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Research Paper

Bio-waste Crude Extracts as Alternatives to Synthetic Antioxidants in Petroleum Lubricants

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Abstract

The increasing environmental concerns and the need for enhanced lubricant stability in petroleum industry necessitate sustainable solutions. This paper reports the use of crude extracts from bio-wastes of lemongrass and pepper fruits, as eco-friendly antioxidants to improve thermal and oxidation stability in petroleum lubricants. The bio-wastes samples were collected from Buguruni market in Ilala district of Dar es Salaam, Tanzania. The samples were dried, ground into powder, methanol-extracted, and concentrated to yield crude extracts. The crude extracts were then analyzed via phytochemical tests, Fourier Transform Infrared (FTIR) and gas Chromatography Mass Spectrometry (GC-MS) to identify antioxidant compounds. The extracts were blended with petroleum base oils and tested for oxidation and thermal stability using a Seta oxidation stability bath and Thermogravimetric Analysis, respectively. Kinematic viscosity and volatility analyses were also conducted. The phytochemical, FTIR, and GC-MS analyses confirmed that the extracts were rich in radical scavengers. The oxidation tests showed that base oils added with crude extracts had an induction time of 400 min, compared to the 320 min for those without, demonstrating that the extracts suppress oxidation. Thermal stability tests indicated that the oils blended extracts exhibited higher temperatures at maximum weight loss (>250 °C) and had fewer insoluble residues, suggesting improved stability. Moreover, kinematic viscosity increased and volatility reduced, implying enhanced lubrication and high-temperature stability. Both lemongrass and pepper fruits extracts had similar antioxidant effectiveness, validating their potential in petroleum lubricants. This research underlines bio-waste's viability as an antioxidant source, contributing to a circular economy in the energy sector.

1. Introduction

Petroleum lubricant is a substance that helps to reduce friction between surfaces in mutual contact, ultimately reducing the heat generated when the surfaces move. It is formed by two major components: base stock (or base oil) and additives. Base oil has an oily consistency characteristic, chemical composition, and lubricating properties. It is a mixture of hydrocarbon molecules of different sizes (C-17 to C-95) and compositions (Kramer et al., 2000). Base oil is the major contributor of lubricant oil as it accounts for 70 – 90 %, and the remaining part is covered by additives (Owuna, 2020). The effectiveness of these lubricants largely depend on their viscosity index, oxidation resistance, and the ability to prevent corrosion (Oladimeji et al., 2018).

Petroleum lubricants heavily rely on additives to enhance their thermal and oxidation stabilities. However, the synthetic antioxidants currently used,

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such as zinc dithiophosphates and polysulphides, although common, fall short in several critical areas. They are expensive, harmful to the environment, and prone to degradation under adverse conditions such as contamination during production, storage, and transportation (Jedrzejczyk et al., 2021; Quinchia et al., 2011). These shortcomings limit their effectiveness and raise substantial concerns regarding their overall utility and impact (Garcia et al., 2017; Muala et al., 2021). Given these challenges, there is a compelling need to develop sustainable, cost-effective, and environmentally friendly alternatives that can maintain or even enhance the performance of petroleum lubricants without the associated drawbacks of synthetic additives.

Various alternatives of synthetic antioxidants have been considered. For instance, a study has shown that the use of ionic liquids as lubricants can enhance long-term stability during oxidation by specific chemical modifications (Zhou et al., 2009). Specifically, the study showed the synthesis of oil miscible novel silane functionalized imidazoline-based ionic liquids as lubricant additives for their effect on properties like viscosity, thermal stability, and compatibility. The incorporation of lignin-based additives in bio lubricant formulations has been proposed to improve thermal-oxidative stability based on lignin's known antioxidant properties (De Almeida et al., 2020; Zhou et al., 2009). Furthermore, the development of fully bio-based lubricants from agro-industrial residues has shown elevated stability and higher onset oxidative temperatures, indicating potential as sustainable alternatives (Karmakar et al., 2017). Moreover, the modification of vegetable oils to prepare green lubricants has been explored, with thermally polymerized soybean oil mixed with additives and diluents showing promise as a bio-based gear oil (Pandey et al., 2022).

Amid to the advancements on antioxidants, natural antioxidants derived from biomass have emerged as particularly promising. These biomass-derived antioxidants are known for their broad spectrum of free radical scavenging molecules, including phenolic compounds (flavonoids, phenolic acids, coumarins, lignans, quinines, tannins, and stilbenes) and nitrogen compounds (amines, alkaloids, betalains) which are rich in antioxidant activity (Amri et al., 2017; Shahbaz et al., 2022). The radical scavengers such as phenols and aromatic amines have shown potential as effective alternatives to traditional synthetic antioxidants in lubricant formulations (Erhan et al., 2006). Despite the promising outlook, research into the use of natural antioxidants from biomass in lubricants is still in its emerging stages. There remains a significant need to further investigate their applicability and effectiveness comprehensively. The ongoing exploration and understanding of these natural alternatives are crucial for developing robust, sustainable lubrication technologies that can significantly enhance the stability and reduce the environmental footprint of the lubricants. The pursuit of such research continues to unfold the potential of bio-waste-derived antioxidants, which could ultimately replace synthetic counterparts and align with global sustainability goals.

This study specifically aimed to investigate the potential of crude extracts from bio-wastes of lemongrass (BLG) and pepper fruits (BPF), as promising alternatives to synthetic antioxidants in petroleum lubricants. The findings are anticipated to broaden the source of eco-friendly lubricant antioxidants. Additionally, utilizing bio-waste as a source of antioxidants would aid in reducing the ecological burden of bio-waste, while enhancing biodiversity and mitigating the traditional "take-use-dispose" approach, thereby promoting a circular economy. This research underscores the significance of transitioning towards sustainable raw materials for industrial applications, reflecting a progressive step towards environmental stewardship and resource efficiency.

