Martins et al. [152] highlighted the most important bioactive chemicals linked to byproducts of the processing of tamarind and identified that the primary types of compounds from tamarind byproducts are phenolic compounds, fatty acids, and polysaccharides, which when extracted can be used as beneficial products such as antioxidants. Mota et al. [153] extracted phenolic compounds from tamarind seeds that can be used as potential antioxidants as seen in Table 12. The extract showed higher phenolic contents as well as antioxidant activity when tested with stable radicals. Additional information from Table 12 shows that different conditions, such as temperature and extraction technique, can result in variation of phenolic contents as well as antioxidant

activities, for example, the total phenolic contents for ethanol extract at 60°C were 305.1 ± 2.9 whereas for an ethanol extract with 50% ethanol/water at 60°C was 128.5 ± 1.4 . This suggests that attention should be paid to extraction conditions when extracting antioxidants.

In general, there are a few obstacles that need to be overcome in order to fully utilize the potential of underutilized plant resources and agricultural wastes with plentiful and high-phenolic contents as sources of natural antioxidants. These obstacles include limited knowledge and awareness. There is often limited information accessible regarding their safety characteristics and chemical composition. This lack of knowledge and correct information makes it challenging to identify and utilize these plants effectively. Moreover, underutilized plants can display significant variation in their antioxidant compositions due to factors such as environmental conditions, genetic diversity, and cultivation methods. It is crucial to establish standardized cultivation and processing approaches to ensure consistent antioxidant compositions in the plant material.

6. Extraction of Natural Antioxidants

In order to extract bioactive substances from plants, a number of steps must first be taken, including sample preparation, extraction, purification, and quantification [154]. The required plant parts must be dried in an oven or under the sun to remove the moisture content [150]. To ensure effective extraction, the dried sample is milled, ground, and sieved to the proper sizes [155]. The extract can be utilized for quantification once the extraction is finished, and this is the most effective stage in order to enhance the polyphenol extraction and processing process. Moreover, this stage determines the quality of the polyphenol content and its antioxidant capacity.

Polyphenols, or antioxidants, are extracted from their feedstock (plants) using a variety of methods, such as mechanical agitation, maceration [146], and Soxhlet [156], as well as more advanced ones like microwave-assisted

TABLE 11: Total phenolic contents, total flavonoid contents, and antioxidant activities in *Vitex doniana* fruit pulp and peel [137].

| Sample location | TPC (mg GAE/100 g DW) | | TF (mg QE/100 g DW) | | AAT (mg/ml) | |
|-----------------|-----------------------|--------------|---------------------|--------------|-------------|-------------|
| | Pulp | Peel | Pulp | Peel | Pulp | Peel |
| Ferke | 227.5 ± 3.35 | 225.8 ± 5.89 | 79.43 ± 1.13 | 103.9 ± 0.66 | 1.90 ± 0.27 | 0.91 ± 0.09 |
| Tiébissou | 202.5 ± 4.19 | 383.0 ± 6.54 | 75.71 ± 1.03 | 145.6 ± 1.03 | 2.13 ± 0.18 | 0.53 ± 0.06 |
| Yamoussoukro | 259.8 ± 2.81 | 463.5 ± 6.85 | 77.95 ± 0.72 | 141.5 ± 0.66 | 1.94 ± 0.06 | 0.48 ± 0.01 |

FIGURE 15: *Parinari curatellifolia* plant and fruits.FIGURE 16: *Tamarindus indica* L. plant and fruits.

TABLE 12: Total phenolic contents and antioxidants activities of extract from tamarind seeds [153].

| Method | Extraction solvent | Total phenolic contents (mg GAE/g) | DPPH ($\mu\text{mol TEAC/g}$) | ABTS ($\mu\text{mol TEAC/g}$) |
|--------------------------------|--------------------------|------------------------------------|---------------------------------|---------------------------------|
| Supercritical fluid extraction | CO ₂ (60°C) | 1.6 ± 0.1 | 2.9 ± 0.1 | 1.3 ± 0.1 |
| Pressurized liquid extraction | Ethanol (60°C) | 305.1 ± 2.9 | 1927 ± 13.6 | 2606 ± 10.0 |
| Pressurized liquid extraction | 50% ethanol/water (60°C) | 128.5 ± 1.4 | 1265 ± 39.1 | 1981 ± 9.0 |
| Soxhlet | Hexane (69°C) | 1.7 ± 0.1 | 1.9 ± 0.1 | 1.9 ± 0.1 |

TABLE 13: Total phenolic contents and antioxidants activities of *Citrus sinensis* peels [161].

| Extraction methods | TPC (mg GAE/g DW) | DPPH (IC_{50} , ml extract/l) | ORAC of extract (μ M TE/g) |
|--------------------|-------------------|----------------------------------|---------------------------------|
| MAE | 12.09 \pm 0.06 | 337.2 \pm 8.45 | 482.3 \pm 57.43 |
| UAE | 10.35 \pm 0.04 | 433.1 \pm 7.62 | 456.9 \pm 35.09 |
| ASE | 6.26 \pm 0.23 | 450.4 \pm 9.49 | 338.0 \pm 23.15 |
| CSE | 10.21 \pm 0.01 | 358.5 \pm 5.15 | 523.0 \pm 48.16 |

extraction (MAE) [157], ultrasound-assisted extraction (UAE) [154], supercritical fluid extraction (SFE) [158], and pressurized liquid extraction (PLE) [159]. Different scholars, for instance [157], have highly recommended UAE for extracting polyphenols from natural source matrices since it offers significant advantages over other approaches, including decreased energy usage. However, on the other side, MAE and PLE have recommended a higher yield; nevertheless, it uses more energy during the extraction process with a risk of degrading labile components [160]. Additionally, Nayak et al. [161] compared the recovery of polyphenols from *Citrus sinensis* peels using accelerated-assisted solvent extraction, ultrasound, and microwave. It was concluded that MAE extracts had a higher yield, higher total phenolic contents of 12.09 \pm 0.06 (mg GAE/g DW), and higher total antioxidant activity than other extracts made using different methods, as seen in Table 13. Lower IC_{50} values for MAE extracts when compared to other extraction techniques indicate that MAE extract has significantly higher antioxidant activities and better scavenging of DPPH radicals than UAE, CSE, and ASE methods of IC_{50} values (437.5 \pm 1.30, 357.4 \pm 6.02, and 450.4 \pm 4.48 ml extract/L, respectively).

It can be noted that the efficiency of each strategy is closely correlated with the operating conditions, according to the aforementioned rationale. Certain factors, including solvent composition, solvent-to-solid ratio, extraction temperature and time, stirring, contact surface area, and the properties of the plant matrix, especially its water content, should receive extra care [162]. For example, the total phenolic contents produced by various processes are shown in Table 14. The results can be attributed to the techniques themselves as well as the solvents employed. Thus, while planning for extracting natural antioxidants, both the technique and other operational conditions such as type of solvent, temperature, plant matrix, and others should be taken into consideration. Apart from that, Table 15 shows the advantages and disadvantages of each technique and gives the way forward for researchers to select the technique based on their preferences with consideration of cost and availability. Based on the data in Tables 14 and 15, it can be suggested that the best strategies to take into account for increased yield and quality are microwave-assisted, ultrasound-assisted, and supercritical fluids. This is due to the numerous benefits of those approaches, including their excellent selectivity, quick and easy handling, higher yield, and moderately low extraction times.

6.1. Screening Potential Solvents for Extraction of Natural Antioxidants. The type of solvent to be employed is one of

the most important factors in the extraction of natural antioxidants since it will determine the yield and purity of the antioxidants, which in turn will have an impact on the antioxidants' activity [170]. Preferably, the solvent should be highly selective toward the target compounds while eliminating unwanted matrix constituents [172]. Preferably, the solvent should be highly selective toward the target compounds while eliminating unwanted matrix constituents [173]. Moreover, other critical factors for solvent selection are polarity, cost, and solvent toxicity.

For instance, Pinho et al. [166], by screening various solvents, examined the capability to extract carotenoids while also examining the temperature and time of extraction. The study revealed that, based on the polarity of solvent carotenoids, they can be classified into two groups: nonpolar carotenes and polar carotenoids. Mixed solvents (ethanol: hexane) and (ethanol: ethyl acetate) yielded higher total carotenoid contents than did ethanol, hexane, and ethyl acetate solvents when used alone. It is possible that the mixture of nonpolar solvents like hexane with polar solvents like ethanol contributed to the improved solubility of beta-carotene [174]. Additionally, [175] reported that the extraction yield increases with an increase in solvent polarity which has a direct connection to the "like dissolves like" principle. Further studies reported that a binary solvent works better for phenolic extraction than a mono-solvent [175, 176]. This demonstrates that, in addition to polarity, a number of other solvent properties, including molecular surface area, molecular size or volume, hydrogen bonding strength, and polarizability, are related to solubility either directly or indirectly.

7. Previous Works on Performance of Natural Antioxidants on Oxidation Stability of Biodiesel

Several studies have investigated the use of natural antioxidants to improve the oxidation stability of biodiesel [155, 177]. These antioxidants are derived from natural sources, such as plants and agricultural wastes, and are added to biodiesel to prevent oxidation and increase its shelf life, as seen in Table 16. Studies have shown that different types of natural antioxidants, such as tocopherols [178], phenols [83], and flavonoids [179], can be effective in improving the oxidation stability of biodiesel. The effectiveness of these antioxidants may depend on various factors, such as the type and concentration of the antioxidant, as well as the type of feedstock used to produce the biodiesel. For instance, [45]

TABLE 14: Various methods for synthesis of natural antioxidants.

| Source of antioxidants | Synthesis method | Solvent used | Total phenolic contents (mg GAE/100 g) | Ref. |
|---|--|--|--|-------|
| Clove waste | A steam distillation at high temperature | Ethyl acetate | 220.0 ± 0.1 | [88] |
| Clove buds | Steam-distilled at under reduced pressure | Dichloromethane | 2.75 ± 0.57 | [163] |
| Vegetables | Solvent extraction under room temperature | 70% (v/v) ethanol | 7167 ± 73 | [164] |
| Babul Barks | Soxhlets extraction | Methanol in water (80:20) | 48.0 ± 0.2 | [88] |
| Stem and fruits of clove | Solvent extraction under room temperature | Acetone 50% | 240.7 | [165] |
| Guaraná (<i>Paullinia cupana</i>) byproduct | Ultra sonication, followed by centrifugation | Hexane, ethanol, and ethyl acetate | 65.9 ± 0.4 | [166] |
| Bravo de Esmolfe' apple | MAE | Mixture of ethanol and water (50:50, v : v) | 4.44 ± 0.32 | [167] |
| Bravo de Esmolfe' apple | UAE | Mixture of ethanol and water (50:50, v : v) | 2.82 ± 0.21 | [167] |
| <i>Osmanthus fragrans</i> (Lour) flower | MAE | Deep eutectic solvents, choline chloride, oxalic acid, and lactic acid | 155.05 to 238.09 | [168] |
| Spinach | UAE | Ethanol and HCl | 3100 ± 100 | [159] |

TABLE 15: Advantages and disadvantages of antioxidants extraction techniques with some of their characteristics.

