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High-Quality Bio-Oil Production from Co-Pyrolysis of Acetic Acid Pretreated Nypa Fronds and High-density Polyethylene with Ni–Cu Modified Fly Ash Catalyst

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Abstract

Co-pyrolysis has emerged as a promising thermochemical approach to enhance both the yield and quality of bio-oil compared to conventional pyrolysis. In this study, *Nypa fruticans* frond (NFF) was initially pyrolyzed following pretreatment with acetic acid diluted in peat water (AAPW) at concentrations of 2.5, 5, 7.5, and 10 w/w% to identify the optimal pretreatment condition for bio-oil production. Subsequently, co-pyrolysis was conducted using NFF pretreated at the selected AAPW concentration (2.5 w/w%) with high-density polyethylene (HDPE) at feed ratios of 30:70, 50:50, and 70:30 (NFF/HDPE, w/w). Finally, catalytic co-pyrolysis was performed at the optimal feed ratio (70:30) by adding Ni–Cu/FA catalyst loadings of 5%, 10%, and 15% (w/w). All experiments were conducted at 500 °C for 60 min. Results showed that increasing AAPW concentration enhanced the bio-oil yield, while the incorporation of HDPE significantly improved both yield and quality. Catalytic co-pyrolysis provided the greatest upgrading effect, with 15% Ni–Cu/FA catalyst achieving the highest bio-oil yield (71.87 ± 2.21%), heating value (45.55 MJ/kg), energy yield (89.61%), and superior physicochemical properties, including near-neutral pH (6.82), high density (0.78 g/cm^3), and 98.43% hydrocarbon content. Overall, the combination of AAPW pretreatment, plastic co-feeding, and catalytic upgrading proved effective in producing high-quality bio-oil characterized by elevated hydrocarbon content and near-neutral acidity.

Keywords

bio-oil, co-pyrolysis, fly ash, Ni-Cu catalyst, pretreatment

1 Introduction

The extensive use of fossil fuels has raised significant concerns due to resource depletion and the increasing environmental impact, including greenhouse gas emissions and air pollution. In response to these challenges, renewable energy sources are being developed as more sustainable and environmentally friendly alternatives. Among them, biomass stands out for its potential to reduce carbon emissions and environmental pollutants, as it contains lower levels of sulfur and nitrogen compared to fossil fuels [1, 2].

Biomass is composed mainly of three chemical elements (carbon, hydrogen and oxygen) which form the structural components cellulose, hemicellulose, and lignin [3]. One promising source of biomass in Indonesia is nypa (*Nypa fruticans*), which are abundant in coastal and estuarine regions. According to Evelyn et al. [4], *Nypa fruticans* frond (NFF) contain approximately 61.3% cellulose, 24% hemicellulose, and 17% lignin, making them a potential feedstock for thermochemical conversion processes such as pyrolysis.

Parallel to the issue of fossil energy, plastic waste accumulation has become a growing environmental concern due to its low degradability and limited recycling rate. In Riau Province, Indonesia, daily waste generation has reached 1,309 t/day, with an annual accumulation of approximately 477,809 t/year. Plastic waste accounts for around 20.4% of the total, making it the second-largest

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waste component after food waste [5]. Plastic waste such as high-density polyethylene (HDPE) is characterized by a high hydrogen content and a low oxygen content, making it suitable to function as an effective hydrogen donor in biomass pyrolysis reactions [6–8].

Co-pyrolysis is the simultaneous thermal decomposition of biomass and plastics under oxygen-limited conditions and is widely recognized for producing synergistic effects that enhance bio-oil yield and fuel quality [7–9]. Process performance is strongly governed by temperature, feedstock ratio, and catalyst selection. In this work, fly ash (FA) was used as a catalyst because it is an abundant, low-cost industrial by-product rich in catalytically active oxides (SiO_2, Al_2O_3, CaO, Fe_2O_3). These components promote cracking and deoxygenation reactions, thereby increasing hydrocarbon formation and improving the energy quality of the bio-oil [10, 11]. To further enhance catalytic activity, fly ash was modified with Ni–Cu, as bimetallic Ni–Cu systems offer superior metal dispersion and synergistic deoxygenation performance compared to monometallic catalysts [12].

Recent studies also highlight the benefits of pretreatment techniques. For instance, acetic acid treatment can remove alkali and alkaline earth metals (AAEMs) from biomass, which helps optimize the pyrolysis reaction and bio-oil yield [13]. Furthermore, dissolving the acetic acid in peat water, which contains humic substances, may further enhance the calorific value of the resulting bio-oil due to the removal of mineral impurities.

In this study, NFF and HDPE plastic were used as co-pyrolysis feedstocks, with nickel and copper modified fly ash (Ni-Cu/FA) serving as the catalyst. The research aims to evaluate the effects of pretreatment using acetic acid dissolved in peat water (AAPW) on the characteristics of NFF, and to investigate the influence of feedstock ratio (NFF/HDPE, wt%) and Ni-Cu/FA catalyst concentration on bio-oil yield and quality.