2. Materials and Methods

2.1. Sample collection and preparation

The petroleum base oil sample 1(BO_1) was supplied by General Petroleum Limited Blending Plant, from Temeke district in Dar es Salaam, Tanzania. The other petroleum base oil samples 2, 3 and 4, abbreviated as BO_2, BO_3 and BO_4, respectively, were supplied by Government Chemist Laboratory Authority (GCLA) in Dar es Salaam, Tanzania. The two selected bio-wastes; namely, BLG and BPF, were collected from Buguruni

market located in Ilala district in Dar es Salaam, Tanzania.

The bio-wastes were washed initially with running tap water to remove loose soil and debris, followed by two subsequent washes with distilled water to ensure all residual contaminants were removed. After washing, the bio-wastes were laid out in a single layer and air-dried under ambient conditions for a week. The choice of a seven-day drying period was based on preliminary trials which indicated this duration was sufficient for achieving a consistent level of dryness suitable for milling, as confirmed by reaching a constant weight (weight stabilization). Once thoroughly dried, the bio-wastes were processed using a KHD Humboldt Wedag AG, Millar machine housed at the Department of Botany, University of Dar es Salaam (UDSM), Tanzania. The ground material was then sieved through a 1 mm sieve to ensure uniform particle size and consistency, weighed, and stored in airtight containers to prevent moisture absorption prior to analysis.

2.2. Chemicals and reagents

Analytical grade chemicals were procured from SMACCO FLO (T) LIMITED in Arusha, Tanzania, which sources its products from Merck Chemical and Pharmaceutical Company. The chemicals with their respective percentage purity were methanol (99.85%), ferric chloride (99.9%), sodium nitrite (99%), concentrated sulfuric acid (99.99%), sodium hydroxide (99.99%), bromine water (99%), nitrous acid (95%), toluene (99.7%), and acetone (99.9%). Distilled water was purchased from the College of Engineering and Technology (CoET), University of Dar es Salaam (UDSM), Tanzania.

2.3. Extraction and characterization

Extraction of crude extracts from - was performed through the maceration process with slight modification in methods given by Muala et al. (2021). About 40 g powder of each sample was soaked separately in 1000 mL of methanol for about 72 hours at room temperature. Methanol was chosen as a solvent for extraction due to its ability of extracting bioactive components well, particularly high polar compounds like flavonoids and polyphenols (Venkatayappa and Reddy, 2017). Additionally, methanol has been found to be effective in extracting phenolic materials and preserving the oxidative properties of plants, making it a suitable choice for such extractions (Fazeli-Nasab et al., 2021). Following the maceration, the mixtures were decanted and then filtered through Whatman filter paper No. 1 to obtain clear extract solutions. These solutions were then concentrated using a vacuum rotary evaporator under low pressure at a temperature of 40 °C. This step ensures the removal of methanol under gentle conditions to preserve the integrity of the extracted compounds. The concentrated crude extracts were subsequently air-dried at room temperature to remove any residual solvent and then weighed. The yield of the crude extracts was quantified in percentage using Eq. 1, providing a measure of the extraction efficiency.

$$\%Yield = \frac{weight\ of\ dry\ extract\ (g)}{Intial\ weight\ of\ raw\ material\ (g)} x100 \ldots (1)$$

2.4. Phytochemical analysis of the crude extracts

Chemical tests were conducted to rigorously screen for the presence of radical scavengers, specifically phenols and amines, within the crude extracts (Agatonovic-Kustrin et al., 2016). The screening for phenolic compounds was performed using the Ferric Chloride Test, which is effective in detecting phenols due to their ability to form complexes with ferric ions. A few drops of ferric chloride solution were added to a sample of the extract, and the formation of a green-blue color indicated the presence of phenols, reflecting their complexation with the ferric ions. Additionally, the Libermann's Test was utilized for phenols, involving the treatment of the extract with chloroform and a few drops of acetic anhydride, followed by the careful addition of concentrated sulfuric acid. A shift in color from yellow to deep red upon standing confirmed the presence of phenolic structures.

For the detection of amines, the Halogenation Test was employed, which identifies aromatic amines through their reaction with bromine water. When bromine water was added to the extract, the presence of aromatic amines was confirmed by the disappearance of the bromine's brown color, indicating the formation of a halogenated amine. The Libermann's Nitroso Test was also performed to assess the presence of amines. This test involved adding nitrous acid to the extract, which

reacts with any amines to form a nitroso derivative, indicated by a color change to deep blue or green, depending on the type of amine present.

2.5. Moisture content of crude extracts

To ascertain the suitability of the bio-waste for long-term storage and its resistance to microbial degradation, the moisture content of the crude extracts was determined using the procedures outlined by Clark and Snyder (1991). Initially, two crucibles were weighed empty, and then each was weighed again after adding 10 g of crude extract. These filled crucibles were placed in an oven and dried at 105 °C for 24 h. After drying, the crucibles were transferred to a desiccator to cool for 6 h. Once cooled, the crucibles were weighed again. The moisture content was then calculated using Eq. 2, providing insights into the extract's stability and storage potential.

$$MC(\%) = \frac{W_2 - W_3}{W_2 - W_1} x100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where: MC = Moisture Content, W_1 = Weight of crucible (g), W_2 = Weight of crucible + sample (g), and W_3 = Weight of crucible + sample after drying and cooling (g)

2.6. Chemical functional groups and composition of crude extracts

Fourier transform infrared (FTIR) spectroscopy (Shimadzu IR affinity 1, Japan) was used to identify the chemical functional groups present in the crude extract samples, utilizing potassium bromide (KBr) as a standard (Younis et al., 2021). Initially, two clean discs were scanned to establish background spectra. Subsequently, 1 mg of potassium bromide (KBr) was placed on a disc, and a mixture of the crude extract with KBr was placed on the second disc. The discs were then loaded into an FTIR Spectrometer. The spectrometer was set to scan from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, providing detailed spectral data that facilitated the analysis of the various functional groups within the extracts.

