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Preparation of Bio-Oil and Biochar through Co-Pyrolysis of *Pennisetum purpureum* and HDPE Plastic Waste at Various Feedstock Ratios and Temperatures

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Abstract

This study investigates the co-pyrolysis process of elephant grass (Pennisetum purpureum) and HDPE plastic waste and evaluates the properties of the resulting bio-oil and biochar. The process was conducted in a pilot-scale reactor under a nitrogen atmosphere using a two-stage heating scheme at 300°C and 450°C, with biomass–HDPE weight ratios of 100:0, 90:10, 75:25, 60:40, and 50:50. The method used in this work includes product yield analysis, thermophysical characterization, GC–MS-based chemical composition analysis, and ANOVA statistical validation to determine the optimum conditions for Pennisetum purpureum–HDPE co-pyrolysis process. The results indicate that the addition of HDPE does not increase the absolute yield of bio-oil but significantly enhances its energy quality. The calorific value of the bio-oil increased from 10,579 cal/g for pure biomass to a maximum of 12,029 cal/g at a 75:25 biomass–HDPE weight ratio, accompanied by a compositional shift from oxygenated compounds toward the dominance of fatty acid methyl esters (FAME) and medium- to long-chain hydrocarbons. At the same ratio, biochar achieved the highest yield (44.93% w/w) while maintaining characteristics suitable for energy applications. These findings identify the 75:25 biomass–HDPE ratio as the optimum condition based on both experimental and statistical evidence, and demonstrate that biomass–HDPE co-pyrolysis is an effective strategy for waste utilization and for enhancing the quality of renewable energy products.

Keywords: co-pyrolysis, Pennisetum purpureum, HDPE, bio-oil, biochar, GC–MS

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INTRODUCTION

The conversion of biomass into energy through pyrolysis continues to be developed in line with the increasing demand for renewable fuels and the abundant availability of biomass. Pennisetum purpureum is a promising candidate due to its high land productivity and thermochemical characteristics that support the formation of bio-oil and biochar (Lessa *et al*., 2021).

Besides the liquid fraction, the solid fraction produced from pyrolysis in the form of biochar also plays an important role in biomass-based energy systems. Biochar derived from lignocellulosic biomass under appropriate thermal conditions has been reported to exhibit high fixed carbon content and good thermal stability (Effendy *et al*., 2024). However, bio-oil from pure biomass still has inherent weaknesses such as high oxygen content, low stability, and a calorific value that is not yet competitive with fossil fuels. Various studies show that the pyrolysis process often produces bio-oil dominated by oxygenated compounds such as phenols, organic acids, and furfural, which significantly reduce fuel quality (Xia *et al*., 2022).

The limitations in bio-oil quality highlight the need for upgrading strategies to improve its fuel properties. A study by (No *et al*., 2025) demonstrated that bio-oil derived from biomass pyrolysis can be effectively upgraded through Ni-zeolite–based catalytic cracking, which reduces oxygen content and increases the hydrocarbon fraction, making the fuel characteristics closer to those of conventional fuels.

On the other hand, HDPE plastic waste is increasingly abundant and has the potential to be processed into an energy source due to the ability of polyolefins to degrade into high-value hydrocarbons. Studies on the co-pyrolysis of biomass with plastic show that there is a hydrogen donation mechanism that can reduce the oxygen content of bio-oil and improve its calorific value and stability (Hoque & Rashid, 2021).

However, research on the co-pyrolysis of Pennisetum purpureum and HDPE is still very limited, especially in explaining how variations in the mixture ratio affect the chemical composition of bio-oil, fuel physical parameters, and biochar properties simultaneously (Altıkat *et al*, 2024).

This gap highlights the need for studies that can evaluate the relationship between the biomass–HDPE ratio and the quality of the resulting energy products. Therefore, this study was conducted to assess the effect of varying Pennisetum purpureum–HDPE ratios on yield, bio-oil characteristics, and biochar quality through two-stage co-pyrolysis. The evaluation includes GC–MS analysis, testing of bio-oil physical properties, and ANOVA statistical analysis to test the significance of differences between ratios.

The novelty of this study lies in its integrative approach, which not only assesses the quality of bio-oil or biochar separately, but also links them through changes in chemical composition, energy parameters, and thermal response to variations in the biomass–HDPE mixture. Thus, this study provides a more comprehensive understanding of the potential of co-pyrolysis as a simultaneous strategy for improving energy quality and utilizing plastic waste.

MATERIAL AND METHOD

Materials and Equipment

The main raw materials are elephant grass (*Pennisetum purpureum*) and high-density polyethylene (HDPE) plastic waste. Elephant grass was collected from farmers around Lhokseumawe, then dried under the sun for about five days and chopped into 1–5 cm pieces. HDPE plastic waste was sourced from used engine oil bottles collected from vehicle repair shops in Lhokseumawe. The plastic was sorted according to type and condition, thoroughly washed with detergent and hot water to remove residual oil contaminants, dried, and then crushed using a mechanical crusher to particles ranging in size from approximately 5 mm to 1 cm.

The pyrolysis apparatus mainly consists of a 25-liter volume batch reactor equipped with an LPG burner for heating, a nitrogen gas supply to create an inert atmosphere, and a water-cooled condenser circuit to condense the liquid fraction. For the chemical composition analysis of the bio-oil product, a Thermo Scientific TRACE 1610 Gas Chromatograph coupled with an ISQ 7610 Single Quadrupole Mass Spectrometer (GC–MS) was used. A Koehler K88900 bomb calorimeter was employed for heating value analysis. The viscosity was determined manually using an Ostwald viscometer at 40°C, referring to ASTM D445. Density was measured manually using a 10 mL pycnometer at 25°C. The flash point was determined using a closed-cup Pensky–Martens apparatus in accordance with ASTM D93.

Preparation of Raw Material Mixture

Dried elephant grass and cleaned HDPE flakes were mixed based on varying ratios of elephant grass to HDPE of 100:0, 90:10, 75:25, 60:40, and 50:50. Each composition was weighed with digital scales, then homogenized manually using a mixer to ensure even distribution of plastic in the biomass before being fed into the reactor.