2 Material and methods

2.1 Material

The materials used in this study include NFF, HDPE plastic, acetic acid 99% (MKR Chemicals, Indonesia), peat water, fly ash, $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, Germany), copper(II) sulfate pentahydrate (Merck, Germany), hydrochloric acid 1 M (Alkemi, Indonesia), and nitrogen gas with 99% purity.

2.2 Methods

This research was conducted through several main stages, including the preparation and pretreatment of raw materials, catalyst synthesis and characterization, co-pyrolysis process, and analysis of the resulting bio-oil and catalyst.

2.2.1 Treatment of *Nypa fruticans* frond and high-density polyethylene

NFFs were first cut into pieces of approximately 1–2 cm in length and sun-dried, resulting in a moisture content of 10.6% prior to pretreatment. The fronds were then subjected to pretreatment using AAPW at concentrations of 2.5, 5.0, 7.5, and 10.0 w/w%, prepared by diluting glacial acetic acid into peat water. Each solution was applied to 100 g of NFF biomass under controlled conditions. The pretreatment was carried out at a temperature of 60 °C for 2 h, with continuous stirring to ensure uniform soaking. After treatment, the fronds were shade-dried, followed by oven-drying at 100 °C until a constant mass was achieved.

HDPE plastic was also cut into pieces of 1–2 cm. The plastic fragments were washed with clean water to remove surface contaminants and subsequently sun-dried before use.

2.2.2 Activation and leaching of Ni-Cu/fly ash catalyst

Fly ash was initially sieved using two successive mesh sizes: 120 mesh and 200 mesh. The material retained on the 200-mesh sieve was collected and used for further processing. A total of 100 g of sieved fly ash was placed in a glass beaker and mixed with 500 mL of hot distilled water (100 °C). The mixture was stirred using a magnetic stirrer and left to stand for 2 h, followed by oven drying at 110 °C for 12 h.

For the leaching process, 60 g of the pre-washed fly ash was added into 360 mL of distilled water, and acetic acid (1 M) was added dropwise until the pH reached 1. The suspension was stirred at 600 rpm for 2 h using a magnetic stirrer. The solid residue was filtered using a Buchner funnel and washed repeatedly with distilled water until the filtrate reached neutral pH. The residue was then dried in an oven at 110 °C for 24 h.

2.2.3 Impregnation of nickel and copper onto fly ash

The impregnation was carried out to achieve a total Ni and Cu loading of 3 wt% on fly ash. 200 g of fly ash was first wet-impregnated with 14.863 g of $Ni(NO_3)_2 \cdot 6H_2O$, slowly added under continuous stirring. The impregnated sample was kept in a desiccator for 12 h and then oven-dried at 110 °C for 12 h. Copper was subsequently introduced using 11.796 g of $CuSO_4 \cdot 5H_2O$ following the same procedure. The dual-metal impregnated material was calcined at 550 °C for 3 h to activate the Ni–Cu species on the fly ash support.

2.2.4 Co-pyrolysis process

The pyrolysis and co-pyrolysis experiments were conducted using a fixed-bed batch reactor. The single-feed pyrolysis of NFF was performed on samples pretreated with AAPW at concentrations of 2.5, 5.0, 7.5, and 10.0 w/w%, under operating conditions of 500 °C for 60 min. Pretreatment condition which provided the highest bio-oil energy yield, was selected as the fixed pretreatment condition for all subsequent co-pyrolysis experiments.

In the co-pyrolysis stage, the pretreated NFF was blended with HDPE at mass ratios of 30:70, 50:50, and 70:30 and subjected to pyrolysis under identical operating conditions (500 °C, 60 min). The NFF/HDPE ratio that produced the most favorable performance (highest bio-oil yield, calorific value, and overall energy yield) was then established as the fixed feed ratio for the catalytic co-pyrolysis stage. Catalytic co-pyrolysis was subsequently carried out using the selected feed ratio with Ni–Cu/FA catalyst loadings of 5, 10, and 15 wt% relative to the total mass of feedstock. Experiments were repeated three times, and the results were presented as mean ± standard deviation.

2.2.5 Product analysis and characterization

The bio-oil produced was collected, weighed to determine yield, and analyzed for heating value (bomb calorimeter, IKA C2000, Germany), density, viscosity, pH, and chemical composition using gas chromatography–mass spectrometry (GC-MS, Shimadzu QP-2010, Japan). Char yield was obtained from the mass of solid residue after pyrolysis, while gas yield was calculated by subtracting the liquid and char yields from 100%. The energy yield of the bio-oil was determined using the formula adapted from Awad et al. [14], which accounts for both the mass and calorific value of the bio-oil relative to the total energy content of the feedstock. The Ni-Cu/FA catalyst was characterized before and after pyrolysis using X-ray diffraction (XRD, Bruker D2 Phaser diffractometer, Germany), X-ray fluorescence (XRF, Bruker S8 Tiger spectrometer, Germany), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX, JEOL JSM-6510LA, Japan).