| Name of technique | Advantage (s) | Disadvantage (s) | Extraction time | Driving force | Ref. |
|----------------------|---|--|-----------------|---|-------|
| Microwave assisted | Moderate use of solvent, fast and easy to handle. Higher yield. Lower extraction times. | Risk of explosion (solvent used must have the ability absorb microwave power). Expensive and requires filtration step. Energy consuming. | 3–30 min | Microwave power | [159] |
| Ultrasound assisted | Easy to handle and safe. It runs under atmospheric pressure and room temperature. Moderate solvent is used reproducible. Lower extraction times. | Possibilities of degradation of compounds at high frequencies. Required filtration step. Low yield compared to Microwave-assisted method. | 10–60 min | Acoustic cavitation | [169] |
| Supercritical fluids | High selectivity No filtering required. Fast and safe. | There are many parameters to be optimize. | 10–60 min | Combined supercritical fluid and pressure | [170] |
| Soxhlet extraction | No sophisticated equipment used. | Exposure risk to organic vapors. It can result into degradation of thermos-labile compounds. Time consuming. Leaving trace amounts of solvents. | 6–24 h | Heat | [171] |
| Mechanical agitation | No sophisticated equipment used. | Exposure risk to organic vapors. It can result into degradation of thermos-labile compounds. Risk of spills. Compounds require filtration process. Time consuming. Increased consumption of energy. | 24-76 h | Depends on solvent contact | [161] |

analyzed the value of potato peel extract as a natural antioxidant on the stability of biodiesel oxidation. The study evaluated the effectiveness of natural antioxidants in varying concentrations and compared them with synthetic antioxidants. The results showed that, with varying concentrations of potato peel extracts (from 100 ppm to

250 ppm), the induction period of biodiesel increased from 5.95 h to 7.02 h, which was higher than that of synthetic antioxidants (TBHQ). The higher performance of potato peel was attributed to higher total phenolic contents and a higher number of hydroxyl groups in the phenolic antioxidants.

TABLE 16: Performance of natural antioxidants from underutilized plants and agricultural wastes on oxidation stability of biodiesel.

| Source of natural antioxidants | TPC (mg GAE/100 g) | Dominant antioxidants compound | Performance test on biodiesel induction period (h) | Observations | Ref. |
|---|--------------------|---|--|---|-------|
| Clove | 220.0 ± 0.1 | Eugenol | 2.41–6.1 | Antioxidant production from clove wastes is a simple and inexpensive process. Clove waste antioxidants show promise as biodiesel oxidation stability boosters. | [88] |
| Babul barks | 48.0 ± 0.2 | Catechin | 2.41–8.1 | Due to the presence of many hydroxyl groups in catechin structure, the most prevalent bioactive component, pure natural Babul antioxidants at 800 ppm increased a longer induction period. | [88] |
| <i>Larrea tridentata</i> | 211.2 ± 0.39 | Caffeic acid, epicatechin, and catechin | 1.25–32.27 | The methanolic <i>Larrea tridentata</i> extract demonstrated a higher antioxidant activity, improves the oxidative stability of biodiesel, and has demonstrated efficacy as an alternative to synthetic antioxidants. | [181] |
| Potato peels | | Gallic acid | 5.95–7.02 | Potato peel extract can improve biodiesel's oxidation stability just as effectively as a synthetic antioxidant TBHQ, and it can thus take the role of synthetic antioxidants. | [45] |
| <i>Thuja oreantalis</i> L. | 69.44 | α -cedrol | 6.79–11.04 | The induction time of the biodiesel produced increased at a minimum concentration of 100 ppm of thuja extract, meeting both the European (ENE14214) and American standards for biodiesel oxidation stability (ASTM D-6751). | [182] |
| Thyme | — | Thymol | 8.00–10.75 | Thyme oil is a tradition extract that is simpler to use and less expensive than synthetic antioxidants. | [183] |
| Waste grape seeds | — | Catechin | 0.18–9.81 | As long as they can be effectively extracted and solubilized, natural antioxidants found in grapeseed could play a significant role in improving the oxidative stability of the biodiesel. | [184] |
| Barley waste | | α -tocopherol | 5.76 ± 0.11 | Increased induction period is due to the presence of higher amount of phenolic antioxidants in the extract | [185] |
| Passion fruit seed | 74.9 | Catechin and epicatechin | 6.00–10.8 | The high concentration of phenolic compounds of 74.9 mgGAE/g with excellent antiradical activity against the model radical DPPH are the reason for the increased induction period. | [186] |
| <i>Annona muricata</i> L. (soursop fruit peels) | 49.08 | Terpenoid | 10.30 ± 0.36 | The soursop peel can be used as a source of an antioxidant for biodiesel because of the protective effect demonstrated against biodiesel degeneration. | [187] |

TABLE 17: Effect of natural antioxidants of biodiesel storage (Jatropha biodiesel-lemongrass oil binary blend) [190].

| Source of antioxidants | Total phenol content (mg GAE/100 g) | Scavenging effect (%) | Induction period from 2.06 (h) |
|------------------------|-------------------------------------|-----------------------|--------------------------------|
| Sesame | 97.37 | 76 | 9.92 |
| Horse gram | 39.99 | 86.51 | 8.10 |
| Sweet basil | 35.07 | 75.28 | 7.74 |
| Coffee | 30.15 | 74.15 | 7.10 |
| Peas | 25.25 | 70.78 | 4.10 |

Moreover, some studies have also explored the use of a combination of different natural antioxidants to improve the oxidation stability of biodiesel [179, 180]. For example, Buosi et al. [155] evaluated the performance of combined natural antioxidants in comparison to syn-

thetic ones. The results showed that the best formulation to prevent the oxidative process in biodiesel B100 was that containing 50.00% of rosemary, 12.50% of oregano, and 37.50% of basil extract. The resultant mixture of antioxidants with higher phenolic contents and a larger

number of hydroxyl groups is responsible for the better performance.

7.1. Effect of Natural Antioxidants on Biodiesel Storage. As previously stated, biodiesel is susceptible to oxidation when exposed to factors that trigger oxidation reactions, such as light, temperature, humidity, and impurities. As a result, biodiesel can degrade while being stored, resulting in the formation of unwanted byproducts that can harm engines and reduce fuel efficiency [188]. Antioxidants are commonly added to biodiesel to prevent oxidation and increase its shelf life. Research has shown that the addition of natural antioxidants to biodiesel can significantly increase its induction period and improve its storage characteristics [189]. For example, the induction period of the *Jatropha* biodiesel-lemongrass oil binary blend was increased by adding antioxidants extracted from peas, coffee, sweet basil, horse gram, and sesame to 4.10, 7.10, 7.74, 8.10, and 9.92 h, respectively, in comparison to the binary blend without antioxidants, in which the induction period was only 2.06 h, as shown in Table 17 [190]. The higher phenolic contents of sesame were the reason for higher induction period.

On the other hand, during long storage, the physical chemical parameters such as the acid number, peroxide value, and viscosity tend to increase significantly due to oxidation [35]. The addition of antioxidants has been reported to reduce the acid number, peroxide value, and viscosity by quenching the free radicals formed during biodiesel's oxidation [39]. Tables 18(a)–18(c) show the changes in physical and chemical parameters with the addition of antioxidants. For example, the peroxide value in Table 18(a) decreased with the addition of leaf extract due to the presence of carotene antioxidants. The drop in peroxide values demonstrates that the addition of antioxidants slows down the oxidation of biodiesel during storage by scavenging the free radicals and hence inhibiting the production of peroxides. Moreover, the degradation of biodiesel results in the formation of short-chain products, such as aldehydes, ketones, and organic acids, or polymeric products, which result in increased acid value [191]. Table 18(b) shows the increase in acid values of biodiesel upon storage for a long time; however, the addition of antioxidants has reduced the acid value, which is explained by a decrease in the production of acid as a secondary oxidation product.

Additionally, another crucial physical and chemical parameter of the biodiesel used in compression ignition engines is viscosity [192]. The chemical composition of biodiesel, which is a complex mixture of many fatty esters with varied chain lengths and degrees of saturation, affects its viscosity [193]. The viscosity of the biodiesel increases due to the production of free fatty acids, isomerization at the double bond positions, often from *cis* to *trans*, and the formation of products with a larger molecular weight [194]. The addition of antioxidants leads to a reduction in viscosity because antioxidants inhibit the autooxidation of biodiesel, which is the primary source of free fatty acids, and other products with a higher molecular weight. Table 18(c) shows the decrease in viscosity upon the addition of antioxidants.

TABLE 18: (a) Changes in peroxide value (PV) of biodiesel doped with antioxidants [189]. (b) Changes of acid values (AV) of biodiesel doped with antioxidants [189]. (c) Changes in viscosity of biodiesel doped with antioxidants [189].

| (a) | | |
|--------------|-------------|--|
| Storage days | PV (mEq/kg) | PV after adding 20 ml of leaf extract (mEq/kg) |
| 0 | 6 | 2 |
| 15 | 10 | 4 |
| 30 | 14 | 6.5 |
| 45 | 18 | 9 |
| 60 | 20 | 11 |
| 75 | 20 | 13 |
| 90 | 17.5 | 15 |

| (b) | | |
|--------------|---------------|---------------------------------------|
| Storage days | AV (mg KOH/g) | AV after adding 20 ml of leaf extract |
| 0 | 0.06 | 0.04 |
| 15 | 0.08 | 0.05 |
| 30 | 0.13 | 0.05 |
| 45 | 0.17 | 0.05 |
| 60 | 0.21 | 0.07 |
| 75 | 0.25 | 0.15 |
| 90 | 0.31 | 0.21 |

| (c) | | |
|--------------|------------------------|-----------------------------------|
| Storage days | Viscosity of B20 (cSt) | Viscosity with 20 ml leaf extract |
| 0 | 3.20 | 3.17 |
| 15 | 3.21 | 3.16 |
| 30 | 3.25 | 3.16 |
| 45 | 3.31 | 3.18 |
| 60 | 3.39 | 3.21 |
| 75 | 3.50 | 3.30 |
| 90 | 3.6 | 3.39 |

7.2. Analytical Methods Utilized to Monitor/Analyze the Oxidation of Biodiesel. Monitoring the oxidation of biodiesel during storage is essential for maintaining fuel quality, complying with regulations, ensuring safety, and advancing research in the field [195]. For example, in the safety aspect, oxidation of biodiesel can also lead to the formation of byproducts such as peroxides and other reactive compounds that can pose a safety risk [196]. Therefore, by monitoring the oxidation, one can detect the formation of these compounds and take appropriate measures to ensure safe handling and storage of the fuel [197]. There are several analytical methods that can be utilized to monitor and analyze the oxidation of biodiesel, as tabulated in Table 19.