Two-Stage Co-Pyrolysis Procedure

The elephant grass–HDPE mixture for each ratio was fed into the reactor with a total weight of approximately 1.5 kg per experiment. Before heating began, a flow of nitrogen gas was injected into the reactor at a constant rate to purge air and maintain minimal oxygen conditions during the process, thus thermal oxidation could be avoided.

The heating profile was arranged in two stages according to the thermal characteristics of the biomass and plastic components. In the first stage, the reactor was heated to 350°C and held for 30 minutes. In this range, the elephant grass hemicellulose decomposes and some of the cellulose begins to break down, producing volatile compounds such as CO, CO_2, organic acids, and furfural. The second stage was carried out by raising the temperature to 450°C and holding it for 30 minutes to complete the decomposition of lignin and trigger thermal cracking of HDPE, thereby producing the expected medium-chain hydrocarbon fraction that improves the energy quality of bio-oil and biochar, in line with the trend of operating conditions in biomass-plastic pyrolysis in the literature *(Awad et al.,* 2024*)*.

During heating, the steam and gases produced by pyrolysis were fed into a water-cooled condenser to be condensed into bio-oil. Uncondensed products were discharged into the exhaust gas stream, and some can be reused as external heating fuel, following common practices for utilizing pyrolysis gas in energy recovery systems (Vamvuka & Chatzifotiadis, 2022). After the holding time was achieved, the heater was then turned off and the reactor was allowed to cool to near room temperature in a nitrogen flow. The biochar remaining at the bottom of the reactor was then removed and weighed. The regulation of the heating profile plays a crucial role in determining the distribution of pyrolysis products. (Al-yaqoobi, 2023) reported that increasing energy intensity and controlling the heating duration significantly influence the shift of products from biochar toward bio-oil and gas as a result of secondary cracking reactions.

Pre-treatment of Bio-Oil

Bio-oil exiting the condenser was collected in a storage vessel. Since there were still suspended solids, the bio-oil was filtered or centrifuged to separate the solid and liquid phases, thereby obtaining a more homogeneous liquid fraction prior to analysis. This initial separation approach is consistent with the bio-oil purification strategy in other biomass pyrolysis studies that utilize mechanical separation and light evaporation to reduce the content of solids and heavy fractions (Maulinda *et al*., 2023).

Characterization of Bio-Oil

Bio-oil from co-pyrolysis was analyzed to determine the main fuel characteristics. The composition of organic compounds was analyzed by GC–MS to identify hydrocarbon, ester, and oxygenate fractions, so that it could be compared with the composition profiles reported for pyrolysis of Pennisetum purpureum and other biomass (Reza *et al*., 2023).

The higher heating value (HHV) was determined using a bomb calorimeter based on the combustion energy per unit mass. Density measurements were performed at a specific reference temperature, while viscosity was determined with a viscometer according to liquid fuel testing standards. The flash point was measured using the Pensky–Martens closed cup method (ASTM D93), measuring the flash point of bio-oil to obtain information on the minimum temperature for the formation of flammable vapor mixtures. The cetane number is estimated using an empirical correlation based on calorific value, density, and hydrocarbon composition, as used in the evaluation of liquid biofuels in biomass and waste pyrolysis studies (Awad *et al*., 2024).

Biochar Characterization

Biochar was dried to a constant mass, then analyzed using a proximate test to determine the moisture content, volatile matter, ash, and fixed carbon. The testing procedure followed the biochar characterization approach used in studies of the relationship between pyrolysis conditions and biochar quality, in which variations in temperature and feedstock type affect pore structure, ash content, and carbon content (Mogaji *et al*., 2020). The calorific value of biochar is measured with a bomb calorimeter to assess its suitability as a substitute solid fuel for low-grade coal and to compare it with the characteristics of biochar from other biomass reported in the literature (Bennani *et al*., 2023).

Biochar samples were subjected to proximate analysis to quantify moisture content, volatile matter, ash content, and fixed carbon in accordance with ASTM D1762-84. This standardized method was employed to ensure methodological consistency and analytical reliability.

The proximate parameters were determined using the following equations:

Moisture Content (MC):

$$MC\ (\%) = \frac{W_1 - W_2}{W_1}\, x\ 100 \qquad (1)$$

Volatile Matter (VM):

$$VM\ (\%) = \frac{W_2 - W_3}{W_1}\, x\ 100 \qquad (2)$$

Fixed Carbon (FC):

$$VM\ (\%) = 100 - (MC + VM + Ash) \qquad (3)$$

Where W_1 represents the initial sample mass, W_2 corresponds to the mass after oven drying at 105°C to constant weight, and W_3 denotes the residual mass after heating at 950°C under an inert atmosphere.

The application of this standardized proximate analysis enables systematic evaluation of the degree of carbonization and thermal stability of the produced biochar, thereby facilitating comparison with previously reported pyrolysis studies.

Yield Calculations

Bio-oil and biochar yields were calculated based on the ratio of product mass to dry feedstock mass, expressed as a percentage by weight. The pyrolysis gas fraction was obtained indirectly as the difference between the total feed mass and the mass of bio-oil and biochar. This mass and energy balance approach is in line with the modeling of bio-oil and biochar yields against temperature and biomass composition developed by (Awad *et al.*, 2024) and (Altıkat *et al.*, 2024).

The energy potential of each product is determined from the product of the yield and the calorific value, yielding the energy contribution of bio-oil and biochar for each elephant grass–HDPE mixture ratio. This indicator is used to identify the ratio that produces the best combination of energy quantity and quality, as well as to assess the extent to which co-pyrolysis can increase the utilization of biomass and plastic energy.

RESULTS AND DISCUSSION

Co-Pyrolysis Products

Figure 1 presents the distribution of these three fractions obtained from the co-pyrolysis of RG and HDPE at different blending ratios, highlighting the influence of feedstock composition on product formation.