3 Result and discussion

3.1 Analysis of Ni-Cu/fy ash catalyst characteristics

XRF analysis was conducted to evaluate the elemental composition of fly ash before and after Ni–Cu impregnation. As presented in Table 1, the modified catalyst shows substantial increases in NiO (from 0.014 to 12.070 wt%) and CuO (from 0.017 to 10.870 wt%), confirming effective incorporation of both metals. The enrichment of NiO is associated with enhanced hydrogen and carbon monoxide formation, which promotes hydrodeoxygenation (HDO) reactions [15], while CuO functions as a co-catalyst that facilitates the removal of oxygenated functional groups and improves catalyst stability [12].

Table 1 XRF analysis of fly ash and Ni-Cu/FA catalyst

Compounds	Fly ash (wt%)	Ni-Cu/FA (wt%)
Al_2O_3	17.200	15.130
SiO_2	32.800	36.760
SO_3	0.110	3.573
CaO	9.430	6.797
TiO_2	1.120	1.788
Fe_2O_3	11.800	12.590
NiO	0.014	12.070
CuO	0.017	10.870
SrO	0.115	0.127
BaO	0.134	0.303
MgO	2.870	-

The characterization results in Tables 2 and 3 show that Ni-Cu metal loading significantly alters the structural and textural properties of fly ash [16, 17]. The crystallite size decreases from 43.98 nm [16] to 27.55 nm, accompanied by a reduction in crystallinity from 62.90% to 57.49%, indicating lattice distortion and improved dispersion of NiO and CuO phases on the fly ash surface. These structural changes are beneficial for catalytic activity because smaller crystallites generally provide more exposed active sites [18].

BET analysis further supports these structural enhancements. The surface area increases from 5 [17] to 10 m^2/g, accompanied by a substantial rise in pore width from 0.680 to 5.086 nm, indicating that metal impregnation facilitates the formation of larger and more accessible pores. Despite a slight reduction in pore volume (0.059 to 0.026 cm^3/g), the combined increase in surface area and pore diameter enhances reactant diffusion and the availability of active sites. Overall, these textural improvements demonstrate that Ni–Cu/FA exhibits superior catalytic characteristics compared to raw fly ash.

The XRD analysis of the Ni–Cu/fly ash catalyst (Fig. 1) confirms the formation of NiO and CuO phases in addition to the original SiO_2 and Fe_2O_3 components of the fly ash. The appearance of these metal oxide phases corresponds to the reduction in crystallite size (from 43.98 to 27.55 nm) and the slight decrease in crystallinity (from 62.90% to 57.49%) shown in Table 2. These structural changes

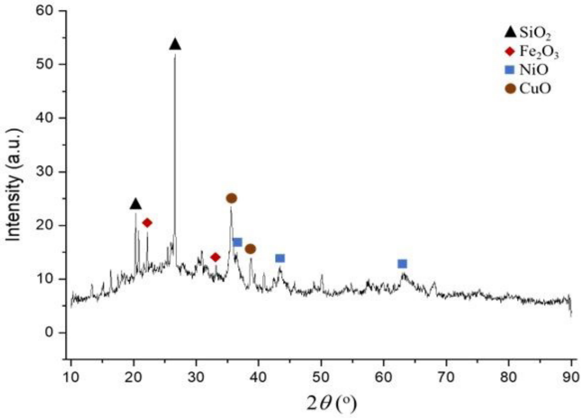

Fig. 1 XRD diffractogram of Ni-Cu/FA catalyst

Table 2 Comparison of crystal properties of fly ash and Ni–Cu/FA

Compounds	Fly ash [16]	Ni-Cu/FA
Crystal size (nm)	43.98	27.55
Crystallinity degree (%)	62.90	57.49

indicate improved metal dispersion and the generation of more defect sites within the catalyst matrix, which is consistent with the increased BET surface area and larger pore width observed in Table 3.

Fig. 2 (1000x SEM) shows that the Ni–Cu/FA catalyst consists mainly of spherical particles with some irregular and agglomerated structures. This morphology aligns with typical fly ash characteristics reported by Liu et al. [19], who noted predominantly spherical particles with variable size and occasional porosity that can enhance catalytic activity. The presence of irregular and aggregated particles is consistent with observations by Turmuzi et al. [20] and likely results from mineral phase diversity and structural changes induced during Ni–Cu impregnation and subsequent thermal treatment.

Table 3 BET analysis of Ni-Cu/FA catalyst

Parameters	Fly ash [17]	Ni-Cu/FA
Surface area (m^2/g)	5	10
Pore width (nm)	0.680	5.086
Pore volume (cm^3/g)	0.059	0.026

Note: Pore volume testing was carried out using the BET analysis setup with the BJH method.