The chemical compositions of crude extract samples were analyzed using a gas chromatograph-mass spectrometer, GC-MS (Shimadzu QP2010 Ultra, Japan) equipped with an Rtx-5MS (30 m × 0.25µm ×0.25µm) capillary column (Belguith et al., 2024). High-purity helium was used as the carrier gas at a flow rate of 1.21 mL/min and an average velocity of 54.6 cm/sec. The oven temperature started at 90 ºC, was held for 2 min, then increased at a rate of 5 ºC/min to 280 ºC and held for 4 min. The injector temperature was maintained at 250 ºC in splitless mode with a 3 mL/min purge flow. The internal pressure was set at 150 kPa, and the interface temperature was maintained at 300 ºC. The ionization mode of the mass spectrometer was electron impact (EI) set at 0.2 volts with an ion source temperature of 230 ºC, operating in full scan mode in the 45-500 m/z range. The Mass Spectral Library and Search Software (NIST 11) was used to identify phytochemicals in the extracts. The peak integration method (area normalization) was employed to quantify the phytochemicals in the extracts. For injection, 10 µL of the sample was dissolved in dichloromethane to make a 1 mL solution, and about 1 µL of this sample solution was then injected into the GC-MS. In qualitative analyses, the results were reported as percentage compositions derived from the peak area of all scanned compounds in the extracts.

2.7. The blending of base oils with crude extracts

The blending process followed the method stated by Okoye et al. (2010). The process was carefully designed to integrate bio-waste crude extracts into base oils to enhance their properties. Specifically, approximately 0.1 g of BLG crude extract and 0.1 g of BPF crude extract were separately measured and placed into dry, tared 250 mL capacity borosilicate glass beakers. An additional mixture of equal parts, 0.05 g each, of BLG and BPF extracts, was also prepared in another beaker. To these beakers, 100 mL of each selected base oil (BO_1, BO_2, BO_3, and BO_4) was added, resulting in a total of 12 distinct sets. The equal ratios of 0.05 g each extract was considered to assess if their synergistic effects could provide a compounded benefit to the base oils without the dominance of one extract over the other, which could mask individual contributions. The chosen ratios of 0.1 g of each extract per 100 mL of base oil were determined through preliminary testing where these concentrations showed the most significant modifications in oxidative stability and viscosity without compromising the fluid's inherent properties. Higher concentrations were tested but led to issues such as solubility problems, phase separation, or negative effects on the lubricant's

performance. The mixtures were then blended using a laboratory stirrer set at 500 rpm on a heated plate to ensure thorough mixing and uniform temperature distribution, reaching 45 °C over approximately 40 min. After cooling to room temperature, the blends were transferred into screw-cap glass bottles for subsequent analysis. This methodological approach ensured the effective integration of bio-waste extracts, optimizing the enhancement of oil properties.

2.8. Characterization of the blended lubricants

The kinematic viscosity of each oil sample was measured at 40 °C and 100 °C using a Seta KV-8 viscometer (Stanhope-Seta, United Kingdom), in accordance with the ASTM D88 standard method. Additionally, to evaluate the volatility of the engine oils, a test following ASTM D5800 was carried out. For this test, 40 mg samples of both the base oils and those enhanced with crude extracts were placed in aluminum crucibles, each normalized to the same weight. These samples were then subjected to a controlled heating process in an oven with a consistent airflow, with temperatures gradually increasing from 50 to 250 °C over a period of 60 min. The specific temperature range and duration were chosen to simulate extreme operating conditions that oils might encounter during engine operation, ensuring the test's relevance to real-world engine scenarios. After heating, the crucibles were removed from the oven and allowed to cool in a desiccator before being weighed again. The difference in weight before and after heating was used to calculate the percentage of mass loss, providing insights into the volatility characteristics of the oils.

The thermal analysis of the crude extracts was conducted using a TGA- Model TGA/ STA PT-1000 (Linseis, Germany). The experimental conditions included a heating rate of 10 °C/min, an oxygen atmosphere of 30 mL/min, and initial base oil masses of 7.87467, 7.75099, 7.71046, and 7.21544 mg for BO_1, BO_2, BO_3, and BO_4, respectively. The thermogravimetric (TG) curves were plotted as mass loss as a temperature (°C) function. Furthermore, an engine oil degradation test was performed by ASTM D5533 to determine the insoluble formation. The experiment involved filling four clean open crucibles with 10 mL of base oils without crude extracts, followed by four sets of crucibles containing base oils added with BLG crude extract, four sets containing BPF crude extract, and four sets of base oils containing the mixture of the two crude extracts. All crucibles were weighed and then heated for 180 min in a hot air oven set to 150 °C before being exposed to air for aging. The average filterable insoluble was measured by gravity after the oil samples had aged and cooled using a digital balance and filter paper with a nominal porosity of 11 µm. Finally, the oxidation stability experiments were performed on a Seta oxidation stability bath using the ASTM D943 standard methods. The analysis was performed under maximum operating pressures and temperatures of 690 to 705 kPa and 95 to 103 °C, respectively.

3. Results and Discussion

3.1. Moisture content and yield of crude extracts

The BLG extraction resulted in a dried crude extract of 2.45 gm weight, which corresponds to a yield of 6.11 %. The crude extract contained 8.25 % moisture. Whereas the extraction of BPF produced a higher yield, with a dried crude extract weight of 4.53 gm, equivalent to a percentage yield of 11.32 %. However, the crude extract from BPF displayed a slightly higher moisture content of 10.09 % compared to that of BLG. The values of moisture content are lower than the moisture content of 10.09 and 11.35 % for extracts of BLG and BPF, respectively, reported in previous studies (Adeyemo et al., 2018; Basera et al., 2019; Simonovska et al., 2016). The lower moisture contents observed in this study may be attributed to factors such as variations in the drying and storage conditions. Moreover, improvements in extraction and drying technologies over time may also contribute to more efficient removal of moisture, resulting in the lower percentages observed. These factors underscore the importance of controlling environmental and procedural conditions to achieve consistent and reproducible extract qualities in research. The low moisture content of both crude extracts were suitable for long storage, meaning they could be used as lubricant additives (Fotouo-M et al., 2020).