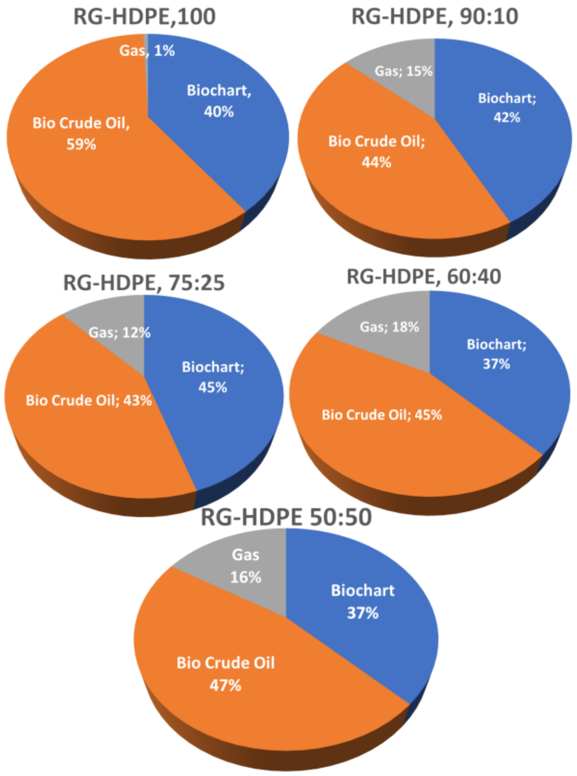


Figure 1. Co-pyrolysis Product Distribution

In the RG–HDPE 100:0 sample, bio-oil was the dominant product with a yield of approximately 59.50% w/w, followed by biochar at 39.87% w/w, while gas accounted for only 0.63% w/w. This composition is consistent with the characteristics of pure biomass pyrolysis, where the liquid fraction tends to be higher due to the decomposition of hemicellulose, cellulose, and some lignin, which produce large amounts of volatile compounds (Zhao *et al.*, 2021). The relatively high biochar yield is also in line with previous reports that lignin in tropical biomass produces significant amounts of solid residue due to its aromatic structure that is resistant to degradation (Tomczyk *et al.*, 2020).

In the 90:10 RG–HDPE composition, changes in the distribution pattern began to appear. Biochar yield increased to 42.33% w/w, while bio-oil decreased to 44.17% w/w, and gas increased to 13.50% w/w. The increase in the gas fraction indicates an increase in the secondary cracking reaction due to the addition of HDPE, which is known to produce light gases (C_1–C_4) through the mechanism of polyethylene chain scission at high temperatures (Oh & Sohn, 2022). Similar phenomenon was also observed in other biomass–polymer co-pyrolysis studies, where plastic accelerates the conversion of volatiles into gas through hydrogen donation and free radical reactions (Aljaziri *et al.*, 2023).

Product distribution reached optimal conditions at RG–HDPE 75:25, where biochar obtained the highest yield of 44.93% w/w, while bio-oil was at 43.00% w/w, and gas was at 12.07% w/w. This ratio shows a balance between biomass decomposition and the contribution of hydrogen from HDPE, which increases the formation of volatile compounds but does not excessively trigger cracking into gas. This pattern is in line with modeling showing that biomass–plastic interactions can produce an optimum zone, where a portion of the volatile fraction is converted to bio-oil while the rest forms a more stable solid residue (Awad *et al.*, 2024).

Notably, the gas fraction at 75:25 did not continue to increase despite the higher HDPE content compared to the 90:10 ratio, indicating that the system does not follow a simple linear cracking trend. This suggests that interactions between biomass-derived fragments and polymer radicals may moderate excessive secondary decomposition, allowing more carbon to remain in the solid phase. Therefore, the 75:25 composition can be interpreted as a transitional zone in which hydrogen transfer and radical stabilization are sufficiently balanced to enhance char formation without promoting over-cracking into permanent gases.

At RG–HDPE 60:40, the biochar yield decreased again to 37.53% w/w, bio-oil to 44.83% w/w, and gas increased to 17.63% w/w. The significant increase in the gas fraction with increasing HDPE indicates that the dominance of plastic promotes more intensive cracking, resulting in a larger proportion of gas and a reduction in the biochar fraction, as reported in co-pyrolysis with high polyolefin fractions (Wantaneeyakul *et al.*, 2021). This suggests that large amounts of HDPE shift the product balance toward gas, as end-thermal cracking volatilization reactions increase.

This shift implies that beyond the intermediate blending ratio, polymer-derived radicals increasingly dominate the reaction environment, reducing the stabilizing influence of lignocellulosic structures on char formation.

At RG–HDPE 50:50, the shift toward gas formation became more evident. The gas fraction further increased to 16.17% w/w, while biochar remained lower at 37.33% w/w, and bio-oil slightly increased to 46.5% w/w. This behavior suggests that when the plastic fraction becomes comparable to biomass, thermal cracking reactions dominate the process. The higher availability of polymer chains enhances radical formation and promotes secondary decomposition of volatiles into lighter gaseous products. As a result, the balance observed at 75:25 is no longer maintained, and the system tends to favor gas production over solid residue formation.

The increasing trend of gas fraction due to advanced cracking was also reported by (Al-yaqoobi, 2023), who showed that at higher energy intensities, pyrolysis volatiles tend to undergo secondary reactions, thereby enhancing the formation of non-condensable gases. The relatively high biochar yield still obtained at the RG–HDPE ratio of 75:25 indicates that the solid residue formed possesses good thermal stability and has not undergone excessive degradation. This finding is consistent with the report by (Effendy *et al.*, 2024), which demonstrated that biochar derived from biomass under controlled thermal treatment retains a high fixed carbon content and has strong potential for further development as a functional carbon material.

Overall, increasing HDPE content shifts the reaction pathway from biomass-controlled volatilization toward plastic-driven cracking. The peak biochar yield at 75:25 indicates a non-linear interaction rather than a simple additive blending effect. Above this ratio, gas formation becomes dominant, suggesting that excessive plastic weakens the synergistic stabilization that supports char retention.

These findings are consistent with the concept of biomass plastic thermal reactivity reported in various pyrolysis studies, where feedstock composition determines the direction of product formation, cracking effectiveness, and char stability (Aboelela *et al., 2023).*

Pyrolysis Product Characteristics

Table 3.1 shows the characteristics of biochar produced from the pyrolysis of *Pennisetum purpureum* (RG:100) and several RG–HDPE mixture ratios (90:10, 75:25, 60:40 and 50:50). The parameters analyzed include moisture content, volatile matter content, fixed carbon content, ash content, and density. In general, changes in biochar composition follow patterns that have been reported in the literature regarding the effects of pyrolysis temperature, biomass type, and the presence of polymer components on the structure and quality of biochar. (Mogaji *et al.*, 2020).