TABLE 19: Analytical methods utilized to monitor/analyze the oxidation of biodiesel.

| S/N | Methods | Analyzed parameters and remarks | Ref. |
|-----|--|---|-------|
| 1 | Rancimat | Oxidation stability (induction period) Only the highly volatile oxidation products are detected through a combination of distillation and conductivity which might provide an incomplete analysis of the oxidation stability of the sample | [198] |
| 2 | PetroOXY | Oxidation stability (induction period) Includes all volatile and nonvolatile oxidation products | [82] |
| 3 | Ultraviolet spectrophotometry | Monitoring of peroxide value and acid value | [199] |
| 4 | Nuclear magnetic resonance | It can analyze the signal intensities of the olefinic, bis-allylic, and allylic protons of the chemical bonds and saturated acyl group proportions and classify some oxidation products | [200] |
| 5 | Vibrational techniques | Monitoring oxidative stability index, acid number, and water content | [201] |
| 6 | Fluorescence spectroscopy | Can predict the biodiesel oxidation stability | [202] |
| 7 | UV-visible spectroscopy | The method can be used to monitor changes in the color and absorbance of the sample, which can be indicative of the degree of oxidation | [203] |
| 8 | GC-MS | Monitoring oxidation products, for example, higher and lower molecular weight products such as polymeric products | [204] |
| 9 | Fourier-transform infrared spectroscopy (FTIR) | Monitoring the degradation process of biodiesel associated with structural and compositional changes | [203] |
| 10 | Viscometer | Can monitor the changes of viscosity of the biodiesel | [205] |

8. Technoeconomic and Environmental Aspects of Using Natural Antioxidants for Improving Biodiesel Stability

To improve the stability of biodiesel, various methods can be applied including the use of natural antioxidants. This approach has both technoeconomic and environmental benefits.

8.1. Technoeconomic aspect. Technoeconomic aspects of using natural antioxidants include feedstock costs and production costs. Feedstocks for natural antioxidant production are often agricultural waste or plants, which are generally cheaper and more abundant than the raw materials used to produce synthetic antioxidants [89]. Additionally, natural antioxidants are often cheaper than synthetic antioxidants in terms of production cost, and natural antioxidants can often be produced using simpler and more cost-effective production processes than synthetic antioxidants [206]. For instance, the extraction of antioxidants from plant sources can be a relatively simple process compared to the complex and costly synthesis of synthetic antioxidants, making even the total production cost of biodiesel cheaper [207].

8.2. Environmental Aspects. When biodiesel is burned in engines, the byproducts produced during the process of oxidation can cause undesirable emissions to be released into the atmosphere and contribute to air pollution [208]. Therefore, the addition of natural antioxidants reduces the formation of harmful compounds during oxidation, which leads to a reduction in emissions and improved air quality [209]. Moreover, natural antioxidants are often derived from renewable sources, making them a more sustainable option than synthetic antioxidants. Biodegradability is another benefit of using natural antioxidants as compared to synthetic ones. This is because natural antioxidants break down natu-

rally in the environment and do not contribute to pollution [210].

9. Practical Implication and Limitation of the Study

9.1. Practical Implication. Natural antioxidants can improve the stability of biodiesel by reducing oxidation reactions that can lead to the formation of harmful byproducts. This can help ensure that biodiesel maintains its quality over time and reduces the need for additional stabilizers [16]. Biodiesel with antioxidants may have reduced emissions compared to conventional diesel due to the lower levels of oxidation and the resulting decrease in particulate matter [211]. Using underutilized plants and agricultural wastes as sources of natural antioxidants for biodiesel production can promote sustainable production practices, reduce waste, and provide economic benefits to farmers and communities [212]. Moreover, using natural antioxidants from underutilized plants and agricultural wastes can reduce costs associated with the production of biodiesel, as these sources are often readily available and low cost.

9.2. Limitation of the Study. While natural antioxidants have the potential to be effective in stabilizing biodiesel, there are several limitations and challenges associated, including the composition of natural antioxidants can vary depending on various factors, such as plant species, growing conditions, and harvest time [213]. This can result in inconsistent performance of the antioxidants in biodiesel stabilization. Moreover, some natural antioxidants may not be stable at high temperatures, which can limit their effectiveness in biodiesel stabilization. This is particularly problematic during the production and storage of biodiesel, where high temperatures can be present. Some natural antioxidants may have

negative impacts on engine performance, such as reduced fuel efficiency and increased emissions. Apart from that, the use of natural antioxidants in biodiesel may be subject to regulatory restrictions, which could limit their use or make their use more complicated and costly.

10. Future Perspectives

While there are challenges associated with utilizing underutilized plant resources and agricultural waste as sources of natural antioxidants like the quantity and quality that vary depending on factors such as crop yield, seasonal variations, and harvesting practices, the future scope is promising when the following is attained. For successful utilization of underutilized plants, the sustainable cultivation and processing should be developed. Developing sustainable cultivation practices for underutilized plants can promote their availability and minimize environmental impact. Furthermore, optimizing processing techniques can help preserve and maximize the antioxidant contents of these feedstocks, leading to improved utilization. The use of natural antioxidants for improving the stability of biodiesel has promising future perspectives, including the development of new sources, combination with other stabilizers, commercialization, application of nanotechnology, and standardization of testing methods. These future perspectives will contribute to the wider adoption of natural antioxidants in biodiesel stabilization and promote the use of sustainable and renewable energy sources.

11. Conclusions

The potential of natural antioxidants with high phenolic content from underutilized plant resources and agricultural wastes as additives for improving the stability of biodiesel was reviewed. Underutilized plant resources and agricultural wastes are potential sources of natural antioxidants because they are locally available, making them sustainable and eco-friendly sources. Moreover, because of their higher phenolic contents, they have been proven to have higher antioxidant activities for scavenging free radicals. It has been reported that the use of natural antioxidants has been increasing from 1.24% in 2015 to 28.57% in 2022 for underutilized plant and from 7.21% in 2015 to 18.69% in 2022 for agricultural waste. Therefore, more research is needed. Additionally, the potentiality of phenolic antioxidants present in underutilized plants and agricultural wastes lies on its ability to chelate metal ions and break oxidation chain reactions, thereby preventing the degradation of biodiesel.

12. Recommendations

The following are our recommendations based on the cited literatures that need further research:

- (1) To explore and realize the full potential of agricultural waste as a source of natural antioxidants, research and development efforts must continue. Optimizing extraction procedures, finding fresh

sources of agricultural waste and underutilized plants with high antioxidant content, and researching the synergistic effects of mixing antioxidants from various waste sources are some of the things that are to be covered

- (2) More study is needed to determine the shelf life of natural antioxidants, including how long they may be stored and under what media and environmental circumstances that they will not degrade
- (3) To tackle the challenge of biodiesel oxidation, several upgrading/removing oxygen processes can be used. These processes include hydrotreating, fractionation, and catalytic hydrodeoxygenation
- (4) The use of nanotechnology to encapsulate the antioxidants in nanoparticles to enhance their stability and solubility in biodiesel should also be studied.
- (5) The study of predictive modeling and optimization for the determination of the optimum concentration or quantity of antioxidants to be added to biodiesel for effective performance while maintaining the quality of biodiesel should be done

Abbreviations

| | |
|--------------------|--------------------------------|
| BHA: | Butylated hydroxyanisole |
| TBHQ: | Tertiary butyl hydroquinone |
| BHT: | Butylated hydroxytoluene |
| PY: | Pyrogallol |
| FAMES: | Free fatty acid methyl esters |
| DPA: | Diphenylamine |
| PG: | Propyl gallate |
| DPPH: | Diphenyl-1-picrylhydrazyl |
| TPC: | Total phenolic contents |
| TF: | Total flavonoid |
| AAT: | Antioxidant activity |
| MAE: | Microwave-assisted extraction |
| UAE: | Ultrasound-assisted extraction |
| SFE: | Supercritical fluid extraction |
| PLE: | Pressurized liquid extraction |
| IP: | Induction period |
| PV: | Peroxide value |
| AV: | Acid value |
| R [•] : | Fatty acid free radical |
| ROO [•] : | Peroxy radicals |
| ROOH: | Fatty acid hydroperoxide. |