It was also observed that the percentage yield of crude extract from BLG was lower than that from BPF. The difference could be due to factors such as the intrinsic properties of the bio-wastes themselves. Different bio-wastes have diverse compositions and

densities, influencing the efficiency of the extraction process. For instance, Plaza and Turner (2015) reported that reducing the particle size of leaves can enhance the yield of bio-actives, which could explain the higher yield observed in BPF compared to BLG. Additionally, Abbattista et al. (2021) found that using pressurized liquid extraction under optimized conditions significantly increased the total amount of extractable compounds, indicating that extraction methods play a crucial role in obtaining higher yields.

3.2. Phytochemical contents

Results on the phytochemical constituents present in the crude extracts of BLG and BPF are shown in Table 1. Both extracts were found to contain phenolic and aromatic amine compounds. The findings agree with previous research works (Duru and Enyoh, 2020; El Kaaby Ekhlas et al., 2016). The phytochemical contents indicate that the crude extracts are ideal for use as antioxidants in petroleum lubricants.

3.3. FTIR spectra of crude extracts

The FTIR spectra of the two crude extracts, which display various peaks indicating their antioxidant nature, are shown in Figure 1. According to Adeyemo et al. (2018), the broad peaks at around 3324 cm^{-1} (extract of BPF) and 3320 cm^{-1} (extract of BLG) indicate OH stretching, which suggests the presence of phenols. The sharp peaks at 2925 cm^{-1} (BPF extract) and 2928 cm^{-1} (BLG extract) correspond to asymmetric -CH_2 stretching, while the peak at 2850 cm^{-1} (extract of BPF) represents symmetric -CH_2 stretching. This indicates the presence of methyl or methylene groups, which are characteristic of organic compounds with long carbon chains. The peaks at 1627 cm^{-1} (extract of BPF) and 1614 cm^{-1} (extract of BLG) are attributed to the C=C stretching frequencies of aromatics and olefins, while the peak at 1600 cm^{-1} confirms the presence of lignin.

Table 1: Phytochemical constituents present in crude extracts of BLG and BPF

Crude Extract of	Phytochemical Constituent	Ferric Chloride Test	Libermann's Test	Halogenation test	Liebermann's Nitroso test
BLG	Phenols	+++	+++		
	Amines			+	+
BPF	Phenols	+	+		
	Amines			+++	+++

+++ = high, + = average

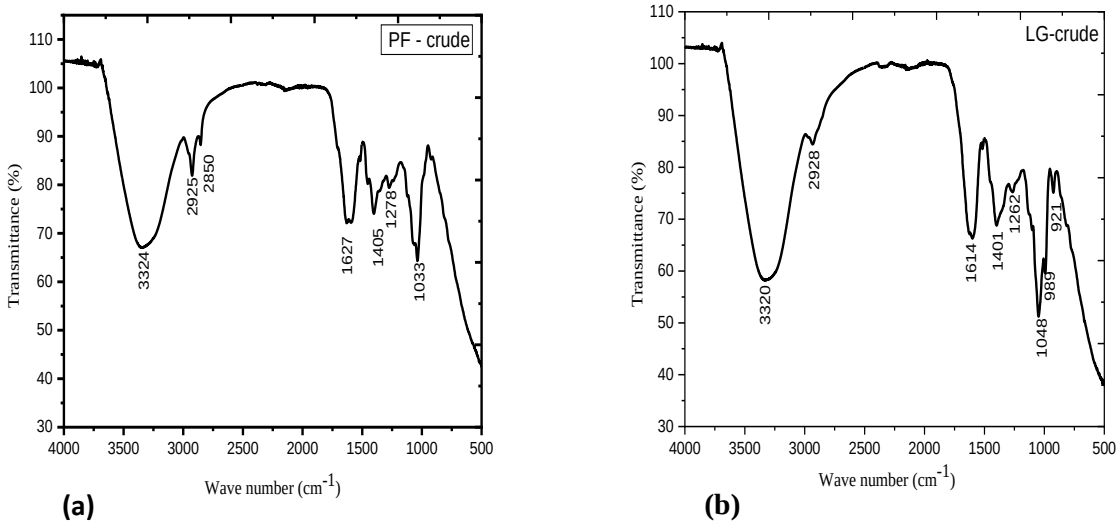

Figure 1: Fourier transform infrared spectra for crude extracts of (a) bio-waste of pepper fruits (PF) and (b) bio-waste of lemongrass (LG)

The peaks at 1405 cm^{-1} (extract of BPF) and 1401 cm^{-1} (extract of BLG) are attributed to the bending vibrations of C-H in methyl and methylene groups, which further confirms the presence of aliphatic hydrocarbons, and 1278 cm^{-1}(extract of BPF), and 1262 cm^{-1}(extract of BLG) correspond to C-O-C asymmetric stretch, suggesting the presence of alcohols, esters, ethers, or carboxylic acids. Furthermore, the peak between 1075-996 cm^{-1} corresponds to the polysaccharides peak (Simonovska et al., 2016; El Kaaby Ekhlas et al., 2016; Basera et al., 2019). Peaks between 900 and 667 cm^{-1} are often attributed to out-of-plane bending vibrations of C-H bonds, which are generally indicative of aromatic compounds. On the flip side, the peak at approximately 3324 cm^{-1} may suggest the N-H stretching vibrations associated with primary or secondary amines. Additionally, the peak near 1627 cm^{-1} could be indicative of N-H bending vibrations. While these peaks could be attributed to various functional groups, which is the case under this study, the likelihood of amines contributing to these signals is plausible. Complementing the FTIR results, the GC-MS analysis detailed in section 3.4 provides a more comprehensive breakdown of the chemical composition of the extracts, affirming their complex molecular nature and potential utility.