In pure biomass (RG:100), the moisture content is 8.9% w/w, volatile matter 31.34% w/w, fixed carbon 56.26% w/w, ash content 3.5% w/w, and density 1.68 g/cm³.

Table 1. Biochar Properties at Various RG–HDPE Ratios

Parameter (% w/w)	100:0	90:10	75:25	60:40	50:50
Moisture Content	8.9	10.4	11.3	12	14.78
Volatile Matter	31.1	35.4	41.14	44.5	46.96
Fixed Carbon	56.26	49.4	42.7	38.7	36.6
Ash Content	3.5	4	4.3	4.5	5.4
Density (g/cm³)	0.52	0.48	0.42	0.37	0.33

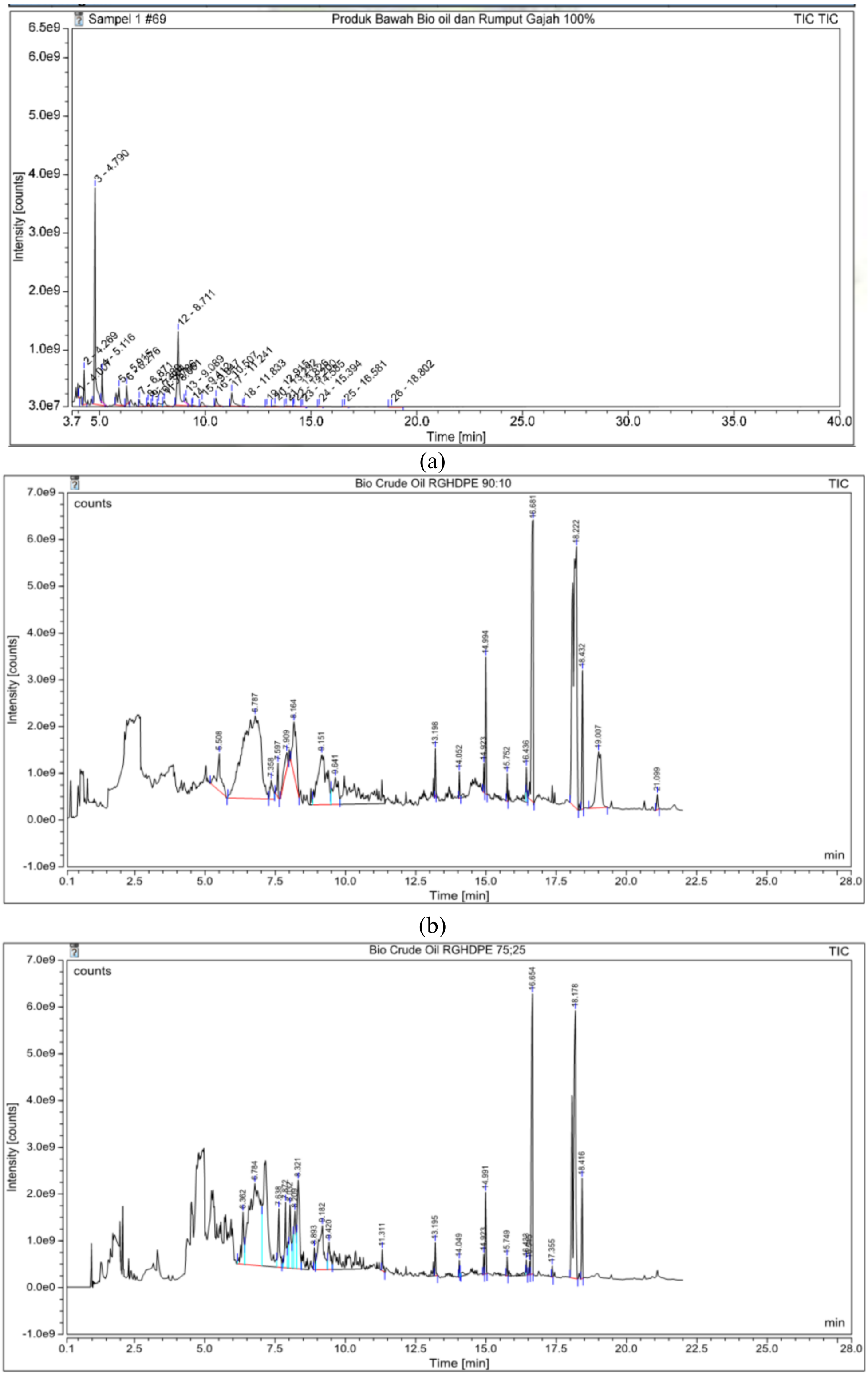
The relatively high fixed carbon content reflects the contribution of lignin, which is thermally more stable and tends to form char with higher carbon content, as reported in lignocellulosic pyrolysis studies (Reza *et al.*, 2023).

With the gradual addition of HDPE, changes in proximate composition become evident. The moisture content increases from 8.9% w/w (RG:100) to 10.4% w/w (90:10), 11.3% w/w (75:25), 12% w/w (60:40), and reaches 13.08% w/w at the 50:50 RG–HDPE ratio. This steady rise suggests that the structure of the resulting biochar becomes more open as the plastic fraction increases. The release of volatile compounds during HDPE depolymerization may contribute to the development of pores, making the char more susceptible to moisture adsorption after exposure to ambient conditions (Altıkat *et al.*, 2024).

A similar trend is observed in volatile matter content. The value increases from 31.34% w/w in pure biomass to 36.2% w/w (90:10), 41.7% w/w (75:25), 44.8% w/w (60:40), and further to 47.62% w/w at 50:50 RG–HDPE ratios. This progressive increase indicates that a larger portion of thermally unstable components remains in the solid residue as the plastic fraction rises. Part of this effect may be associated with plastic-derived hydrocarbons that are not fully converted into permanent gases under the applied pyrolysis conditions (Farobie *et al.*, 2024).

In contrast, the fixed carbon content shows a continuous decrease with increasing HDPE proportion, dropping from 56.26% w/w (RG:100) to 49.4% w/w, 42.7% w/w, 38.7% w/w, and finally 36.6% w/w at 50:50 RG–HDPE ratios. This decline reflects a reduced contribution of stable aromatic carbon structures in the char matrix. Since HDPE does not generate aromatic carbon in the same way lignin does, increasing its fraction gradually shifts the composition toward a less carbonized material (Mogaji *et al.*, 2020).