Data Availability

The corresponding author can provide the data upon request.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] T. Tamoradi, A. R. Kiasat, H. Veisi, V. Nobakht, and B. Karmakar, "RSM process optimization of biodiesel production from rapeseed oil and waste corn oil in the presence of green and novel catalyst," *Scientific Reports*, vol. 12, no. 1, pp. 1–15, 2022.
- [2] S. Abel, L. T. Jule, L. Gudata et al., "Preparation and characterization analysis of biofuel derived through seed extracts of *Ricinus communis* (castor oil plant)," *Scientific Reports*, vol. 12, no. 1, pp. 1–11, 2022.
- [3] IEA, "Global Energy Review 2019 - The latest trends in energy and emissions in 2019," *Global Energy Trends*, pp. 1–50, 2020, <https://webstore.iea.org/download/direct/2994>.
- [4] Ö. Andersson and P. Börjesson, "The greenhouse gas emissions of an electrified vehicle combined with renewable fuels: Life cycle assessment and policy implications," *Applied Energy*, vol. 289, article 116621, 2021.
- [5] P. S. Priya, Y. Deora, R. A. Verma, C. G. Muhal, and T. Singh, "Biofuels: an alternative to conventional fuel and energy source," *Materials Today: Proceedings*, vol. 48, pp. 1178–1184, 2021.
- [6] B. Sarkar, B. Mridha, S. Pareek, M. Sarkar, and L. Thangavelu, "A flexible biofuel and bioenergy production system with transportation disruption under a sustainable supply chain network," *Journal of Cleaner Production*, vol. 317, article 128079, 2021.
- [7] M. M. Aslam, A. A. Khan, H. M. N. Cheema, M. A. Hanif, M. W. Azeem, and M. A. Azmat, "Novel mutant camelina and jatropha as valuable feedstocks for biodiesel production," *Scientific Reports*, vol. 10, no. 1, pp. 1–9, 2020.
- [8] Y.-T. Wang, W.-J. Cong, Y.-N. Zeng et al., "Direct production of biodiesel via simultaneous esterification and transesterification of renewable oils using calcined blast furnace dust," *Renewable Energy*, vol. 175, pp. 1001–1011, 2021.
- [9] M. A. Shaah, F. Allafi, M. S. Hossain et al., "Candlenut oil: review on oil properties and future liquid biofuel prospects," *International Journal of Energy Research*, vol. 45, no. 12, pp. 17057–17079, 2021.
- [10] R. Manimaran, K. M. M. Kumar, and N. S. Narayanan, "Synthesis of bio-oil from waste *Trichosanthes cucumerina* seeds: a substitute for conventional fuel," *Scientific Reports*, vol. 10, no. 1, pp. 1–12, 2020.
- [11] A. A. Babadi, S. Rahmati, R. Fakhlaei et al., "Emerging technologies for biodiesel production: processes, challenges, and opportunities," *Biomass and Bioenergy*, vol. 163, article 106521, 2022.
- [12] M. Kariminejad, A. Naimabadi, A. Morshedi, T. Mohammadi-Moghaddam, A. Shokuhi, and M. Bordbar, "Oxidative stability of sunflower and soybean oils enriched with black plum peel extract in comparison with synthetic antioxidants," *PLoS One*, vol. 18, no. 1, article e0279735, 2023.
- [13] C. K. Suraj, G. Sudarshan, K. Anand, and T. Sundararajan, "Effects of autooxidation on the fuel spray characteristics of Karanja biodiesel," *Biomass and Bioenergy*, vol. 149, article 106084, 2021.
- [14] N. Acharya, P. Nanda, S. Panda, and S. Acharya, "A comparative study of stability characteristics of mahua and jatropha biodiesel and their blends," *Journal of King Saud University - Engineering Sciences*, vol. 31, no. 2, pp. 184–190, 2019.
- [15] K. A. Sorate and P. V. Bhale, "Experimental investigation of elastomer compatibility and engine performance of biodiesel derived from deodorizer distillate," *Biofuels*, vol. 14, pp. 1–11, 2023.
- [16] L. F. Cavalheiro, M. Y. Misutsu, R. C. Rial, L. H. Viana, and L. C. S. Oliveira, "Characterization of residues and evaluation of the physico chemical properties of soybean biodiesel and biodiesel: diesel blends in different storage conditions," *Renewable Energy*, vol. 151, pp. 454–462, 2020.
- [17] P. Kumar, D. Kumar, R. Shankar, S. Kumar, P. Saini, and N. Kumar, "Effect of synthesized lemongrass biodiesel on the performance and emission characteristics of a CI engine," *Sustainable Energy Technologies and Assessments*, vol. 57, article 103221, 2023.
- [18] S. Dharma, A. S. Silitonga, A. H. Shamsuddin et al., "Properties and corrosion behaviors of mild steel in biodiesel-diesel blends," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 45, no. 2, pp. 3887–3899, 2023.
- [19] D. Kumar and B. Singh, "Tinospora cordifolia stem extract as an antioxidant additive for enhanced stability of Karanja biodiesel," *Industrial Crops and Products*, vol. 123, pp. 10–16, 2018.
- [20] C. H. Lau, S. Gan, H. L. N. Lau, L. Y. Lee, S. Thangalazhy-Gopakumar, and H. K. Ng, "Insights into the effectiveness of synthetic and natural additives in improving biodiesel oxidation stability," *Sustainable Energy Technologies and Assessments*, vol. 52, article 102296, 2022.
- [21] K. R. Spacino, D. Borsato, G. M. Buosi, and L. T. Chendynski, "Determination of kinetic and thermodynamic parameters of the B100 biodiesel oxidation process in mixtures with natural antioxidants," *Fuel Processing Technology*, vol. 137, pp. 366–370, 2015.
- [22] K. R. Spacino, E. T. da Silva, K. G. Angilelli, I. Moreira, O. F. Galao, and D. Borsato, "Relative protection factor optimisation of natural antioxidants in biodiesel B100," *Industrial Crops and Products*, vol. 80, pp. 109–114, 2016.
- [23] M. Lopes, A. Sanches-Silva, M. Castilho, C. Cavaleiro, and F. Ramos, "Halophytes as source of bioactive phenolic compounds and their potential applications," *Critical Reviews in Food Science and Nutrition*, vol. 63, pp. 1–24, 2023.
- [24] H. Hosseinzadeh-Bandbafha, D. Kumar, B. Singh et al., "Biodiesel antioxidants and their impact on the behavior of diesel engines: a comprehensive review," *Fuel Processing Technology*, vol. 232, article 107264, 2022.
- [25] J. O'Connor, B. S. Mickan, K. H. M. Siddique, J. Rinklebe, M. B. Kirkham, and N. S. Bolan, "Physical, chemical, and microbial contaminants in food waste management for soil application: a review," *Environmental Pollution*, vol. 300, 2021.
- [26] E. M. Abdo, O. E. Shaltout, and H. M. M. Mansour, "Natural antioxidants from agro-wastes enhanced the oxidative stability of soybean oil during deep-frying," *LWT*, vol. 173, article 114321, 2023.
- [27] A. A. Casazza, B. Aliakbarian, E. Sannita, and P. Peregó, "High-pressure high-temperature extraction of phenolic

- compounds from grape skins,” *International Journal of Food Science & Technology*, vol. 47, no. 2, pp. 399–405, 2012.
- [28] J. Chen, X. Jiang, G. Yang, Y. Bi, and W. Liu, “Green and efficient extraction of resveratrol from peanut roots using deep eutectic solvents,” *Journal of Chemistry*, vol. 2018, Article ID 4091930, 9 pages, 2018.
- [29] M. Kehili, M. Kammlott, S. Choura et al., “Supercritical CO₂ extraction and antioxidant activity of lycopene and β -carotene-enriched oleoresin from tomato (*Lycopersicon esculentum* L.) peels by-product of a Tunisian industry,” *Food and Bioproducts Processing*, vol. 102, pp. 340–349, 2017.
- [30] S. K. Karmee, “A spent coffee grounds based biorefinery for the production of biofuels, biopolymers, antioxidants and biocomposites,” *Waste Management*, vol. 72, pp. 240–254, 2018.
- [31] A. Devi, V. K. Das, and D. Deka, “Evaluation of the effectiveness of potato peel extract as a natural antioxidant on biodiesel oxidation stability,” *Industrial Crops and Products*, vol. 123, pp. 454–460, 2018.
- [32] R. K. Das, S. K. Brar, and M. Verma, “A fermentative approach towards optimizing directed biosynthesis of fumaric acid by *Rhizopus oryzae* 1526 utilizing apple industry waste biomass,” *Fungal Biology*, vol. 119, no. 12, pp. 1279–1290, 2015.
- [33] R. C. Rial, O. N. de Freitas, G. dos Santos, C. E. D. Nazário, and L. H. Viana, “Evaluation of the oxidative and thermal stability of soybean methyl biodiesel with additions of dichloromethane extract ginger (*Zingiber officinale* Roscoe),” *Renewable Energy*, vol. 143, pp. 295–300, 2019.
- [34] E. Amruth and L. J. Sudev, “Ageing effect and storage stability of fish biodiesel and its blends with diesel treated with orange peel extract as economical green-antioxidant additive,” *Brazilian Journal of Chemical Engineering*, vol. 40, pp. 1–8, 2023.
- [35] R. Bharti, D. Kumar, and B. Singh, “Assessing the effectiveness of bael leaf extract towards stabilization of biodiesel during accelerated oxidation tests,” *Biomass Conversion and Biorefinery*, vol. 13, no. 4, pp. 3391–3403, 2023.
- [36] M. A. Clemente, G. G. Marcheafave, H. H. Silva et al., “Addition of jaboticaba peel extract with antioxidant properties in biodiesel,” *Fuel Processing Technology*, vol. 243, article 107678, 2023.
- [37] N. Chana, A. Muengpoon, S. Pethkaew, N. Kulsin, A. Mahasuk, and S. Srirat, “Screening for phenolic compounds and oxidative capacity of fruit peels, agricultural waste, and traditional herbal medicine for use as biodiesel fuel additive,” *Songklanakarin Journal of Science & Technology*, vol. 44, no. 4, 2022.
- [38] G. Uğuz, A. Çakmak, C. D. Bento, and N. Türköz Karakullukçu, “Experimental investigation of fuel properties and engine operation with natural and synthetic antioxidants added to biodiesel,” *Biofuels*, vol. 14, no. 4, pp. 405–420, 2023.
- [39] E. D. Witt, G. Johann, C. C. Triques et al., “Potential application of supercritical extract of pomegranate peel as bio-antioxidant for biodiesel,” *Environmental Progress & Sustainable Energy*, vol. 41, no. 2, article e13755, 2022.
- [40] M. Govindasamy, S. Ramalingam, R. Dhairiyasamy, and S. Rajendran, “Investigation on thermal and storage stability of the Calophyllum inophyllum ester with natural leaf extract as antioxidant additive,” *Energy*, vol. 253, article 124117, 2022.
- [41] D. Kusumaningsih, “Mendeley as a reference management and citation generator for academic articles,” in *Proceedings of the International Conference on Applied Science and Engineering (ICASE 2018)*, vol. 175, pp. 81–83, Atlantis Press, 2018.
- [42] E. Sneha, G. V. S. Karthik, A. D. Thampi, A. Krishna, A. Revikumar, and S. Rani, “Experimental and quantum chemical investigation of bio-fuels/lubricants for its oxidative stability,” *Journal of Molecular Liquids*, vol. 340, article 117292, 2021.
- [43] S. Rajamohan, A. H. Gopal, K. R. Muralidharan et al., “Evaluation of oxidation stability and engine behaviors operated by Prosopis juliflora biodiesel/diesel fuel blends with presence of synthetic antioxidant,” *Sustainable Energy Technologies and Assessments*, vol. 52, article 102086, 2022.
- [44] W. Wang, F. Li, and H. Wang, “Study of light wavelength on the oxidative stability of Jatropha biodiesel,” *Fuel*, vol. 292, article 120230, 2021.
- [45] D. Chandran, H. K. Ng, H. L. N. Lau, S. Gan, and Y. M. Choo, “Deterioration of palm biodiesel fuel under common rail diesel engine operation,” *Energy*, vol. 120, pp. 854–863, 2017.
- [46] R. Bharti and B. Singh, “Green tea (*Camellia assamica*) extract as an antioxidant additive to enhance the oxidation stability of biodiesel synthesized from waste cooking oil,” *Fuel*, vol. 262, 2020.
- [47] N. V. P. Rangel, L. P. da Silva, V. S. Pinheiro et al., “Effect of additives on the oxidative stability and corrosivity of biodiesel samples derived from babassu oil and residual frying oil: an experimental and theoretical assessment,” *Fuel*, vol. 289, article 119939, 2020.
- [48] A. V. Kiran, J. Jayapriya, and M. Ravi, “Evaluation and predictive model development of oxidative stability of biodiesel on storage,” *Chemical Engineering Communications*, vol. 203, no. 5, pp. 676–682, 2016.
- [49] M. A. Hazrat, M. G. Rasul, M. M. K. Khan et al., “Techniques to improve the stability of biodiesel: a review,” *Environmental Chemistry Letters*, vol. 19, no. 3, pp. 2209–2236, 2021.
- [50] C. V. Jemima Romola, M. Meganaharshini, S. P. Rigby, I. Ganesh Moorthy, R. Shyam Kumar, and S. Karthikumar, “A comprehensive review of the selection of natural and synthetic antioxidants to enhance the oxidative stability of biodiesel,” *Renewable and Sustainable Energy Reviews*, vol. 145, article 111109, 2021.
- [51] M. V. da Silva, M. R. C. Santos, I. R. A. Silva et al., “Synthetic and natural antioxidants used in the oxidative stability of edible oils: an overview,” *Food Reviews International*, vol. 38, pp. 349–372, 2021.
- [52] G. Knothe, “Some aspects of biodiesel oxidative stability,” *Fuel Processing Technology*, vol. 88, pp. 669–677, 2007.
- [53] D. M. Ohlmann, N. Tschauder, J.-P. Stockis, K. Gooßen, M. Dierker, and L. J. Gooßen, “Isomerizing olefin metathesis as a strategy to access defined distributions of unsaturated compounds from fatty acids,” *Journal of the American Chemical Society*, vol. 134, no. 33, pp. 13716–13729, 2012.
- [54] P. Y. Furlan, P. Wetzel, S. Johnson, J. Wedin, and A. Och, “Investigating the oxidation of biodiesel from used vegetable oil by FTIR spectroscopy: used vegetable oil biodiesel oxidation study by FTIR,” *Spectroscopy Letters*, vol. 43, no. 7–8, pp. 580–585, 2010.
- [55] W. Tsuzuki, “Cis–trans isomerization of carbon double bonds in monounsaturated triacylglycerols via generation of free radicals,” *Chemistry and Physics of Lipids*, vol. 163, no. 7, pp. 741–745, 2010.