Overall, the FTIR spectra of the crude extracts reveal phenolic compounds, aliphatic hydrocarbons, aromatic structures, and functional groups such as esters and lignin. Phenolics enhance oxidation resistance by neutralizing free radicals. Aliphatic and aromatic compounds improve thermal stability, with aliphatics reducing volatility and aromatics forming protective films at high temperatures. Esters, ethers, and lignin provide additional barriers against thermal and oxidative breakdown (Zhang et al., 2013). Collectively, these components can significantly enhance the oxidation resistance and thermal stability of lubricants, leading to more durable and efficient performance.

3.4. GC-MS analyses of crude extracts

The GC-MS analysis of BLG and BPF methanol crude extracts revealed that the two bio-wastes contained a diverse array of phytochemicals that could be responsible for their antioxidant activities. Capsaicin (53.2%) and dihydrocapsaicin (40.5%) were the two main components of the BPF crude extract (Table 2). Dereli et al. (2022) also identified capsaicin and dihydrocapsaicin as predominant components. The other phytochemicals are present in smaller amounts, and they include methyl stearate, ascorbic acid, pentadecanoic acid, quercetin, and linoleic acid. Notably, Hexahydro-3,5,5,9-tetramethyl(1H) benzo-cycloheptene was present as well, although not in the same proportion in the BPF extract as the other components.

The detected phytochemicals in the BLG methanol crude extract are fatty acids, alcohols, esters, and phenols (Table 3). The most significant chemical components of the bio-waste extract are 2,6 Bis (1,1-dimethylethyl)-4-[(4-chloro-6-(3,5, bis (1,1-dimethyl-ethyl)-4-hydroxyanilino)-1,3,5-triazin-2-yl) amino] phenol (48.5%) and 1-ethoxyoctadecane (35.9%). Thorat et al. (2021) also documented these compounds in bio-waste extracts.

Table 2: Phytochemical Compounds from bio-waste of pepper fruits (BPF) methanolic extract

Retention time (min)	Compound Name	Molecular Formula	Molecular Weight	Peak Area (%)
9.349	Hexahydro-3,5,5,9-tetramethyl(1H)benzocycloheptene	$C_{15}H_{10}$	204.351	0.04169
13.787	Palmitic acid, methyl ester	$C_{17}H_{34}O_2$	270.450	0.11618
14.156	Pentadecanoic acid, 14-methyl-, methyl ester	$C_{17}H_{34}O_2$	270.451	1.64691
14.567	l-(+)-Ascorbic acid 2,6-dihexadecanoate	$C_{38}H_{68}O_8$	652.900	2.15198
14.813	Palmitic acid, ethyl ester	$C_{18}H_{36}O_2$	284.477	0.18493
15.779	Linoleic acid, methyl ester	$C_{18}H_{32}O_2$	280.447	0.89764
16.054	Methyl stearate	$C_{19}H_{38}O_2$	298.500	0.32212
16.199	Linoleic acid, ethyl ester	$C_{20}H_{36}O_2$	308.499	0.93948
19.805	Capsaicin	$C_{18}H_{27}NO_3$	305.410	53.20471
19.966	Dihydrocapsaicin	$C_{18}H_{29}NO_3$	307.430	40.49439

Table 3: Phytochemical Compounds from bio-waste lemongrass (BLG) Methanolic Extract

Retention time (min)	Compound Name	Molecular formula	Molecular weight	Peak Area (%)
16.23	Hexadecanoic acid	$C_{16}H_{32}O_2$	256.48	3.89
19.84	Hepta-9,10, and 11-trienioc acid	$C_{18}H_{36}O_2$	264.40	3.03
20.66	Octadecenoic acid	$C_{18}H_{36}O_2$	284.48	3.05
20.67	2-ethenyltradecan-1-ol	$C_{16}H_{31}O$	239.42	0.96
22.82	Eicosane aldehyde	$C_{21}H_{41}O$	309.59	4.64
22.86	1-ethoxyoctadecane	$C_{20}H_{41}O$	297.54	35.93
23.12	2,6 Bis (1,1-dimethylethyl)-4-[(4-chloro-6-(3,5, bis (1,1-dimethylethyl)-4-hydroxyanilino)-1,3,5-triazin-2-yl)amino]phenol	$C_{31}H_{44}CIN_5O_2$	553	48.46

In general, the GC-MS analysis of BLG and BPF methanol crude extracts reveals a diverse array of phytochemicals with notable antioxidant properties, such as capsaicin, dihydrocapsaicin, and various fatty acids and phenols. These compounds can significantly enhance the thermal and oxidation stability of lubricants. Antioxidants like these prevent the oxidation process that degrades lubricant quality, while compounds with stable molecular structures, such as fatty acids and phenols, maintain effective lubrication even at high temperatures. The presence of amino groups further suggests potential antioxidative benefits, contributing to overall lubricant stability and longevity. Integrating these extracts could therefore lead to lubricants with improved performance, longer life, and enhanced protection under thermal and oxidative stress. This finding is particularly notable as amino compounds are often associated with antioxidant activity, which could contribute to the overall antioxidative potential of the BLG crude extract.