The ash content follows a moderate upward trend, increasing from 3.5% in pure biomass to 4.0–4.5% at intermediate ratios and reaching 5.4% at 50:50.

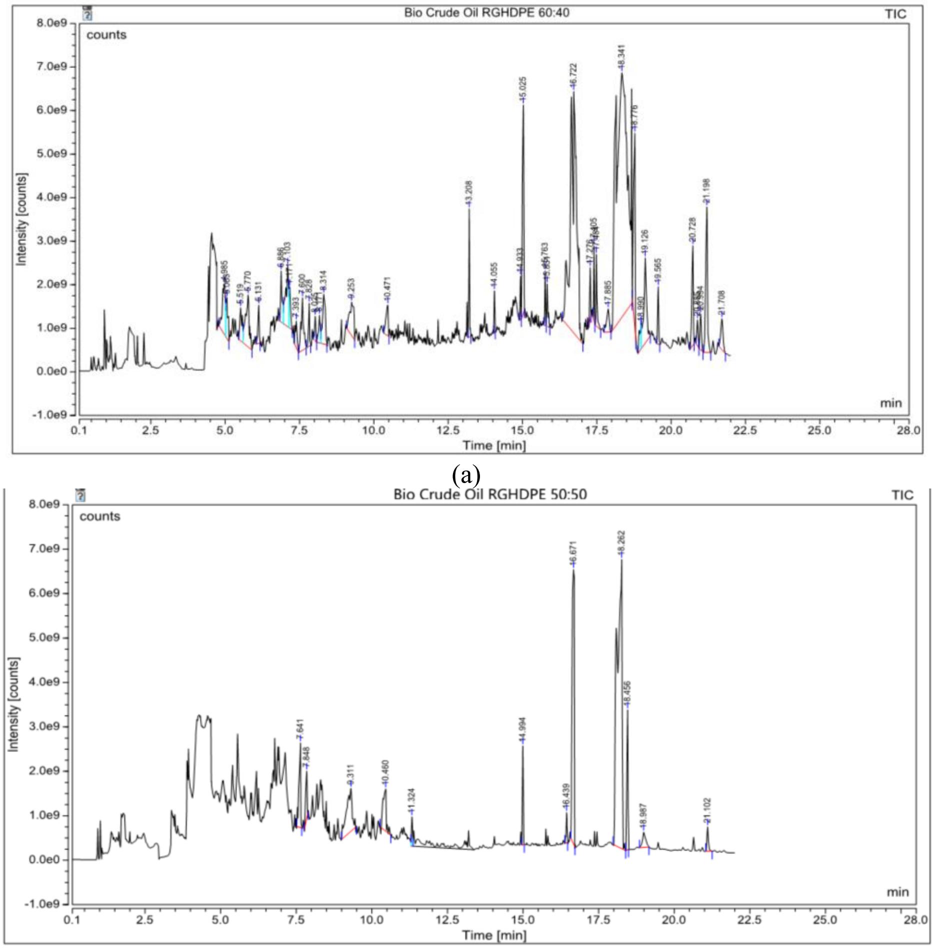


(a)

(b)

(c)

Figure 2. GC-MS Spectra of (a) RGHDPE 100, (b) RGHDPE 90:10, (c) RGHDPE 75:25



(a)

(b)

Figure 3. GC-MS Spectra of (a) RGHDPE 60:40, (b) RGHDPE 50:50

This increase may be explained by the relative concentration of inorganic components as more organic fractions are volatilized during co-pyrolysis (Wantaneeyakul *et al*., 2021).

Consistent with these compositional changes, the density decreases steadily from 1.68 g/cm³ (RG:100) to 1.48, 1.24, 1.04, and 1.01 g/cm³ at the 50:50 ratio. The lower density supports the observation of a more porous and less compact carbon structure, which aligns with the increased volatile content and reduced fixed carbon (Tomczyk *et al*., 2020).

Overall, increasing the HDPE fraction leads to a gradual transition in biochar characteristics: higher moisture and volatile content, lower fixed carbon, slightly higher ash, and reduced density. At moderate blending (75:25), a balance between yield and carbon stability is still maintained.

However, at the highest proportion (50:50), the char becomes noticeably less carbonized and more volatile in nature. These findings suggest that the blending ratio plays a key role in controlling the structural and compositional properties of the resulting biochar.

Chemical Composition of Bio-Crude Oil

The composition of organic compounds was analyzed by GC–MS (Figure 2 and Figure 3) to identify hydrocarbon, ester, and oxygenated compound fractions, so that it could be compared with the composition profiles reported for the pyrolysis of Pennisetum purpureum and other biomass (Reza *et al*., 2023).

GC–MS analysis results on 100% elephant grass BCO (RG–HDPE 100:0) show the dominance of oxygenated compounds characteristic of lignocellulose pyrolysis. The main peaks were identified as furfural and 3-furaldehyde (degradation of hemicellulose/cellulose fractions), various pyridine derivatives (pyridine, methyl-pyridine), lactones (butyrolactone), and phenols and methyl/methoxy-phenol derivatives originating from the breakdown of lignin structures. This composition is in line with the biomass pyrolysis literature, which reports a bio-oil rich in aldehydes, ketones, phenols, and other oxygenated compounds, resulting in relatively low calorific value and poor thermal stability (Maulinda *et al*., 2023).

In the co-pyrolysis system, the GC–MS spectrum changed significantly. For the RG–HDPE ratio of 90:10, in addition to traces of light aromatic compounds (e.g., 1-ethyl-3-methylbenzene) and several oxygenated compounds, there are quite dominant fractions of fatty acid methyl esters

(FAME) and medium–long chain hydrocarbons, such as dodecanoic acid methyl ester, hexadecanoic acid methyl ester, 9,12-octadecadienoic acid (Z,Z) methyl ester, 9-octadecenoic acid (Z) methyl ester, and methyl stearate. The C_{12}–C_{18} FAME fraction and these hydrocarbons contribute to an increase in calorific value and a decrease in bio-oil density at a 90:10 ratio, as also observed in bio-oil from the pyrolysis of other hydrocarbon-rich biomass *(Reza et al.*, 2023).