- [56] E. D. Christensen and R. L. McCormick, "Water contamination impacts on biodiesel antioxidants and storage stability," *Energy & Fuels*, vol. 37, no. 7, pp. 5179–5188, 2023.
- [57] H. Deviren and H. Aydın, "Production and physicochemical properties of safflower seed oil extracted using different methods and its conversion to biodiesel," *Fuel*, vol. 343, article 128001, 2023.
- [58] A. Demirbas, "Thermal degradation of fatty acids in biodiesel production by supercritical methanol," *Energy Exploration & Exploitation*, vol. 25, no. 1, pp. 63–70, 2007.
- [59] R. W. Browne and D. Armstrong, "HPLC analysis of lipid-derived polyunsaturated fatty acid peroxidation products in oxidatively modified human plasma," *Clinical Chemistry*, vol. 46, no. 6, pp. 829–836, 2000.
- [60] M. M. Rashed, M. A. Kalam, H. H. Masjuki et al., "Stability of biodiesel, its improvement and the effect of antioxidant treated blends on engine performance and emission," *RSC Advances*, vol. 5, no. 46, pp. 36240–36261, 2015.
- [61] E. Christensen, R. L. McCormick, and O. Con, "Long-term storage stability of biodiesel and biodiesel blends," *Fuel Processing Technology*, vol. 128, pp. 339–348, 2014.
- [62] N. Jeyakumar, B. Narayanasamy, D. Balasubramanian, and K. Viswanathan, "Characterization and effect of Moringa oleifera Lam. antioxidant additive on the storage stability of Jatropha biodiesel," *Fuel*, vol. 281, article 118614, 2020.
- [63] Y. Huang, F. Li, G. Bao, M. Li, and H. Wang, "Qualitative and quantitative analysis of the influence of biodiesel fatty acid methyl esters on iodine value," *Environmental Science and Pollution Research*, vol. 29, no. 2, pp. 2432–2447, 2022.
- [64] R. Sipayung, "Optimization of biodiesel production from used cooking oil using modified calcium oxide as catalyst and N-hexane as solvent," *Materials Today: Proceedings*, vol. 63, pp. S32–S39, 2022.
- [65] L. Zhang, Q. Qi, Z. Wang, G. Ren, and Z. Liu, "Development of a reduced oxidation mechanism with low-temperature chemistry for real biodiesel methyl esters," *Fuel*, vol. 338, article 127289, 2023.
- [66] Z. Dong, F. Li, H. Zhang et al., "Effects of oxidation degree and antioxidant addition on the carbon deposition tendency of jatropha biodiesel," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 45, no. 2, pp. 4917–4930, 2023.
- [67] G. S. Jatadhara, N. R. Banapurmath, T. K. Chandrashekar, S. B. Nagesh, and P. A. Harari, "Effect of diesel engine modification operated with karanja biodiesel and its blends," *Materials Today: Proceedings*, vol. 80, pp. 409–414, 2023.
- [68] E. Khethiwe, K. Clever, and G. Jerekias, "Effects of fatty acids composition on fuel properties of Jatropha curcas biodiesel," *Smart Grid and Renewable Energy*, vol. 11, no. 10, pp. 165–180, 2020.
- [69] A. E. Martínez, L. M. Magallanes, L. V. Tarditto, M. C. Pramparo, and M. F. Gayol, "Fatty acids methyl esters from soybean oil for biobased surfactants industry: obtention C16/C18 concentrate for use as feedstock," *Industrial Crops and Products*, vol. 190, article 115892, 2022.
- [70] R. N. Vilas Bôas and M. F. Mendes, "A review of biodiesel production from non-edible raw materials using the transesterification process with a focus on influence of feedstock composition and free fatty acids," *Journal of the Chilean Chemical Society*, vol. 67, no. 1, pp. 5433–5444, 2022.
- [71] P. D. Kabudke, Y. R. Kharde, and R. A. Parkhe, "Experimental investigation on performance of cotton seed biofuel blended with diesel on variable compression ratio diesel engine," *Materials Today: Proceedings*, vol. 72, pp. 846–852, 2023.
- [72] M. Muhammed Niyas and A. Shaija, "Effect of repeated heating of coconut, sunflower, and palm oils on their fatty acid profiles, biodiesel properties and performance, combustion, and emission, characteristics of a diesel engine fueled with their biodiesel blends," *Fuel*, vol. 328, article 125242, 2022.
- [73] Z. B. Njezić, M. D. Kostić, B. D. Marić et al., "Kinetics and optimization of biodiesel production from rapeseed oil over calcined waste filter cake from sugar beet processing plant," *Fuel*, vol. 334, no. July, article 126581, 2022.
- [74] T. T. Kivevele, M. M. Mbarawa, A. Bereczky, T. Laza, and J. Madarasz, "Impact of antioxidant additives on the oxidation stability of biodiesel produced from Croton megalocarpus oil," *Fuel Processing Technology*, vol. 92, no. 6, pp. 1244–1248, 2011.
- [75] K. Thakkar, S. S. Kachhwaha, and P. Kodgire, "A novel approach for improved in-situ biodiesel production process from gamma-irradiated castor seeds using synergistic ultrasound and microwave irradiation: Process optimization and kinetic study," *Industrial Crops and Products*, vol. 181, article 114750, 2022.
- [76] Y. Xue, Y. Teng, M. Chen, Z. Li, and G. Wang, "Antioxidant activity and mechanism of avenanthramides: double H+/e-processes and role of the catechol, guaiacyl, and carboxyl groups," *Journal of Agricultural and Food Chemistry*, vol. 69, no. 25, pp. 7178–7189, 2021.
- [77] C. J. Romola, P. K. Samuel, M. M. Harshini et al., "Improvement of fuel properties of used palm oil derived biodiesel with butyl ferulate as an additive," *Renewable Energy*, vol. 175, pp. 1052–1068, 2021.
- [78] N. A. Amran, U. Bello, and M. S. H. Ruslan, "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*, vol. 8, no. article e09846, 2022.
- [79] G. Uğuz, A. E. Atabani, M. N. Mohammed et al., "Fuel stability of biodiesel from waste cooking oil: a comparative evaluation with various antioxidants using FT-IR and DSC techniques," *Biocatalysis and Agricultural Biotechnology*, vol. 21, article 101283, 2019.
- [80] V. D. Kancheva, M. A. Dettori, D. Fabbri et al., "Natural chain-breaking antioxidants and their synthetic analogs as modulators of oxidative stress," *Antioxidants*, vol. 10, no. 4, p. 624, 2021.
- [81] K. Varatharajan and D. S. Pushparani, "Screening of antioxidant additives for biodiesel fuels," *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 2017–2028, 2018.
- [82] J. Zhou, Y. Xiong, and S. Xu, "Evaluation of the oxidation stability of biodiesel stabilized with antioxidants using the PetroOXY method," *Fuel*, vol. 184, pp. 808–814, 2016.
- [83] I. D. Figueredo, M. A. Rios, C. L. Cavalcante Jr., and F. M. Luna, "Effects of amine and phenolic based antioxidants on the stability of babassu biodiesel using rancimat and differential scanning calorimetry techniques," *Industrial & Engineering Chemistry Research*, vol. 59, no. 1, pp. 18–24, 2019.
- [84] G. Uğuz, "Antioxidant effect of clove oil on biodiesel produced from waste cooking oil," *Biomass Convers. Biorefinery*, vol. 13, no. 1, pp. 367–373, 2023.
- [85] L. T. Chendynski, T. Cordeiro, G. B. Messias et al., "Evaluation and application of extracts of rosemary leaves, araçá pulp