3.5. Thermal stability analyses of crude extracts

The thermogravimetric analysis (TGA) curves of the crude extracts showed various stages of weight reduction below 600 °C (Figure 2). The TG profiles indicated just an evaporation stage and quick mass loss in the BLG extracts. However, the graphics did not reveal a plateau indicating thermal stability. The initial mass for BLG extract was 7.5661 mg, and the mass loss started at about 110 °C and terminated at 560 °C. For the BPF crude extracts, the initial mass was 7.7105 mg, and the intense slope in the first segment began at room temperature and increased to 100 °C, representing water loss. The second zone, from 100 to 170 °C, corresponded to the first weight loss of crude extracts, during which lower molecular weight components disintegrate. The cellulose started to break down in the third zone at temperatures ranging from 210 °C to 300 °C. Hemicellulose continued to degrade at 304 °C. Finally, lignin components broke down at temperatures ranging from 392 to 573 °C (Simonovska et al., 2016).

Overall, the TGA results indicate the thermal degradation profiles of the crude extracts, suggesting their potential as antioxidants for petroleum lubricants. Despite the absence of a plateau indicating thermal stability, the delineated decomposition temperatures of various components within the extracts provide insights for formulating lubricants resilient to thermal stress. This knowledge would aid in optimizing blend ratios and processing conditions to enhance lubricant performance and longevity in real-world operating conditions.

3.6. Kinematic viscosity and volatility

In agreement with the findings of Okoye et al. (2010), the kinematic viscosity of the oil samples decreased as temperature increased (Table 4). The untreated base oils had different kinematic viscosities at 40 °C and 100 °C. When treated with both crude extracts at 40 °C, the kinematic viscosities increased. However, when treated with an equal proportional mixture of crude extracts of BPF and BLG, the kinematic viscosities of the base oils increased even more. At 100 °C, adding crude extracts of BLG and BPF, and an equal mixture of the crude extracts also increased the kinematic viscosities of the base oils. Overall, base oils containing the bio-s crude

extract had higher kinematic viscosity than those without. On the other hand, the volatility test results showed that base oils with crude extract had lower volatility values (Table 4), possibly due to the presence of higher molecular weight polyphenols and aromatic amine compounds from the crude extracts. These findings potentially of benefit to automotive engines that require low-volatility lubricants to minimize oil consumption and maintain proper lubrication under high-temperature conditions.

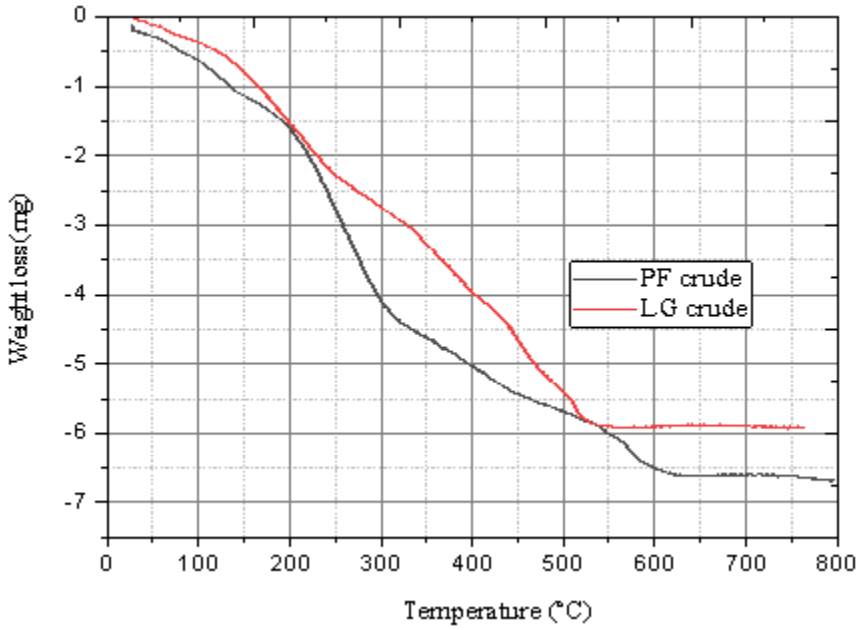

Figure 2: Thermogravimetric analysis of PF and LG, which are crude extracts of bio-wastes of pepper fruits and lemongrass, respectively

Table 4: Kinematic viscosity and volatility of base oils with and without crude extracts

Base oil/Aadditized base oil	Appearance	KV at 40 °C (cSt)	KV at 100 °C (cSt)	Volatility % (w/w)
BO_1	Light yellow	40.65	7.01	6.633
BO_2	Clear	84.56	9.88	17.688
BO_3	Light yellow	34.07	5.51	21.352
BO_4	Clear	101.80	10.03	20.467
BO_1 + LG	Green	47.81	7.50	2.843
BO_2 + LG	Green	117.30	13.44	4.675
BO_3+ LG	Green	46.39	7.47	5.749
BO_4+ LG	Green	113.70	13.11	5.748
BO_1+ PF	Brick red	57.49	9.14	0.632
BO_2+ PF	Light yellow	146.99	17.24	1.201
BO_3+ PF	Brick red	65.17	9.79	1.768
BO_4+ PF	Light yellow	136.30	15.21	1.516
BO_1 + PF + LG	Brown amber	73.64	11.29	1.579
BO_2 + PF + LG	Brown amber	156.50	18.58	1.958
BO_3 + PF + LG	Brown amber	85.41	12.59	3.159
BO_4 + PF + LG	Brown amber	159.50	18.53	2.653

BO_1, BO_2, BO_3 and BO_4 are base oil samples number 1, 2, 3 and 4, respectively; PF and LG are crude extracts from bio-wastes of pepper fruits and lemongrass, respectively

When heating the four base oils and their corresponding additized base oils with crude extracts of BLG, BPF, (BPF + BLG) in an inert atmosphere from room temperature to 600 ºC for 1 h, vaporization and single-step decomposition of their components occurred. The first step began at different temperature ranges for each type of oil, with the second regime starting from 360 to 480 ℃ for all four types of base oils and their corresponding additized oils. During the first temperature range of 150 to 350 ℃, evaporation of hydrocarbons with lower molecular weight distribution and degradation of base oil components occurred. The second weight loss regime was likely attributed to the decomposition of long-chain hydrocarbons resulting in oxygenated organics such as alcohols, diols, and sulfurous acid esters (Lehrle et al., 2002; Tripathi and Vinu, 2015). It was also observed that the oils were pyrolyzed completely before 500 ℃ without any residue formation, while in certain cases, small residue was observed at 500 ℃. Complete decomposition was observed at much higher temperatures, such as 600 ℃. These findings are consistent with those described in the literature for various types of mineral oils (Kupareva et al., 2013; Parajo et al., 2018).