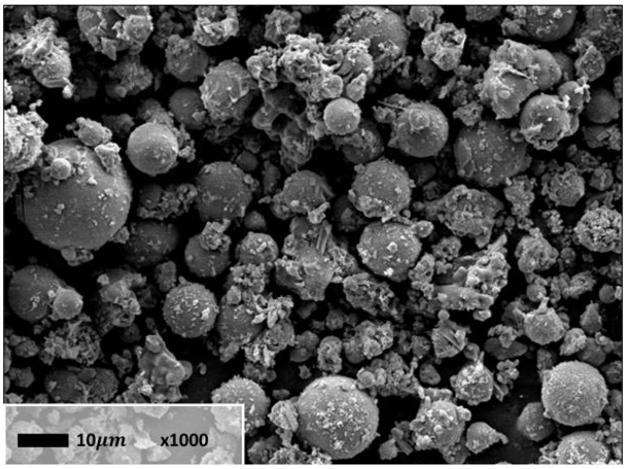

Fig. 2 SEM analysis of Ni-Cu/FA catalyst

The morphological variations observed in the Ni–Cu/FA catalyst are consistent with the XRF results (Table 1) showing substantial increases in NiO and CuO. The presence of porous and irregular structures is beneficial for catalytic applications, as it may provide more active sites and improve the interaction between the catalyst and reactants during the co-pyrolysis process.

The EDX results further presented in Table 4 support the successful modification of the catalyst. The detection of Ni (22.23 mass%) and Cu (11.36 mass%) confirms effective metal impregnation onto the fly ash surface, complementing the XRD observation of NiO and CuO crystalline phases. Meanwhile, the dominant Al, Si, and Fe contents reflect the natural aluminosilicate and iron oxide components of fly ash, which form the structural backbone of the catalyst.

3.2 Analysis of the effect of pre-treatment on the yield and calorific value of bio-oil

The pretreatment of NFF using AAPWplays a crucial role in enhancing the bio-oil yield during co-pyrolysis. Acetic acid functions to remove AAEMs, which are known to catalyze secondary cracking reactions and promote char formation [13]. Additionally, peat water naturally contains humic and fulvic acids, which can help in mineral dissolution and possibly enhance the fuel quality of the derived bio-oil [21].

Fig. 3 illustrates the effect of AAPW concentration on the pyrolysis products (bio-oil, char, and gas) yields. It is evident that increasing the concentration of AAPW from 0 to 7.5 w/w% leads to a consistent rise in bio-oil yield, peaking at 43.74 ± 1.13%. This increase can be attributed to the more effective removal of AAEMs at higher acid

Table 4 EDX analysis results of Ni-Cu/FA catalysts

Element	Mass (%)	Atom (%)
Al	13.24	20.15
Si	24.59	35.95
Fe	28.57	21.01
Ni	22.23	15.55
Cu	11.36	7.34

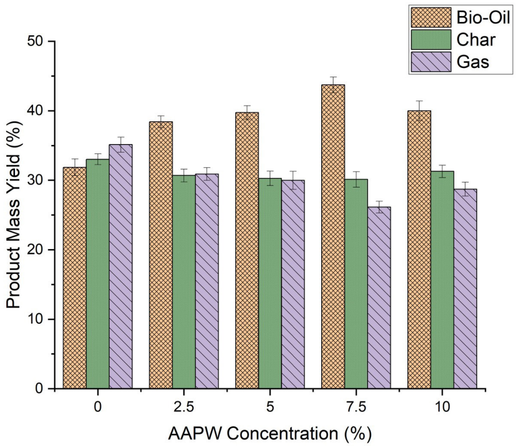

Fig. 3 Effect of acetic acid peat water concentration in NFF pretreatment on product mass yield (%)

concentrations, thereby reducing catalytic cracking and favoring the formation of liquid products.

However, at 10% AAPW, a slight decline in bio-oil yield is observed. This may indicate that excessive acid treatment could alter the biomass structure and possibly degrading essential volatiles or promoting partial hydrolysis during pretreatment, leading to increased gas formation or even re-polymerization of bio-oil precursors into solid residue (char).

Although higher AAPW concentrations increased bio-oil yield, Table 5 shows that the highest calorific value (23.74 MJ/kg) and energy yield (56.54%) were achieved at 2.5% AAPW. At higher concentrations (5–10%), bio-oil yield continued to increase, but the calorific value decreased to around 19.6–21 MJ/kg, resulting in lower overall energy yield. This decline can be attributed to higher water content and oxygenated compounds such as acids and aldehydes in produced bio-oil. These components lower energy density despite higher mass yield. Therefore, while AAPW pretreatment improves bio-oil production, optimizing acid concentration is key to balancing yield with fuel quality.