- and peel of bacuri in the inhibition of the oxidation reaction of biodiesel,” *Fuel*, vol. 261, article 116379, 2020.
- [86] L. S. De Sousa, C. V. R. De Moura, J. E. De Oliveira, and E. M. De Moura, “Use of natural antioxidants in soybean biodiesel,” *Fuel*, vol. 134, pp. 420–428, 2014.
- [87] G. Karunanithi and A. M. S. Varadappan, “Exploring the effectiveness of novel *Coffea Arabica* leaf pigment as a natural antioxidant additive for date seed biodiesel,” *Fuel*, vol. 324, article 124561, 2022.
- [88] E. J. Waweru, T. Pogrebnya, and T. T. Kivevele, “Effect of antioxidants extracted from clove wastes and babul tree barks on the oxidation stability of biodiesel made from water hyacinth of Lake Victoria origin,” *Waste and Biomass Valorization*, vol. 11, no. 11, pp. 5749–5758, 2020.
- [89] U. Bello, N. A. Amran, and M. S. H. Ruslan, “Improving antioxidant scavenging effect of fruit peel waste extracts and their applicability in biodiesel stability enhancement,” *Journal of Saudi Chemical Society*, vol. 27, no. 4, article 101653, 2023.
- [90] S. Fairus, H. M. Cheng, and K. Sundram, “Antioxidant Status Following Postprandial Challenge of Two Different Doses of Tocopherols and Tocotrienols,” *Journal of Integrative Medicine*, vol. 18, no. 1, pp. 68–79, 2020.
- [91] L. S. de Sousa, C. V. R. de Moura, and E. M. de Moura, “Action of natural antioxidants on the oxidative stability of soy biodiesel during storage,” *Fuel*, vol. 288, 2021.
- [92] G. Rodríguez, G. Squeo, L. Estivi et al., “Changes in stability, tocopherols, fatty acids and antioxidant capacity of sacha inchi (*Plukenetia volubilis*) oil during French fries deep-frying,” *Food Chemistry*, vol. 340, article 127942, 2021.
- [93] B. Ozturk, C. Parkinson, and M. Gonzalez-Miquel, “Extraction of polyphenolic antioxidants from orange peel waste using deep eutectic solvents,” *Separation and Purification Technology*, vol. 206, pp. 1–13, 2018.
- [94] W. Tan, F. Dong, J. Zhang, X. Zhao, Q. Li, and Z. Guo, “Physical and antioxidant properties of edible chitosan ascorbate films,” *Journal of Agricultural and Food Chemistry*, vol. 67, no. 9, pp. 2530–2539, 2019.
- [95] L. Lauberte, G. Telysheva, G. Cravotto et al., “Lignin - Derived antioxidants as value-added products obtained under cavitation treatments of the wheat straw processing for sugar production,” *Journal of Cleaner Production*, vol. 303, article 126369, 2021.
- [96] S. Chavoshizadeh, S. Pirsá, and F. Mohtarami, “Sesame oil oxidation control by active and smart packaging system using wheat gluten/chlorophyll film to increase shelf life and detecting expiration date,” *European Journal of Lipid Science and Technology*, vol. 122, no. 3, article 1900385, 2020.
- [97] H. E. A. Ali, E. A. El-fayoumy, W. E. Rasmy, R. M. Soliman, and M. A. Abdullah, “Two-stage cultivation of *Chlorella vulgaris* using light and salt stress conditions for simultaneous production of lipid, carotenoids, and antioxidants,” *Journal of Applied Phycology*, vol. 33, no. 1, pp. 227–239, 2021.
- [98] J. Li, X. Han, C. Huyan et al., “Hindered phenolic antioxidant modified waterborne polyurethane films with excellent thermal stability and anti-aging performance at high temperature,” *Progress in Organic Coatings*, vol. 176, article 107398, 2023.
- [99] W. U. Rahman, A. Fatima, A. H. Anwer et al., “Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst,” *Process Safety and Environmental Protection*, vol. 122, pp. 313–319, 2019.
- [100] J. S. Rodrigues, C. P. do Valle, A. F. J. Uchoa et al., “Comparative study of synthetic and natural antioxidants on the oxidative stability of biodiesel from tilapia oil,” *Renewable Energy*, vol. 156, pp. 1100–1106, 2020.
- [101] P. Li, X. Yang, W. J. Lee, F. Huang, Y. Wang, and Y. Li, “Comparison between synthetic and rosemary-based antioxidants for the deep frying of French fries in refined soybean oils evaluated by chemical and non-destructive rapid methods,” *Food Chemistry*, vol. 335, article 127638, 2021.
- [102] C. X. Li, F. R. Wang, B. Zhang, Z. Y. Deng, and H. Y. Li, “Stability and antioxidant activity of phenolic compounds during in vitro digestion,” *Journal of Food Science*, vol. 88, no. 2, pp. 696–716, 2023.
- [103] B. Narayanasamy, N. Jeyakumar, and D. Balasubramanian, “Effect of star anise as a natural antioxidant additive on the oxidation stability of lemon grass oil,” *Waste and Biomass Valorization*, vol. 12, no. 6, pp. 2983–2997, 2021.
- [104] R. Rashid, S. M. Wani, S. Manzoor, F. A. Masoodi, and M. M. Dar, “Green extraction of bioactive compounds from apple pomace by ultrasound assisted natural deep eutectic solvent extraction: optimisation, comparison and bioactivity,” *Food Chem.*, vol. 398, article 133871, 2023.
- [105] F. De Canio, “Consumer willingness to pay more for pro-environmental packages: the moderating role of familiarity,” *Journal of Environmental Management*, vol. 339, article 117828, 2023.
- [106] L. S. Schaumlöffel, L. A. M. Fontoura, S. J. Santos, L. F. Pontes, and M. Gutterres, “Vegetable tannins-based additive as antioxidant for biodiesel,” *Fuel*, vol. 292, p. 2021, 2020.
- [107] A. Arias, G. Feijoo, and M. T. Moreira, “Exploring the potential of antioxidants from fruits and vegetables and strategies for their recovery,” *Innovative Food Science & Emerging Technologies*, vol. 77, article 102974, 2022.
- [108] D. Aggarwal, A. Bhardwaj, A. K. Sobti, S. Fatma, N. Sharma, and V. Bansal, “Processing induced changes on coarse cereals (majorly millets) derived antioxidant compounds - a review,” *Functional Food Science*, vol. 2, no. 8, p. 163, 2022.
- [109] N. Dinkçi, V. Akdeniz, and A. S. Akalın, “Probiotic whey-based beverages from cow, sheep and goat milk: antioxidant activity, culture viability, amino acid contents,” *Foods*, vol. 12, no. 3, p. 610, 2023.
- [110] N. S. Mat Aron, K. S. Khoo, K. W. Chew, P. L. Show, W. H. Chen, and T. H. P. Nguyen, “Sustainability of the four generations of biofuels – a review,” *International Journal of Energy Research*, vol. 44, no. 12, pp. 9266–9282, 2020.
- [111] H. S. Hafid, F. N. Omar, N. Abdul Rahman, and M. Wakisaka, “Innovative conversion of food waste into biofuel in integrated waste management system,” *Critical Reviews in Environmental Science and Technology*, vol. 52, no. 19, pp. 3453–3492, 2022.
- [112] R. Okigbo and C. Anyaegbu, “Underutilized plants of Africa,” *Journal of Biology and Nature*, vol. 13, no. 2, pp. 1–17, 2021.
- [113] M. Wei, M. I. Mínguez, and S. Tavoletti, “Intercropping systems for sustainable agriculture,” *Agriculture*, vol. 12, no. 2, pp. 10–13, 2022.
- [114] J. Niyukuri, J. Raiti, V. Ntakarutimana, and A. Hafidi, “Lipid composition and antioxidant activities of some underused wild plants seeds from Burundi,” *Food Science & Nutrition*, vol. 9, no. 1, pp. 111–122, 2021.
- [115] L. Benchagra, H. Berrougui, M. O. Islam, and M. Ramchoun, “Antioxidant effect of Moroccan pomegranate (*Punica*

- granatum* L. Sefri Variety) extracts rich in Punicalagin against the oxidative stress process,” *Foods*, vol. 10, no. 9, p. 2219, 2021.
- [116] F. Djague, P. K. Lungai, K. R. M. Toghueo, D. Y. K. Melogmo, and B. F. Fekam, “*Garcinia kola* (Heckel) and *Alchornea cordifolia* (Schumach. & Thonn.) Müll. Arg. From Cameroon possess potential antisalmonellal and antioxidant properties,” *PLoS One*, vol. 15, no. 8, article e0237076, 2020.
- [117] S. Ahmed, B. M. Moni, S. Ahmed, D. J. Gomes, and A. M. Shohaël, “Comparative phytochemical, antioxidant, and antibacterial study of different parts of Doigota plants (*Bixa orellana* L.),” *Bulletin of the National Research Centre*, vol. 44, no. 1, pp. 1–10, 2020.
- [118] A. Chawafambira, M. M. Sedibe, A. Mpofo, and M. Achilonu, “Multivariate analyses of functional and chemical properties of *Uapaca kirkiana* fruits from Zimbabwe,” *International Journal of Fruit Science*, vol. 20, Supplement 3, pp. 1–18, 2020.
- [119] S. Adjei, I. K. Amponsah, S. O. Bekoe et al., “Fruits of *Vitex doniana* sweet: toxicity profile, anti-inflammatory and antioxidant activities, and quantification of one of its bioactive constituents oleanolic acid,” *Heliyon*, vol. 7, no. 9, p. e07910, 2021.
- [120] B. Issakou, Y. P. Payang, D. Christophe et al., “Antidermatophyte activity of ethanolic extracts of *Daniellia oliveri* (Fabaceae) and *Parinari curatellifolia* (Chrysobalanaceae) in Chad,” *GSC Advanced Research and Reviews*, vol. 13, no. 2, pp. 170–179, 2022.
- [121] N. Baenas, M. Belović, N. Ilic, D. A. Moreno, and C. García-Viguera, “Industrial use of pepper (*Capsicum annum* L.) derived products: technological benefits and biological advantages,” *Food Chemistry*, vol. 274, pp. 872–885, 2019.
- [122] V. P. Cavalcanti, S. Aazza, S. K. V. Bertolucci et al., “Solvent mixture optimization in the extraction of bioactive compounds and antioxidant activities from garlic (*Allium sativum* L.),” *Molecules*, vol. 26, no. 19, p. 6026, 2021.
- [123] X. Zou, A. Bk, A. Rauf et al., “Screening of polyphenols in tobacco (*Nicotiana tabacum*) and determination of their antioxidant activity in different tobacco varieties,” *ACS Omega*, vol. 6, no. 39, pp. 25361–25371, 2021.
- [124] L. S. Borquaye, M. S. Doetse, S. O. Baah, and J. A. Mensah, “Anti-inflammatory and anti-oxidant activities of ethanolic extracts of *Tamarindus indica* L. (Fabaceae),” *Cogent Chemistry*, vol. 6, no. 1, article 1743403, 2020.
- [125] T. T. Shonte, K. G. Duodu, and H. L. de Kock, “Effect of drying methods on chemical composition and antioxidant activity of underutilized stinging nettle leaves,” *Heliyon*, vol. 6, no. 5, 2020.
- [126] M. Errico, J. A. P. Coelho, R. P. Stateva, K. V. Christensen, R. Bahij, and S. Tronci, “Brewer’s spent grain, coffee grounds, burdock, and willow—four examples of biowaste and biomass valorization through advanced green extraction technologies,” *Foods*, vol. 12, no. 6, p. 1295, 2023.
- [127] W. K. Chishimba, E. Lingumbwanga, L. M. Tembo, and A. K. Hang’andu, “Effect of cytokinins on in vitro propagation of *Uapaca kerkiana*,” *Journal of Tropical Forest Science*, vol. 12, no. 1, pp. 28–36, 2000.
- [128] M. Muchuweti, A. R. Ndhkala, and A. Kasiamhuru, “Analysis of phenolic compounds including tannins, gallotannins and flavanols of *Uapaca kirkiana* fruit,” *Food Chemistry*, vol. 94, no. 3, pp. 415–419, 2006.
- [129] A. R. Ndhkala, K. Chitindingu, C. Mupure et al., “Antioxidant properties of methanolic extracts from *Diospyros mespiliformis* (jackal berry), *Flacourtia indica* (Batoka plum), *Uapaca kirkiana* (wild loquat) and *Ziziphus mauritiana* (yellow berry) fruits,” *International Journal of Food Science & Technology*, vol. 43, no. 2, pp. 284–288, 2008.
- [130] A. Chawafambira, M. M. Sedibe, A. Mpofo, and M. Achilonu, “*Uapaca kirkiana*, an indigenous fruit tree in sub-Saharan Africa: a comprehensive review,” *Cogent Food & Agriculture*, vol. 6, no. 1, 2020.
- [131] K. Padmalatha, K. Jayaram, N. L. Raju, M. N. Prasad, and R. Arora, “Ethnopharmacological and biotechnological significance of vitex,” *Bioremediation, Biodiversity and Bioavailability*, vol. 3, no. 1, pp. 6–14, 2009.
- [132] O. Lasekan, “Identification of the aroma compounds in *Vitex doniana* sweet: free and bound odorants,” *Chemistry Central Journal*, vol. 11, pp. 4–11, 2017.
- [133] N. Parthasarathy, “Horticulture and forestry society of Transylvania,” *Notulae Scientia Biologicae*, vol. 13, no. 1, pp. 1–12, 2022.
- [134] B. Lamage, A. Hegano, A. Tesfaye, and M. Ayele, “Evaluation of leaf litter nutrient composition, decomposition and releasing potential of *Cordia Africana*, *Terminalia Brownie* and *Vitex Doniana* tree species,” *Journal of Agriculture and Aquaculture*, vol. 4, no. 4, 2022.
- [135] P. R. Barry, A. Sanou, K. Konaté, R. R. Aworet-Samseny, O. Sytar, and M. H. Dicko, “Toxicological profile, phytochemical analysis and anti-inflammatory properties of leaves of *Vitex doniana* sweet. (Verbenaceae),” *Heliyon*, vol. 8, no. 8, pp. 4–11, 2022.
- [136] D. Charles and C. Mgina, “Antioxidant activities in *Vitex doniana* and *Saba comorensis* fruits from coastal forests of Tanzania,” *International Journal of Food Properties*, vol. 24, no. 1, pp. 1222–1228, 2021.
- [137] K. F. Traore, K. Y. Kone, A. P. Ahi et al., “Phenolic compounds characterisation and antioxidant activity of black plum (*Vitex doniana*) fruit pulp and peel from Côte d’Ivoire,” *Journal of Food Measurement and Characterization*, vol. 15, no. 2, pp. 1281–1293, 2021.
- [138] S. Ogbonnia, “Extracts of mobola plum (*parinari curatellifolia* planch ex benth, chrysobalanaceae) seeds and multiple therapeutic activities,” in *Nuts and Seeds in Health and Disease Prevention*, R. W. Victor and R. Preedy, Eds., pp. 767–774, Elsevier, 2011.
- [139] B. Mwatope, I. Chikowe, D. T. Tembo, J. F. Kamanula, F. F. F. Masumbu, and F. D. Kumwenda, “Phytochemical composition and antioxidant activity of edible wild fruits from malawi,” *BioMed Research International*, vol. 2023, Article ID 2621434, 9 pages, 2023.
- [140] M. Gororo, T. Chimponda, E. Chirisa, and S. Mukanganyama, “Multiple cellular effects of leaf extracts from *Parinari curatellifolia*,” *BMC Complementary and Alternative Medicine*, vol. 16, no. 1, pp. 1–14, 2016.
- [141] O. O. Crown, T. R. Komolafe, A. C. Akinmoladun, M. T. Olaleye, A. A. Akindahunsi, and A. A. Boligon, “*Parinari curatellifolia* seed flavonoids protect against Triton-induced dyslipidemia and atherogenicity in rats,” *Traditional & Kampo Medicine*, vol. 5, no. 1, pp. 11–18, 2018.
- [142] M. T. Olaleye, A. E. Amobonye, K. Komolafe, and A. C. Akinmoladun, “Protective effects of *Parinari curatellifolia* flavonoids against acetaminophen-induced hepatic necrosis