As shown in Table 5, the onset of temperature and the temperature at maximum weight loss rate varied for each type of oil and their corresponding additized oils, indicating differences in thermal stability. For example, the onset temperature for BO_1 was 150 ℃, while the onset temperature for BO_4 was 120 ℃; while the maximum weight loss rate for BO_1 was at 267 ℃, while the maximum weight loss rate for BO_4 was at 275 ℃. Overall, the results suggest that the crude extracts may effectively influence the thermal behavior of base oils, which could have implications for industries such as automotive and lubricant manufacturing.

Table 5: Thermogravimetric analysis of base oils and addicted base oils

Base Oil/Additized Base Oil	T_{onset}(°C)	%Weight Loss	T_{offset}(°C)	% Weight Loss	DTG T_{max} (°C)
BO_1	150	2.90	300	85.40	267
BO_2	220	0.91	370	80.70	309
BO_3	210	0.90	370	84.20	309
BO_4	120	0.85	300	81.13	266
BO_1 + LG	214	0.92	350	85.70	305
BO_2 + LG	230	0.68	400	85.11	323
BO_3 + LG	213	0.72	374	82.10	316
BO_4 + LG	125	1.16	300	80.28	270
BO_1 + PF	226	0.63	350	94.67	307
BO_2 + PF	240	2.14	400	84.95	332
BO_3 + PF	215	2.11	376	86.18	318
BO_4+ PF	150	0.98	300	85.44	273
BO_1 + PF + LG	200	0.50	304	85.60	276
BO_2 + PF + LG	228	0.32	370	84.90	318
BO_3 + PF + LG	219	0.34	370	88.09	315
BO_4 + PF + LG	156	1.55	300	86.14	275

BO_1, BO_2, BO_3 and BO_4 are base oil samples number 1, 2, 3 and 4, respectively; PF and LG are crude extracts from bio-wastes of pepper fruits and lemongrass, respectively. DTG stands for Differential Thermogravimetric.

3.7. Degradation of base and additized oils

The experimental data presented in Table 6 provide valuable insight into the physicochemical properties of base oils and their additized counterparts after undergoing thermal oxidation at 150°C for 16 h. It was found that base oils without antioxidants had a higher amount of insoluble compared to base oils with antioxidants. Among the four base oils, BO_3 had a relatively higher carbon residue and sludge deposit content, leading to a higher thermal oxidation insoluble percentage. This highlights the importance of selecting base oils with appropriate properties to minimize degradation products during service. As the oxidation time increased, the viscosity of the oils also increased due to the poly-condensation of the oxygenated products formed during the oxidation phase. The high molecular weight intermediates also underwent further poly-condensation and polymerization reactions, forming products that were no longer soluble in the hydrocarbon.

In general, the presence of antioxidants in base oils effectively reduced the formation of insoluble materials during thermal oxidation, indicating improved oxidation stability. Additionally, the increase in viscosity with prolonged oxidation time suggests the formation of high molecular weight intermediates, which can impact lubricant performance. These findings highlight the significance of antioxidant additives in enhancing thermal stability and performance of lubricants under oxidative conditions.

3.8. Oxidation Stability of the Oil Samples

The oxidation stability results are shown in Figure 3. It was found that base oils containing crude antioxidants had a linear profile, whereas base oil without crude antioxidants displayed a nonlinear pattern. The induction time for base oils without crude antioxidants was 320 min, while for base oils with crude antioxidants, it was above 400 min, which is in line with the idea reported by Fairus et al. (2020). These results indicate that the crude antioxidant suppressed the oxidation reaction of base oils. Based on GC-MS results, such observation could be due to capsaicin and phenolic compounds in crude extracts.

Table 6: Thermo-oxidative Degradation data of Base Oil, LG-Extract Additized Oil, PF-Extract Additized Oil and LG+ PF- Extracts Additized Oil at 150 ºC for 16 h

Base oil or additized base oil	Initial sample weight	Sample weight after time t	Char weight at end of reaction	% insoluble
BO_1	8.7550	6.8150	1.05	6.633
BO_2	8.0970	5.2970	2.80	17.688
BO_3	8.5560	4.8160	3.38	21.352
BO_4	7.1860	3.9660	3.24	20.467
BO_1 + LG	8.7509	5.6916	0.45	2.843
BO_2 + LG	8.7104	5.3846	0.74	4.675
BO_3 + LG	8.5662	6.9835	0.97	5.749
BO_4 + LG	7.5614	6.6730	0.91	5.748
BO_1 + PF	8.1461	5.6910	0.10	0.632
BO_2 + PF	8.8551	6.0853	0.19	1.201
BO_3 + PF	8.7675	6.9168	0.28	1.768
BO_4 + PF	7.8933	6.1520	0.24	1.516
BO_1 + PF + LG	8.0385	5.6880	0.25	1.579
BO_2 + PF + LG	8.0242	5.4621	0.31	1.958
BO_3 + PF + LG	8.4381	5.3220	0.50	3.159
BO_4 + PF + LG	7.2154	5.8922	0.42	2.653

BO_1, BO_2, BO_3 and BO_4 are base oil samples number 1, 2, 3 and 4, respectively; PF and LG are crude extracts from bio-wastes of pepper fruits and lemongrass, respectively

Furthermore, the synergistic effect of aminic and phenolic antioxidants from extracts of BLG and BPF was revealed to be more effective in minimizing thermal-oxidation effects. This observation could be attributed to phenol's ability to regenerate the more efficient aminic antioxidant as a combination of radical scavengers and peroxide decomposers (Romeo et al., 2020). Overall, the oxidation stability results demonstrate the effectiveness of crude antioxidants derived from BLG and BPF in enhancing the oxidation resistance of base oils. The findings underline the potential of bio-waste-derived antioxidants in improving the performance and longevity of lubricants, highlighting their importance in various industrial applications.