Table 5 Effect of AAPW pretreatment concentration on bio-oil yield and energy performance

Concentration of AAPW (%)	Bio-oil yield (%)	Calorific value (MJ/kg)	Energy yield (%)
0	31.86	19.62	38.73
2.5	38.42	23.74	56.54
5	39.74	20.99	51.68
7.5	43.74	19.61	53.16
10	40.00	19.59	48.56

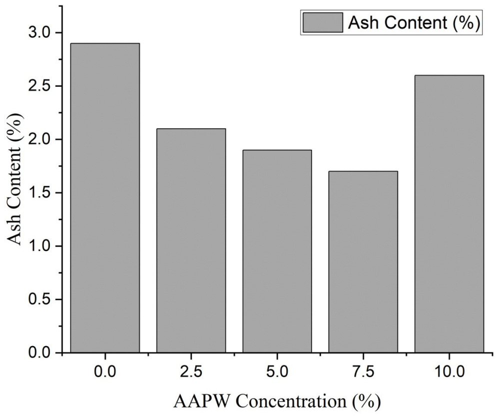

Fig. 4 Influence of AAPW pretreatment concentration on NFF ash content

Fig. 4 shows that AAPW pretreatment reduces the ash content of NFF from 2.9% to about 1.8% at a 7.5% AAPW concentration. This improvement is attributed to the removal of AAEMs, which serve as the main inorganic impurities in biomass. Comparative data from Tamunaidu and Saka [22] indicate that nypa frond ash contains Na (2 wt%), Mg (0.5 wt%), and K (2.1 wt%), which not only catalyze cracking and char formation during pyrolysis, but also contribute to slagging and fouling through the formation of low-melting inorganic deposits [11, 13].

Ash content decreases at 2.5–7.5% acetic acid because AAEMs are effectively leached out. However, at high acid strength (10%), excessive hydrolysis removes more organic components (especially hemicellulose), causing the remaining biomass to become proportionally richer in minerals [23].

The decrease in ash content correlates directly with the reduction in char yield at pretreatment concentrations of 2.5%, 5%, and 7.5%. Without pretreatment, the char yield was 33.02%, and it declined to 30.68 ± 0.91%, 30.28 ± 1.02%, and 30.12 ± 1.12% at these respective concentrations. This reduction reflects the effective removal of inorganic minerals (AAEMs), which normally enhance thermal stability and promote char formation.

However, at 10% AAPW pretreatment, the char yield increases to 31.28 ± 0.89%%. This phenomenon is attributed to over-acidification, in which excessive hydrolysis leads to the removal of more organic constituents, producing a biomass fraction enriched in minerals, which subsequently generates a greater amount of solid residues during pyrolysis [12].

Proximate and ultimate analyses were conducted on two biomass samples: untreated NFF (before pretreatment) and NFF pretreated under the optimal condition of 2.5% AAPW. The proximate analysis (Table 6) [24–30] reinforces the finding that pretreatment with 2.5 w/w% AAPW

Table 6 Proximate and ultimate analysis of NFF

Parameters	Without pretreatment	Pretreatment with 2.5% AAPW	Method
Proximate			
Moisture (wt%)	10.60	5.46	ASTM D 3173/D31773M-17a [24]
Ash content (wt%)	3.40	2.40	ASTM D 3174-12 (2018)e1 [25]
Volatile matter (wt%)	66.88	74.28	ASTM D 3175-20 [26]
Fixed carbon (wt%)	18.12	17.86	ASTM D 3172-2021e1 [27]
Ultimate			
Carbon (wt%)	45.58	46.11	
Hydrogen (wt%)	6.28	6.02	ASTM D5373-21 (Method A) [28]
Nitrogen (wt%)	0.29	0.32	
Sulfur (wt%)	0.10	0.07	ASTM D4239-18e1 (Method A) [29]
Oxygen (wt%)	47.69	45.08	ASTM D 3176-24 [30]

increased volatile matter from 66.88 wt% to 74.28 wt% and decreased ash content from 3.40 wt% to 2.40 wt%. Fixed carbon remained relatively stable, suggesting that the primary shift in composition was due to reduced mineral matter and enhanced devolatilizable content.

Ultimate analysis revealed a slight rise in carbon content (45.58% to 46.11%) and a reduction in sulfur (0.10% to 0.07%), enhancing the calorific quality of the pyrolysis products. This aligns with Table 5, where the highest energy yield occurred at 2.5% AAPW, driven by higher bio-oil yield and improved organic quality, while further AAPW increases showed diminishing benefits due to possible leaching of organics.

3.3 Effect of raw material ratio on bio-oil yield and energy yield

Table 7 and Fig. 5 demonstrate the influence of varying the ratio of NFF and HDPE plastic on product distribution (bio-oil, char, and gas) and energy performance in the co-pyrolysis process. In this study, the NFF used had been pretreated with 2.5% AAPW. As observed, increasing the HDPE content in the mixture significantly enhances the bio-oil yield, with the highest yield of 68.22 ± 1.7% achieved at the NFF/HDPE mass ratio of 30:70. This is notably higher than the yield obtained from the pyrolysis of NFF alone (with 2.5% AAPW pretreatment), which only produced 38.42 ± 0.85% bio-oil with a calorific value of 23.74 MJ/kg and a corresponding energy yield of 56.54%.