- in rats," *Saudi Journal of Biological Sciences*, vol. 21, no. 5, pp. 486–492, 2014.
- [143] F. Boora, E. Chirisa, and S. Mukanganyama, "Evaluation of nitrite radical scavenging properties of selected Zimbabwean plant extracts and their phytoconstituents," *Journal of Food Processing*, vol. 2014, Article ID 918018, 7 pages, 2014.
- [144] E. De Caluwé, K. Halamová, and P. Van Damme, "Tamarind (*Tamarindus indica* L.): a review of traditional uses, phytochemistry and pharmacology," in *ACS Symposium Series*, pp. 85–110, American Chemical Society (ACS), 2009.
- [145] A. A. Ayat, A. R. A. Shima, H. E. Sahar et al., "The effect of blending of extracts of Sudanese *Adansonia digitata* and *Tamarindus indica* on their antioxidant, anti-inflammatory and antimicrobial activities," *Journal of Pharmacognosy and Phytotherapy*, vol. 11, no. 2, pp. 28–34, 2019.
- [146] R. Wandee, K. Sutthanut, J. Songsri et al., "Tamarind seed coat: a catechin-rich source with anti-oxidation, anti-melanogenesis, anti-adipogenesis and anti-microbial activities," *Molecules*, vol. 27, no. 16, p. 5319, 2022.
- [147] S. Natukunda, J. H. Muyonga, and I. M. Mukisa, "Effect of tamarind (*Tamarindus indica* L.) seed on antioxidant activity, phytochemicals, physicochemical characteristics, and sensory acceptability of enriched cookies and mango juice," *Food Science & Nutrition*, vol. 4, no. 4, pp. 494–507, 2016.
- [148] N. Naeem, F. Nadeem, M. W. Azeem, and R. M. Dharmadasa, "Tamarindus indica—a review of explored potentials," *International Journal of Chemical and Biochemical Sciences*, vol. 12, pp. 98–106, 2017.
- [149] S. Luengthanaphol, D. Mongkholkhajornsilp, S. Douglas, P. L. Douglas, L. I. Pengsopa, and S. Pongamphai, "Extraction of antioxidants from sweet Thai tamarind seed coat - preliminary experiments," *Journal of Food Engineering*, vol. 63, no. 3, pp. 247–252, 2004.
- [150] L. Leng, N. Nadzri, A. Shaari, N. A. Razak, and K. Yee, "Antioxidant capacity and total phenolic content of fresh, oven-dried and stir-fried tamarind leaves," *Current Research in Nutrition and Food Science Journal*, vol. 5, no. 3, pp. 282–287, 2017.
- [151] B. B. Mansingh, J. S. Binoj, N. P. Sai et al., "Sustainable development in utilization of *Tamarindus indica* L. and its by-products in industries: A review," *Current Research in Green and Sustainable Chemistry*, vol. 4, article 100207, 2021.
- [152] C. M. Martins, D. M. Ferro, E. S. de Brito, and S. R. S. Ferreira, "Industrial relevance of *Tamarindus indica* L. by-products as source of valuable active metabolites," *Innovative Food Science & Emerging Technologies*, vol. 66, article 102518, 2020.
- [153] C. M. Martins, J. A. C. Guedes, E. S. de Brito, and S. R. S. Ferreira, "Valorization of tamarind seeds using high-pressure extraction methods to obtain rich fractions in fatty acid and phenolic compounds," *The Journal of Supercritical Fluids*, vol. 183, article 105556, 2022.
- [154] A. Palma, M. J. Díaz, M. Ruiz-Montoya, E. Morales, and I. Giráldez, "Ultrasound extraction optimization for bioactive molecules from *Eucalyptus globulus* leaves through antioxidant activity," *Ultrasonics Sonochemistry*, vol. 76, 2021.
- [155] G. M. Buosi, E. T. Da Silva, K. Spacino, L. R. C. Silva, B. A. D. Ferreira, and D. Borsato, "Oxidative stability of biodiesel from soybean oil: comparison between synthetic and natural antioxidants," *Fuel*, vol. 181, pp. 759–764, 2016.
- [156] D. F. Kaoke, E. Siryabe, D. Iya-Sou, E. Talla, and P. M. Kouotou, "Physicochemical potential of *Balanites aegyptiaca* seed kernel oil from Northern Cameroon for biodiesel valorization," *Journal of Energy Research and Reviews*, vol. 9, no. 1, pp. 21–31, 2021.
- [157] M. Stramarkou, T.-V. Missirli, K. Kyriakopoulou, S. Papadaki, A. Angelis-Dimakis, and M. Krokida, "The recovery of bioactive compounds from olive pomace using green extraction processes," *Resources*, vol. 12, no. 7, pp. 1–22, 2023.
- [158] A. I. Talmaciu, I. Volf, and V. I. Popa, "A comparative analysis of the 'green' techniques applied for polyphenols extraction from bioresources," *Chemistry & Biodiversity*, vol. 12, no. 11, pp. 1635–1651, 2015.
- [159] M. F. Montenegro-Landívar, P. Tapia-Quirós, X. Vecino et al., "Fruit and vegetable processing wastes as natural sources of antioxidant-rich extracts: evaluation of advanced extraction technologies by surface response methodology," *Journal of Environmental Chemical Engineering*, vol. 9, no. 4, article 105330, 2021.
- [160] S. S. Ferreira, T. A. Brito, A. P. R. Santana et al., "Greenness of procedures using NADES in the preparation of vegetal samples: Comparison of five green metrics," *Talanta Open*, vol. 6, article 100131, 2022.
- [161] B. Nayak, F. Dahmoune, K. Moussi et al., "Comparison of microwave, ultrasound and accelerated-assisted solvent extraction for recovery of polyphenols from *Citrus sinensis* peels," *Food Chemistry*, vol. 187, pp. 507–516, 2015.
- [162] S. Chakraborty, S. Majumder, A. Ghosh, S. Saha, and M. Bhattacharya, "Metabolomics of potential contenders conferring antioxidant property to varied polar and non-polar solvent extracts of *Edgaria darjeelingensis* C.B. Clarke," *Bulletin of the National Research Centre*, vol. 45, no. 1, 2021.
- [163] K. G. Lee and T. Shibamoto, "Antioxidant property of aroma extract isolated from clove buds [*Syzygium aromaticum* (L.) Merr. et Perry]," *Food Chemistry*, vol. 74, no. 4, pp. 443–448, 2001.
- [164] A. Ismail, Z. M. Marjan, and C. W. Foong, "Total antioxidant activity and phenolic content in selected vegetables," *Food Chemistry*, vol. 87, no. 4, pp. 581–586, 2004.
- [165] I. Muhson and A. Al Mashkor, "Evaluation of antioxidant activity of clove (*Syzygium aromaticum*)," *International Journal of Chemical Science*, vol. 13, no. 1, pp. 23–30, 2015.
- [166] L. S. Pinho, M. P. Silva, M. Thomazini et al., "Guaraná (*Paulinia cupana*) by-product as a source of bioactive compounds and as a natural antioxidant for food applications," *Journal of Food Processing and Preservation*, vol. 45, no. 10, pp. 1–13, 2021.
- [167] A. A. Vilas-Boas, A. Oliveira, T. B. Ribeiro et al., "Impact of extraction process in non-compliant 'Bravo de Esmolfe' apples towards the development of natural antioxidant extracts," *Applied Sciences*, vol. 11, no. 13, 2021.
- [168] R. Wang, R. He, Z. Li, S. Li, C. Li, and L. Wang, "Tailor-made deep eutectic solvents-based green extraction of natural antioxidants from partridge leaf-tea (*Mallotus furetianus* L.)," *Separation and Purification Technology*, vol. 275, article 119159, 2021.
- [169] H. Alasalvar and Z. Yildirim, "Ultrasound-assisted extraction of antioxidant phenolic compounds from *Lavandula angustifolia* flowers using natural deep eutectic solvents: an experimental design approach," *Sustainable Chemistry and Pharmacy*, vol. 22, article 100492, 2021.
- [170] K. Y. Lee, M. S. Rahman, A. N. Kim et al., "Supercritical fluid tomato extract for stabilization of perilla oil subjected to