At a 75:25 RG–HDPE ratio, the composition pattern is similar, but the FAME fraction is more prominent. GC–MS shows the presence of heptane and branched heptane, 1-ethyl-3-methyl-benzene, and a series of C_{12}–C_{18} methyl esters such as dodecanoic, tetradecanoic, pentadecanoic, hexadecanoic, cis-10-heptadecenoic, 9,12-octadecadienoic (Z,Z), and 9-octadecenoic acid methyl ester, with 9,12-octadecadienoic acid (Z,Z) methyl ester recorded as one of the peaks with the largest relative area.

At an RG–HDPE ratio of 60:40, the GC–MS chromatogram shows a combination of aliphatic hydrocarbons (branched heptane and octane, substituted cyclohexane/cyclopentane) and the C_{12}–C_{20} FAME series, with 9-octadecenoic acid (Z) methyl ester as the dominant component, followed by methyl stearate, hexadecanoic acid methyl ester, and various other fatty acid esters.

In bio-oil at an RG–HDPE 50:50 ratio, the composition is increasingly dominated by FAME and heavy hydrocarbons. The main compounds identified include hexadecanoic acid methyl ester and 9,12-octadecadienoic acid (Z,Z) methyl ester with a combined relative area of approximately two-thirds of the total peak, accompanied by 9-octadecenoic acid (Z) methyl ester, methyl tetradecanoate, and heavy alkanes such as substituted octadecane. The very high proportion of hydrocarbon and FAME fractions explains the lowest viscosity and density close to light fuel oil at this ratio, but in this study, the 50:50 ratio actually resulted in the lowest bio-oil yield and biochar presence, making it less advantageous in terms of total system energy.

In general, the shift in composition from the dominance of oxygenated compounds (furfural, ketones, phenols) in RG–HDPE 100:0 toward medium–long chain hydrocarbon and FAME fractions at RG–HDPE ratios of 90:10 to 50:50 is consistent with the results of biomass–plastic co-pyrolysis literature reporting a decrease in oxygen content and an increase in the aromatic/aliphatic fraction in bio-oil (Aljaziri *et al*., 2023).

Mechanism of Biomass-HDPE Co-Pyrolysis Reaction

The co-pyrolysis of *Pennisetum purpureum* and HDPE involves simultaneous thermal degradation of lignocellulosic biomass and polymer cracking reactions. During heating, both materials decompose through different pathways that may interact under pyrolysis conditions (Wang *et al*., 2022).

Lignocellulosic biomass decomposes sequentially according to its structural components. Hemicellulose typically degrades at 200 – 350°C, followed by cellulose at 300 – 400°C, while lignin decomposes more gradually over a wider temperature range (250 –500°C) (Zhao *et al*., 2021). These processes generate oxygenated compounds such as acids, ketones, furans, and phenolic derivatives. The resulting intermediates are reactive and may undergo secondary reactions including cracking and repolymerization, contributing to char formation (Aljaziri *et al*., 2023).

HDPE, on the other hand, decomposes mainly through random free-radical chain scission:

$–(CH_2–CH_2)n– \rightarrow R\bullet + R'\bullet$

This reaction produces alkyl radicals and hydrocarbon fragments such as alkanes and alkenes. Recent studies have reported that plastic-derived radicals can significantly modify the reaction atmosphere by increasing hydrogen availability during co-pyrolysis (Liu & Yu, 2021).

One key interaction between biomass and HDPE is hydrogen transfer. Hydrogen radicals generated from HDPE may react with oxygenated biomass intermediates:

$R–O\bullet + H\bullet \rightarrow R–OH$

This hydrogen donation mechanism reduces oxygenated species and promotes hydrocarbon formation in the liquid phase (Chen *et al*., 2025). Consequently, the oxygen content of bio-oil decreases and its calorific value improves with moderate HDPE addition.

At higher RG-HDPE 50:50, more intensive cracking reactions occur, leading to increased formation of light hydrocarbons (C_1–C_4) and permanent gases (Liu & Yu, 2021). As a result, although the hydrocarbon fraction increases, excessive plastic content may shift the product distribution toward gaseous products and reduce biochar yield.

Overall, the interaction between oxygenated compounds derived from biomass and hydrogen-rich radicals generated from HDPE contributes to the variation in product distribution and fuel properties observed at different feedstock ratios. These findings are consistent with recent co-pyrolysis studies reported in the literature (Wang *et al*., 2022).

Bio-Oil Product Characteristics

The characteristics of bio-oil shown in Table 3.2 were obtained from bio crude oil resulting from the co-pyrolysis process, which then underwent an initial purification stage. The bio-crude oil was centrifuged using an LC-04S Centrifuge to separate fine solids and heavy fractions that were still carried over from the pyrolysis process. This stage aimed to obtain a more homogeneous liquid fraction so that density, viscosity, flash point, and calorific value tests could describe the quality of bio-oil more representatively. This approach is in line with the initial purification practices in biomass and polyolefin waste pyrolysis research, where the presence of suspended solids can affect the interpretation of the physical properties and stability of bio-oil (Farobie *et al*., 2022).

Table 2. Bio-oil Properties at Various RG-HDPE Ratios

Sample	ρ (g/cm³)	η (cP)	Flash Point	Heat Value (Cal/g)
RG-HDPE,100	0.97	1.65	48	10,579
RG-HDPE, 90:10	0.93	2.44	31	11,360
RG-HDPE, 75:25	0.93	2.24	32	12,029
RG-HDPE, 60:40	0.92	1.83	33	11,025
RG-HDPE, 50:50	0.88	1.46	31	10,132

The density of bio-oil showed a decreasing trend from 0.97 g/cm³ in RG–HDPE 100:0 to 0.93 g/cm³ (90:10 and 75:25), 0.92 g/cm³ (60:40), and 0.88 g/cm³ (50:50). This decrease in density is consistent with the composition pattern shown by GC–MS, where pure biomass bio-oil is still rich in oxygenated compounds such as furfural, lactones, and phenols, while mixtures with HDPE are dominated by fatty acid methyl esters (FAME C_{12}–C_{18}) and non-polar, lighter medium-long chain hydrocarbons (Zhao *et al*., 2021).