Table 7 Effect of NFF/HDPE ratio on bio-oil yield, calorific value, and energy yield

NFF/HDPE ratio	Bio-oil yield (%)	Calorific value (MJ/kg)	Energy yield (%)
30:70	68.22	45.81	85.53
50:50	56.84	45.13	83.54
70:30	44.96	31.84	57.54

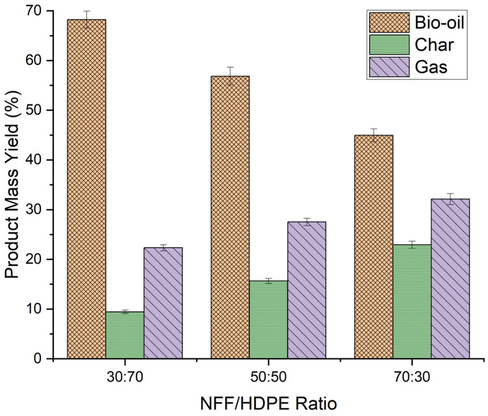

Fig. 5 Effect of NFF/HDPE ratio on bio-oil, char, and gas yields

This substantial improvement can be attributed to the synergistic effect during co-pyrolysis, where HDPE acts as an effective hydrogen donor. During thermal decomposition, HDPE produces aliphatic hydrocarbons and hydrogen radicals that interact with the oxygenated volatiles from biomass. This interaction promotes HDO, reducing the oxygen content and increasing the hydrocarbon content of the resulting bio-oil, which in turn enhances both yield and calorific value [31].

The highest energy yield of 85.53% at the 30:70 (NFF/HDPE) mass ratio corresponds to the highest calorific value of 45.81 MJ/kg, comparable to commercial fossil fuels. This ratio was selected because it provides optimal synergy between biomass and HDPE, enhancing deoxygenation and hydrocarbon formation while minimizing oxygenated compounds.

However, higher biomass fractions (mass ratio 50:50 and 70:30) increase oxygen content, resulting in lower calorific value, reduced oil stability, and decreased conversion efficiency. This trend is evident at the 70:30 mass ratio, where bio-oil yield drops to 44.96 ± 1.31% and energy yield to 57.54%, consistent with the behavior of lignocellulosic bio-oil [32].

Increasing HDPE content also reduces char formation and slightly increases gas yield, as plastics favor volatilization pathways, whereas biomass contributes more to char due to its fixed carbon and lignin content [11, 33].

3.4 Effect of Ni-Cu/FA catalyst ratio on bio-oil yield and energy output

The co-pyrolysis process of pretreated NFF (with 2.5% AAPW) and HDPE at a 30:70 mass ratio was further investigated by varying the percentage of Ni-Cu/FA catalyst to evaluate its impact on product distribution and energy performance. Fig. 6 and Table 8 show that increasing the catalyst ratio from 5% to 15% significantly enhances the bio-oil yield. At a catalyst loading of 5%, the bio-oil yield was 62.31 ± 2.01%, and it increased steadily to 66.30 ± 1.95% at 10% and peaked at 71.87 ± 2.21% at 15% catalyst loading. This enhancement can be attributed to the catalytic activity of Ni and Cu metals impregnated on the fly ash, which effectively promotes cracking reactions and enhances the selectivity towards bio-oil production.

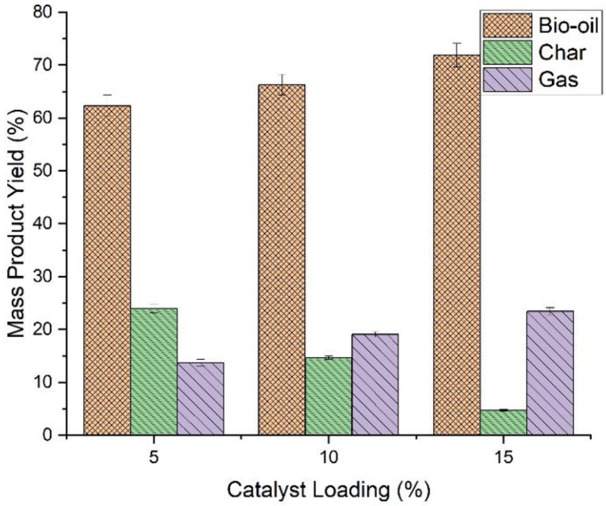

Fig. 6 Effect of catalyst loading on bio-oil, char, and gas yields

Table 8 Effect of Ni-Cu/FA catalyst loading on bio-oil yield, calorific value, and energy yield

Catalyst (%)	Bio-oil yield (%)	Calorific value (MJ/kg)	Energy yield (%)
5	62.31	45.83	78.17
10	66.30	45.81	83.13
15	71.87	45.55	89.61

The catalyst facilitates the breakdown of larger organic molecules and promotes deoxygenation reactions, leading to more efficient conversion of biomass and plastic-derived volatiles into hydrocarbon-rich bio-oil. This is also evident in the corresponding energy yields. As the catalyst ratio increases, the energy yield also improves, reaching a maximum of 89.61% at 15% catalyst usage. This result indicates a synergistic effect of the Ni-Cu/FA catalyst in enhancing both the quantity and quality of the bio-oil produced.