- thermal treatment,” *Journal of Food Processing and Preservation*, vol. 44, no. 3, pp. 1–8, 2020.
- [171] A. Zeroual, E. H. Sakar, F. Mahjoubi, M. Chaouch, A. Chaqroune, and M. Taleb, “Effects of extraction technique and solvent on phytochemicals, antioxidant, and antimicrobial activities of cultivated and wild rosemary (*Rosmarinus officinalis* L.) from Taounate region (Northern Morocco),” *Biointerface Research in Applied Chemistry*, vol. 12, no. 6, pp. 8441–8452, 2022.
- [172] C. F. Poole, “Solvent selection and method development for thin-layer chromatography,” in *Instrumental Thin-Layer Chromatography*, pp. 47–80, Elsevier, 2023.
- [173] T. Ouatmani, H. Haddadi-Guemghar, L. Boulekbache-Makhlouf, D. Mehidi-Terki, A. Maouche, and K. Madani, “A sustainable valorization of industrial tomato seeds (cv Rio Grande): sequential recovery of a valuable oil and optimized extraction of antioxidants by microwaves,” *Journal of Food Processing and Preservation*, vol. 46, no. 1, pp. 1–13, 2022.
- [174] P. Sharayei, E. Azarpazhooh, S. Zomorodi, S. Einafshar, and H. S. Ramaswamy, “Optimization of ultrasonic-assisted extraction of astaxanthin from green tiger (*Penaeus semisulcatus*) shrimp shell,” *Ultrasonics Sonochemistry*, vol. 76, article 105666, 2021.
- [175] X. Cai, M. Xiao, X. Zou, J. Tang, B. Huang, and H. Xue, “Separation of six antioxidants from *Hypsizygus marmoreus* by high-speed countercurrent chromatography utilizing an approach based upon the polarity parameter model,” *Journal of Chromatography A*, vol. 1633, article 461650, 2020.
- [176] M. Monteiro, R. A. Santos, P. Iglesias et al., “Effect of extraction method and solvent system on the phenolic content and antioxidant activity of selected macro- and microalgae extracts,” *Journal of Applied Phycology*, vol. 32, no. 1, pp. 349–362, 2020.
- [177] S. Hosni, S. S. A. Gani, V. Orsat, M. Hassan, and S. Abdullah, “Ultrasound-assisted extraction of antioxidants from *Melastoma malabathricum* Linn.: modeling and optimization using Box–Behnken design,” *Molecules*, vol. 28, no. 2, p. 487, 2023.
- [178] B. A. Ziyad, M. Yousfi, and Y. Vander Heyden, “Effects of growing region and maturity stages on oil yield, fatty acid profile and tocopherols of *Pistacia atlantica* Desf. fruit and their implications on resulting biodiesel,” *Renewable Energy*, vol. 181, pp. 167–181, 2022.
- [179] R. C. Rial, T. C. Merlo, P. H. Michalski Santos et al., “Evaluation of oxidative stability of soybean methyl biodiesel using extract of cagaite leaves (*Eugenia dysenterica* DC.) as additive,” *Renewable Energy*, vol. 152, pp. 1079–1085, 2020.
- [180] L. S. de Sousa, C. V. R. de Moura, and E. M. de Moura, “Influence of binary, ternary and quaternary mixtures on oxidative stability and study of kinetics and thermodynamic parameters of the degradation process of soybean biodiesel,” *Fuel*, vol. 259, article 116235, 2020.
- [181] C. A. Sagaste, G. Montero, M. A. Coronado et al., “Creosote bush (*Larrea tridentata*) extract assessment as a green antioxidant for biodiesel,” *Molecules*, vol. 24, no. 9, p. 1786, 2019.
- [182] A. Devi, V. K. Das, and D. Deka, “A green approach for enhancing oxidation stability including long storage periods of biodiesel via *Thuja orientalis* L. as an antioxidant additive,” *Fuel*, vol. 253, pp. 1264–1273, 2019.
- [183] G. Uguz, “Inhibitory effect of thyme oil as an antioxidant for waste cooking oil biodiesel crystallization,” *Energy & Environment*, vol. 34, no. 1, pp. 176–192, 2023.
- [184] D. Donoso, D. Bolonio, M. Lapuerta, and L. Canoira, “Oxidation stability: the bottleneck for the development of a fully renewable biofuel from wine industry waste,” *ACS Omega*, vol. 5, no. 27, pp. 16645–16653, 2020.
- [185] N. L. Boschen, M. G. P. Valenga, G. A. R. Maia, A. L. Gallina, and P. R. P. Rodrigues, “Synergistic study of the antioxidant potential of barley waste for biodiesel,” *Industrial Crops and Products*, vol. 140, article 111624, 2019.
- [186] S. Jain, S. Purohit, D. Kumar, and V. V. Goud, “Passion fruit seed extract as an antioxidant additive for biodiesel; shelf life and consumption kinetics,” *Fuel*, vol. 289, article 119906, 2021.
- [187] M. A. Molinares, N. L. Bosch, D. Y. Pelegrini et al., “The influence of *Annona muricata* L. peel extract as a potent source of natural antioxidant on soybean oxidation stability,” *Brazilian Journal of Development*, vol. 8, no. 10, pp. 69709–69727, 2022.
- [188] B. H. H. Goh, C. T. Chong, H. C. Ong et al., “Strategies for fuel property enhancement for second-generation multi-feedstock biodiesel,” *Fuel*, vol. 315, article 123178, 2022.
- [189] O. Dorosh, E. Surra, M. Eusebio et al., “Vineyard pruning extracts as natural antioxidants for biodiesel stability: experimental tests and preliminary life cycle assessment,” *ACS Sustainable Chemistry & Engineering*, vol. 11, pp. 8084–8095, 2023.
- [190] N. Jeyakumar, Z. Huang, D. Balasubramanian et al., “Experimental evaluation over the effects of natural antioxidants on oxidation stability of binary biodiesel blend,” *International Journal of Energy Research*, vol. 46, no. 14, pp. 20437–20461, 2022.
- [191] X. Huang, W. Gao, X. Yun, Z. Qing, and J. Zeng, “Effect of natural antioxidants from marigolds (*Tagetes erecta* L.) on the oxidative stability of soybean oil,” *Molecules*, vol. 27, no. 9, p. 2865, 2022.
- [192] A. Gaur, G. Dwivedi, P. Baredar, and S. Jain, “Influence of blending additives in biodiesel on physicochemical properties, engine performance, and emission characteristics,” *Fuel*, vol. 321, article 124072, 2022.
- [193] V. Kumbhar, A. Pandey, C. R. Sonawane, A. S. El-Shafay, H. Panchal, and A. J. Chamkha, “Statistical analysis on prediction of biodiesel properties from its fatty acid composition,” *Case Studies in Thermal Engineering*, vol. 30, article 101775, 2022.
- [194] F. Vetica, A. Sansone, C. Ferreri, and C. Chatgililoglu, “A convenient route to mono-trans polyunsaturated free fatty acids,” *Journal of Chemical Research*, vol. 46, no. 2, 2022.
- [195] N. S. Rao, N. H. M. Zini, M. N. A. Saadun, and F. S. Anuar, “Biodiesel storage stability: evaluation and monitoring advancements,” in *Proceedings of the 7th International Conference and Exhibition on Sustainable Energy and Advanced Materials (ICE-SEAM 2021)*, pp. 241–245, Melaka, Malaysia, 2022.
- [196] B. A. Oni, S. E. Sanni, B. O. Ezurike, and E. E. Okoro, “Effect of corrosion rates of preheated *Schinzochytrium* sp. microalgae biodiesel on metallic components of a diesel engine,” *Alexandria Engineering Journal*, vol. 61, no. 10, pp. 7509–7528, 2022.
- [197] J. A. Melo, L. A. de Aquino Silva, J. M. Santos, and A. Wisniewski Jr., “Advanced characterization of oxidized

- derivatives in alternative fatty esters mixture for biodiesel purposes,” *Fuel*, vol. 309, article 122109, 2022.
- [198] L. Botella, F. Bimbela, L. Martín, J. Arauzo, and J. L. Sánchez, “Oxidation stability of biodiesel fuels and blends using the Rancimat and PetroOXY methods. Effect of 4-allyl-2,6-dimethoxyphenol and catechol as biodiesel additives on oxidation stability,” *Frontiers in Chemistry*, vol. 2, pp. 1–9, 2014.
- [199] T. M. F. S. Vieira and M. A. B. R. Arce, “Ultraviolet spectrophotometric evaluation of corn oil oxidative stability during microwave heating and oven test,” *Journal of Agricultural and Food Chemistry*, vol. 47, no. 6, pp. 2203–2206, 1999.
- [200] A. C. G. Mantovani, L. T. Chendynski, D. Galvan, F. C. de Macedo Júnior, D. Borsato, and E. Di Mauro, “Thermal-oxidation study of biodiesel by proton nuclear magnetic resonance (1H NMR),” *Fuel*, vol. 274, article 117833, 2020.
- [201] L. F. B. de Lira, M. S. de Albuquerque, J. G. A. Pacheco et al., “Infrared spectroscopy and multivariate calibration to monitor stability quality parameters of biodiesel,” *Microchemical Journal*, vol. 96, no. 1, pp. 126–131, 2010.
- [202] F. S. Michels, M. A. G. Trindade, E. A. Falcão, R. C. A. Guimarães, S. L. Oliveira, and A. R. L. Caires, “The effect of the excitation light intensity during on-line monitoring of biodiesel by fluorescence spectroscopy,” *Fuel*, vol. 193, pp. 395–400, 2017.
- [203] J. Zhou, Y. Xiong, Y. Gong, and X. Liu, “Analysis of the oxidative degradation of biodiesel blends using FTIR, UV – Vis, TGA and TD-DES methods,” *Fuel*, vol. 202, pp. 23–28, 2017.
- [204] K. Bacha, A. Ben-Amara, A. Vannier, M. Alves-Fortunato, and M. Nardin, “Oxidation stability of diesel/biodiesel fuels measured by a petrooxy device and characterization of oxidation products,” *Energy and Fuels*, vol. 29, no. 7, pp. 4345–4355, 2015.
- [205] R. A. Usmanov, S. V. Mazanov, A. R. Gabitova et al., “The effect of fatty acid ethyl esters concentration on the kinematic viscosity of biodiesel fuel,” *Journal of Chemical & Engineering Data*, vol. 60, no. 11, pp. 3404–3413, 2015.
- [206] A. Sharma and S. Murugan, “Effect of blending waste tyre derived fuel on oxidation stability of biodiesel and performance and emission studies of a diesel engine,” *Applied Thermal Engineering*, vol. 118, pp. 365–374, 2017.
- [207] J. R. Orives, D. Galvan, J. L. Pereira, R. L. Coppo, and D. Borsato, “Experimental design applied for cost and efficiency of antioxidants in biodiesel,” *Journal of the American Oil Chemists’ Society*, vol. 91, no. 10, pp. 1805–1811, 2014.
- [208] S. Nogales-Delgado, A. Guiberteau, and J. M. Encinar, “Effect of tert-butylhydroquinone on biodiesel properties during extreme oxidation conditions,” *Fuel*, vol. 310, article 122339, 2022.
- [209] N. Jeyakumar and B. Narayanasamy, “Effect of Basil antioxidant additive on the performance, combustion and emission characteristics of used cooking oil biodiesel in CI engine,” *Journal of Thermal Analysis and Calorimetry*, vol. 140, no. 1, pp. 457–473, 2020.
- [210] Z. Khounani, H. Hosseinzadeh-Bandbafha, K. Moustakas et al., “Environmental life cycle assessment of different biorefinery platforms valorizing olive wastes to biofuel, phosphate salts, natural antioxidant, and an oxygenated fuel additive (triacetin),” *Journal of Cleaner Production*, vol. 278, article 123916, 2021.
- [211] P. V. E. B. Dhinesh and J. J. M. Nambiraj, “Effects of antioxidants to reduce the harmful pollutants from diesel engine using preheated palm oil – diesel blend,” *Journal of Thermal Analysis and Calorimetry*, vol. 147, 2022.
- [212] Y.-G. Lee, E.-J. Cho, S. Maskey, D.-T. Nguyen, and H.-J. Bae, “Value-added products from coffee waste: a review,” *Molecules*, vol. 28, no. 8, p. 3562, 2023.
- [213] A. Islam, H. Singh, and A. Sharma, “Impact of regional quality assessment of *Tinospora cordifolia*: a scientific perspective for exploration of harvest strategy as a quality marker,” *Agricultural Research*, vol. 12, pp. 1–8, 2023.