Viscosity increased at low ratios (2.44 cP at 90:10) before decreasing again to 1.46 cP at a ratio of 50:50. This initial increase can be attributed to the presence of a mixture of phenolic compounds and FAME at low ratios, which resulted in a thicker bio-oil. However, in mixtures with a larger HDPE fraction, the dominance of hydrocarbons and FAME causes a weakening of intermolecular interactions, resulting in a decrease in viscosity, a phenomenon consistent with GC–MS results showing a decrease in phenolic peaks and an increase in the fraction of alkanes and FAME (Zhao *et al*., 2021).

The flash point decreased dramatically from 48°C at an RG–HDPE ratio of 100:0 to 31 – 33°C in samples containing HDPE. This decrease is due to an increase in volatile compounds, such as heptane, branched octane, and several C_{12}–C_{16} methyl esters identified by GC–MS. These compounds have high vapor pressure and more easily produce flammable vapor-air mixtures, thereby lowering the flash point of bio-oil (Farobie *et al*., 2024).

The calorific value (HHV) is the clearest indicator of the synergy of biomass-plastic co-pyrolysis. The HHV increased from 10,579 cal/g (RG–HDPE ratio of 100:0) to a maximum of 12,029 cal/g at an RG–HDPE of 75:25 before declines at higher RG–HDPE ratios. This increase is consistent with GC–MS results showing a decrease in the oxygenate fraction and an increase in the peak intensity of FAME C_{16}–C_{18} (methyl palmitate, methyl oleate, methyl linoleate, methyl stearate) and medium-chain hydrocarbons. Because FAME and alkanes have a higher H/C ratio and lower oxygen content, the dominance of these compounds increases the energy content of bio-oil (Awad *et al*., 2024).

The combination of physical parameters and chemical composition shows that an RG–HDPE ratio of 75:25 produces bio-oil with the best energy quality. At this feed condition, density and viscosity have decreased, the flash point is within a stable range, and the calorific value has peaked. The presence of C_{12}–C_{18} FAME and hydrocarbons in large quantities in GC–MS shows that HDPE acts as an effective hydrogen donor, reducing oxygenation and enriching the high-energy hydrocarbon fraction (Hoque & Rashid, 2021).

Thus, this discussion confirms that the improvement in bio-oil quality does not only depend on the mixture ratio but is also understood through the transformation of the chemical composition shown by GC–MS. The synergy of both biomass and plastic sources produces a bio-oil fraction with characteristics close to conventional liquid fuels at an optimum RG–HDPE ratio of 75:25.

ANOVA Calculations

Effect of RG–HDPE ratio on biochar quality parameters

The ANOVA test results show that variations in the *Pennisetum purpureum*–HDPE mixture ratio have a significant effect on all biochar parameters tested, including moisture content, volatile matter, fixed carbon, ash content, and density. This statistical significance confirms that changes in biochar characteristics are not random, but rather a systematic response to modifications in feedstock composition during the co-pyrolysis process. This finding is in line with studies on biomass pyrolysis optimization, which emphasize that feedstock composition is a dominant factor in determining the properties of solid products resulting from thermochemical conversion

The increase in volatile matter and decrease in fixed carbon at higher HDPE ratios indicate a reduction in the degree of carbonization due to the contribution of polymers that do not form stable aromatic carbon structures, a mechanism also reported in biomass–plastic co-pyrolysis studies that highlight the synergistic and competitive effects between biomass and polyolefin components (Puentes *et al*., 2023).

The statistically significant decrease in biochar density reflects the formation of a more porous structure, which has direct implications for combustion properties and its potential use in waste-based energy system (Rashid & Zaini, 2021).

Meanwhile, the significant yet relatively moderate change in ash content indicates that although the mineral content did not increase dramatically, the

Table 3 ANOVA Result for the Effect of RG-HDPE Ratio on Biochar Quality Properties

Var	**Src**	**SS**	**df**	**MS**	**F**	**p**
MC	B	92.96	4	23.24	118.63	<0.001
	W	3.92	20	0.196	–	–
	T	96.88	24	–	–	–
VM	B	664.59	4	166.15	198.50	<0.001
	W	16.75	20	0.837	–	–
	T	681.34	24	–	–	–
Ash	B	4.91	4	1.23	41.00	<0.001
	W	0.60	20	0.030	–	–
	T	5.51	24	–	–	–
ρ	B	0.094	4	0.0235	47.00	<0.001
	W	0.010	20	0.0005	–	–
	T	0.104	24	–	–	–
FC	B	1605.10	4	401.28	92.20	<0.001
	W	87.11	20	4.36	–	–
	T	1692.21	24	–	–	–

redistribution of volatile and carbon phases during pyrolysis still affected the concentration of inorganic residues in biochar. Overall, the ANOVA results confirm that adjusting the HDPE biomass ratio is an effective approach to controlling biochar quality, supporting the concept of integrated optimization in modern waste-to-energy systems as emphasized by (Gabbar & Ahmad, 2024), and reinforcing the role of co-pyrolysis as a waste valorization strategy that not only improves energy efficiency but also enables targeted engineering of solid product properties.

Effect of RG–HDPE ratio on bio-oil quality parameters

Table 4. ANOVA Result for the Effect of RGHDPE Ratio on Bio-oil Quality Properties

Var	Src	SS	df	MS	F	p
P	B	0.014	4	0.004	5.250	0.015
	W	0.007	10	0.001	–	–
	T	0.021	14	–	–	–
H	B	1.962	4	0.491	21.548	<0.001
	W	0.228	10	0.023	–	–
	T	2.190	14	–	–	–
FP	B	615.600	4	153.900	85.500	<0.001
	W	18.000	10	1.800	–	–
	T	633.600	14	–	–	–
HHV	B	6,351,885.864	4	1,587,971.466	23,304,541.62	<0.001
	W	0.681	10	0.068	–	–
	T	6,351,886.546	14	–	–	–

A one-way ANOVA test was conducted to assess the effect of the *Pennisetum purpureum*–HDPE ratio on four main bio-oil parameters: density, viscosity, flash point, and calorific value (HHV). The ANOVA test results show that variations in the Pennisetum purpureum–HDPE mixture ratio have a significant effect on all major bio-oil parameters, namely density, viscosity, flash point, and calorific value. This statistical significance confirms that changes in bio-oil characteristics are not merely experimental fluctuations, but rather a direct result of feedstock composition modifications during the co-pyrolysis process. This finding is consistent with the principle of waste-to-energy process optimization, which states that feedstock composition is a key variable in determining the quality of liquid energy products (Gabbar & Ahmad, 2024).