A comparison of heating values clearly demonstrates the superior performance of the Ni–Cu/FA catalyst in upgrading bio-oil quality. The bio-oil produced in this study from the co-pyrolysis of NFF and HDPE using Ni–Cu/FA exhibited a high calorific value ranging from 45.55 to 45.83 MJ/kg, which is remarkably close to the calorific value of commercial kerosene (45.9 MJ/kg) [34]. In contrast, previous work on the co-pyrolysis of NFF and plastic waste using unmodified fly ash reported a substantially lower heating value of 40.93 MJ/kg [11]. The increase in the calorific value observed in the present study indicates that fly ash modification with nickel and copper enhances catalytic activity, particularly by promoting deoxygenation and cracking reactions that increase hydrocarbon formation. This evidence confirms that the incorporation of Ni and Cu into fly ash significantly improves the energy content of bio-oil and strengthens its potential as a renewable liquid fuel. These findings are consistent with previous research by Kumar et al. [35], which reported that NiCu-based catalysts improve bio-oil quality through enhanced catalytic cracking and deoxygenation mechanisms.

3.5 Effect of different treatment conditions to bio-oil physical properties

Table 9 summarizes the characteristics of bio-oil produced from various treatment conditions, including acetic acid pretreatment, raw material ratio variation, and catalyst loading.

Table 9 Physical properties of bio-oil samples under different treatment conditions

Sample	Density (g/cm^3)	Viscosity (m^2/s × 10^{-6})	pH
Untreated NFF	0.93	20.178	2.26
Pretreated NFF (2.5% AAPW)	0.99	18.646	3.57
Pretreated NFF+HDPE (R = 30:70)	0.69	18.561	6.23
Pretreated NFF+HDPE (R = 30:70) Ni-Cu/FA (5%)	0.72	18.305	6.48
Pretreated NFF+HDPE (R = 30:70) Ni-Cu/FA (15%)	0.78	18.476	6.82

The density of the bio-oil varied significantly depending on the treatment conditions, reflecting changes in chemical composition. The highest density (0.99 g/cm^3) was observed in the sample pretreated with 2.5% AAPW, which is consistent with its high content of oxygenated biomass-derived compounds. In contrast, the lowest density (0.69 g/cm^3) was obtained from the 30:70 NFF/HDPE co-pyrolysis sample, indicating a strong shift toward lighter, plastic-derived hydrocarbons. The introduction of the Ni–Cu/FA catalyst increased the density slightly, with values ranging from 0.72 g/cm^3 (5% catalyst) to 0.78 g/cm^3 (15% catalyst).

When compared to kerosene with density range of 0.775–0.820 g/cm^3 [34], the density of bio-oil produced with the addition of 15% catalyst falls within the kerosene range.

The viscosity of the bio-oil was strongly influenced by the feedstock composition and pretreatment. The untreated NFF pyrolysis oil had the highest viscosity (20.178 cSt), consistent with its high lignin content and the formation of complex phenolic structures. This aligns with Wang et al. [36], who reported that lignin-derived compounds significantly increase bio-oil viscosity. After 2.5% AAPW pretreatment, the viscosity decreased to 18.646 cSt, indicating partial breakdown of lignin components. Co-pyrolysis with HDPE and catalytic upgrading further lowered viscosity, with the lowest value (18.476 cSt) observed at 15% catalyst loading. However, these viscosities remain far higher than kerosene (1–2 cSt) [34], showing that further upgrading is required.

The acidity also showed notable changes. The untreated NFF oil had a low pH of 2.26, which increased to 3.57 after AAPW pretreatment. A larger increase occurred in the HDPE co-pyrolysis sample (pH 6.23), and the highest pH (6.82) was achieved with 15% catalyst. This rise in pH results from the dilution of acidic biomass compounds by HDPE-derived hydrocarbons and the deoxygenation promoted by the Ni–Cu/FA catalyst. A higher pH makes the bio-oil less corrosive and more compatible with conventional fuels such as kerosene, which is typically neutral [34].

3.6 Gas chromatography - mass spectrometry analysis of bio-oil composition

The GC–MS analysis reveals a distinct shift in the chemical composition of the bio-oil across the various treatment conditions. Bio-oil produced with 2.5% AAPW is dominated by oxygenated compounds characteristic of conventional biomass pyrolysis (Fig. 7). The introduction of HDPE at a 30:70 ratio significantly modifies this profile, increasing the hydrocarbon fraction to over 90%, which indicates effective hydrogen transfer and enhanced deoxygenation during co-pyrolysis (Fig. 8). The presence of the Ni–Cu/FA catalyst further intensifies this conversion, yielding approximately 98% hydrocarbons and suppressing oxygenated compounds to near-zero levels (Figs. 9 and 10). These trends are consistent with the observations of Soongprasit et al. [37], who reported that fly ash-based catalysts promote hydrocarbon formation and reduce oxygenates in pyrolysis products.