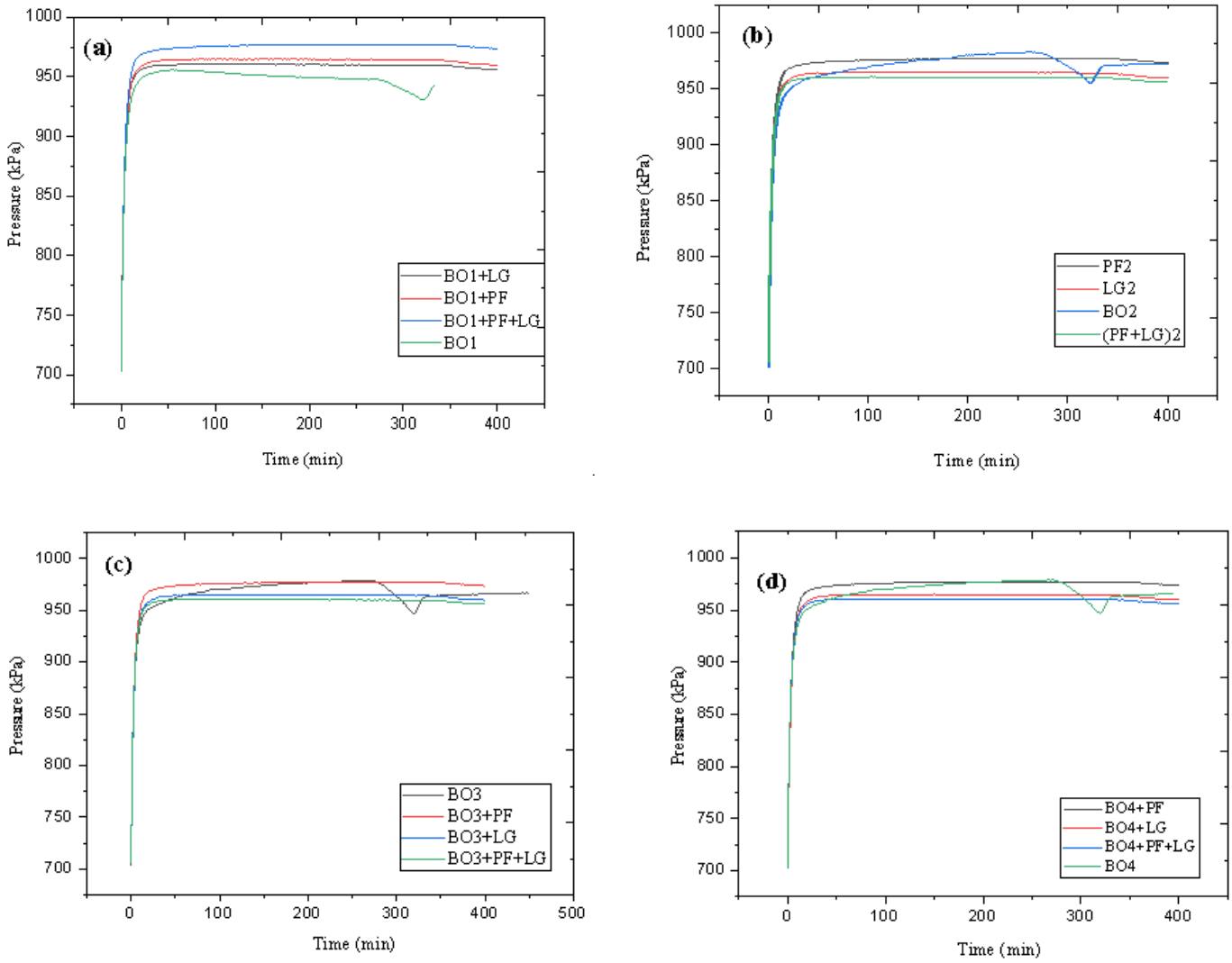

Figure 3: Oxidation pressure profile at 100 ˚C for samples **(a)** BO_1, (BO_1+LG), (BO_1+PF), and (BO_1+PF+LG); **(b)** BO_2, (BO_2+ LG), (BO_2+PF), and (BO_2+PF+LG); **(c)** BO_3, (BO_3+LG), (BO_3+PF), and (BO_3+PF+LG) and **(d)** BO_4, (BO_4+LG), (BO_4+PF), and (BO_4+PF+LG)

4. Conclusion

The study aimed at exploring the use of crude extracts from bio-wastes of lemongrass and pepper fruits as an alternative source of synthetic antioxidants for petroleum lubricants. The crude extracts of the bio-wastes have successfully demonstrated their potential to enhance lubricant stability. The comprehensive analysis employing phytochemical tests, FTIR, and GC-MS revealed that these extracts are rich in radical scavengers like phenols and aromatic amines, which are effective in enhancing the thermal and oxidative stability of lubricants. By extending the induction time for oxidation and increasing the temperatures at maximum weight loss, the extracts improved the performance of the base oils substantially compared to those without additives.

The application of the bio-waste-derived extracts would contribute to the sustainability goals of reducing environmental impact and promoting a circular economy by valorizing waste products. The study has not only shown the feasibility of using these extracts in industrial applications but also it opens up new pathways for further research into similar bio-waste resources. For instance, based on the outcomes of the equal ratio blend of this study, future studies could then explore varying ratios to fine-tune the balance of properties contributed by each extract, optimizing the formulation for specific performance characteristics or cost-efficiency.

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