The statistically significant decrease in bio-oil density and viscosity indicates a shift in chemical composition toward hydrocarbon and ester fractions with weaker intermolecular interactions. These results are in line with biomass pyrolysis optimization studies reporting that the enrichment of non-polar compounds directly contributes to improved flow properties and bio-oil stability (Kusworo *et al*., 2020).

In the context of biomass plastic co-pyrolysis, this phenomenon is reinforced by the synergistic effect between lignocellulose and polyolefin degradation, where HDPE acts as a hydrogen donor that suppresses the formation of heavy oxygenated compounds and increases the fraction of high-energy hydrocarbons (Puentes *et al*., 2023).

The significantly decreased flash point indicates an increased fraction of volatile compounds in the bio-oil, which is a direct consequence of the dominance of light hydrocarbons resulting from HDPE degradation. Operationally, this change is important because it relates to the safety and handling of liquid fuels, while also reflecting the increased volatility commonly found in pyrolysis systems with high plastic fractions (Mohammed *et al*., 2020).

The calorific value shows the strongest statistical influence, confirming that the feedstock ratio is highly determinative of the bio-oil's energy potential. The increase in calorific value at the medium ratio reflects the optimum conditions where the content of high-energy hydrocarbons and esters increases without excessive energy loss to the gas phase. This pattern is consistent with energy optimization studies on biomass pyrolysis processes, which show that control of process parameters and feed composition are dominant factors in maximizing the calorific value of liquid products (Gabbar & Ahmad, 2024).

Overall, the ANOVA results confirm that the biomass HDPE mixture ratio is the main controlling parameter for bio-oil quality, both in terms of physical properties and energy content. These findings reinforce that co-pyrolysis not only serves as a waste management strategy but also as an effective process engineering approach to produce bio-oil with characteristics that can be directed through feedstock composition optimization, in line with the framework of modern waste-to-energy system development.

Implications for Energy Utilization and Waste Management

The co-pyrolysis results show that the addition of HDPE does not increase the overall yield of bio-oil or biochar, but it can improve the energy quality of bio-oil up to a certain ratio and modify the properties of biochar towards lower density and higher volatility. Thus, the hypothesis that HDPE acts as a hydrogen donor that improves the energy quality of the product is confirmed, especially in terms of the calorific value and density of bio-oil, while the effect on total energy yield is more complex and influenced by operating conditions and reactor characteristics (Awad *et al*., 2024).

From a waste management and energy transition perspective, the co-pyrolysis of *Pennisetum purpureum* and HDPE at a ratio of 75:25–60:40 appears promising as a dual energy recovery scenario: bio-oil with high calorific value that has the potential to be further formulated as liquid fuel, and biochar with characteristics that are still relevant for low-rank coal substitution and environmental applications. This is in line with the trend of utilizing biomass and solid waste to produce a combination of energy products and value-added products (Ge *et al*., 2025).

However, for very high HDPE ratios (50:50), the reduced bio-oil yield and loss of biochar make the system less profitable when the research objective is to produce two types of fuel simultaneously. Such ratios are more relevant for process designs that are truly oriented towards liquid/gas fuels and the utilization of plastics as the main raw material, as examined in several advanced gasification and pyrolysis configurations (Aljaziri *et al*., 2023).

In general, these combined results confirm that determining the biomass–plastic mixture ratio in co-pyrolysis cannot be based solely on increasing calorific value, but must also consider yield, the presence of two products (bio-oil and biochar), the end-use application, and the local waste management context. This approach is in line with the concept of multifaceted valorization of biomass and industrial residues, which positions pyrolysis as part of a broader circular energy and economic system (Aboelela *et al*., 2023).

CONCLUSION

This study demonstrates that the mixture ratio of *Pennisetum purpureum* and HDPE plays a decisive role in governing the characteristics of co-pyrolysis products. Among the investigated compositions, the 75:25 RG–HDPE ratio consistently produced the most favorable performance. At this condition, the bio-oil exhibited a higher calorific value, along with reduced density and viscosity, accompanied by a compositional shift toward hydrocarbon- and FAME-rich fractions as identified by GC–MS analysis.

The corresponding biochar also showed distinct structural modification, including increased volatile matter and reduced fixed carbon content and density, indicating alterations in carbonization behavior driven by biomass–plastic interactions. These trends confirm that the observed changes were not random fluctuations but reflected systematic transformations associated with feedstock blending.

Statistical evaluation using ANOVA further verified that variations in bio-oil and biochar properties were significantly influenced by the RG–HDPE ratio, supporting the robustness of the experimental findings. The novelty of this work lies in its integrated analytical framework, which directly correlates feedstock composition, chemical evolution, thermophysical properties, and statistical validation within a single co-pyrolysis system. Such a comprehensive evaluation remains limited for the *Pennisetum purpureum*-HDPE combination. Overall, this study establishes 75:25 as an interaction-optimized composition and provides a scientifically grounded basis for the rational design of biomass-plastic co-pyrolysis systems toward more controllable and targeted waste-to-energy applications.

NOTATION

Table 5. Symbols / Abbreviations and Explanation

Symbols / Abbreviations	Explanation
ASTM	American Society for Testing & Materials
FAME	Fatty Acid Methyl Ester
FC	Fixed Carbon
FP	Flash Point (°C)
GC–MS	Gas Chromatography–Mass Spectrometry
HDPE	High-Density Polyethylene
HHV	Higher Heating Value (cal/g)
η	Viscosity of bio-oil (cP)
ρ	Density (g/cm^3)
RG	*Pennisetum purpureum*
VM	Volatile Matter (%)
Ash	Ash Content (%)
MC	Moisture Content (%)
w/w	Weight percent (%)
Var	Variable
Src	Source (B = Between; W = Within; T = Total)
SS	Sum of Squares
df	Degrees of Freedom
MS	Mean Square
F	F-value
p	p-value

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest in the conduct of the research or the preparation of this manuscript.

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