The dominance of hydrocarbons in the GC–MS results is consistent with the improved heating value and density of the upgraded bio-oil, which are close to those of standard kerosene (Table 10). However, its viscosity remains relatively high, likely due to residual heavier or less saturated hydrocarbons. While catalytic co-pyrolysis markedly improves the chemical quality of the bio-oil, further upgrading is still needed to enhance its flow properties.

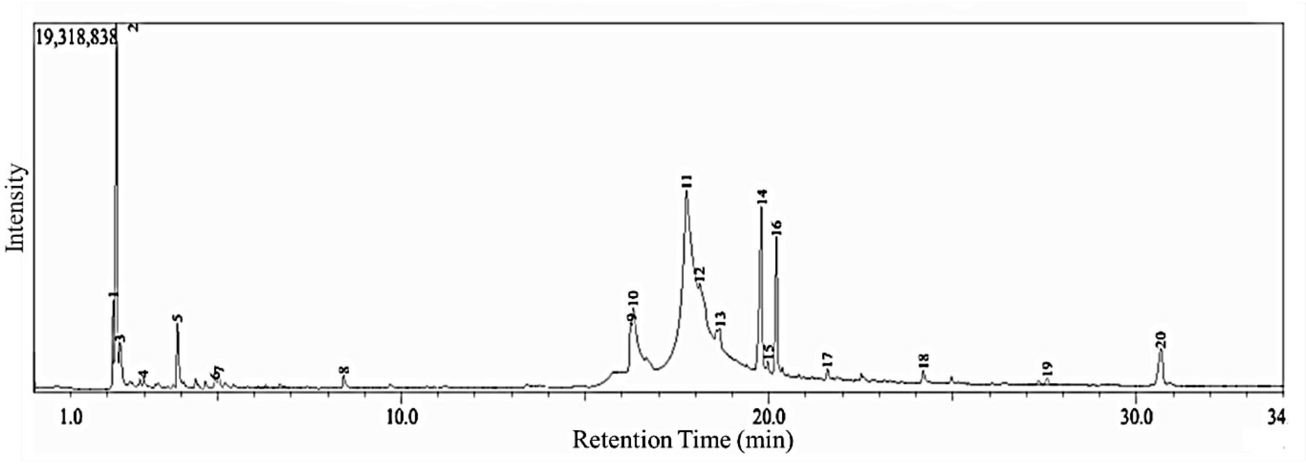

Fig. 7 GC–MS chromatogram of bio-oil from NFF pretreated with 2.5% AAPW

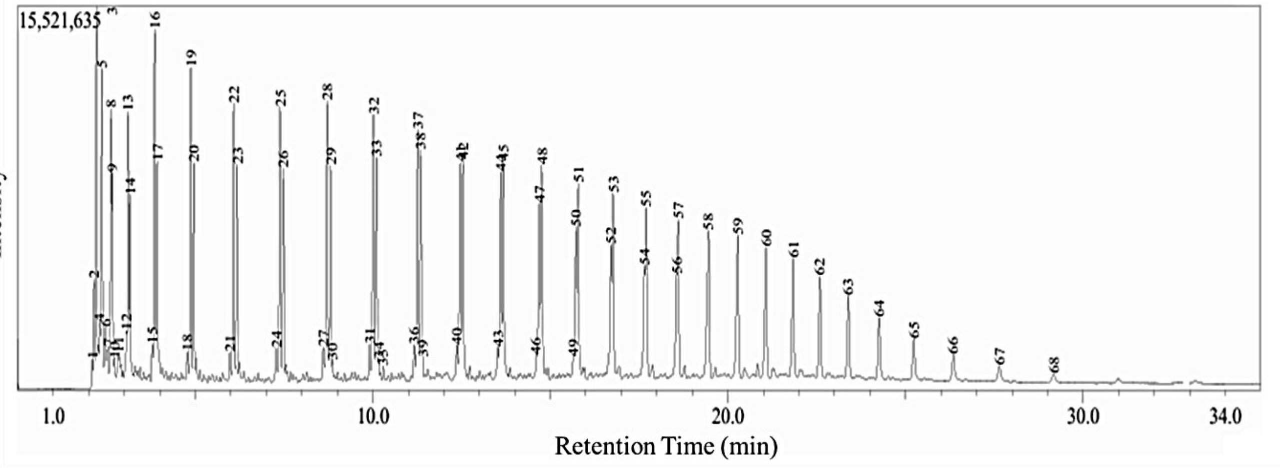

Fig. 8 GC–MS chromatogram of bio-oil from pretreated NFF with HDPE (30:70 wt%)

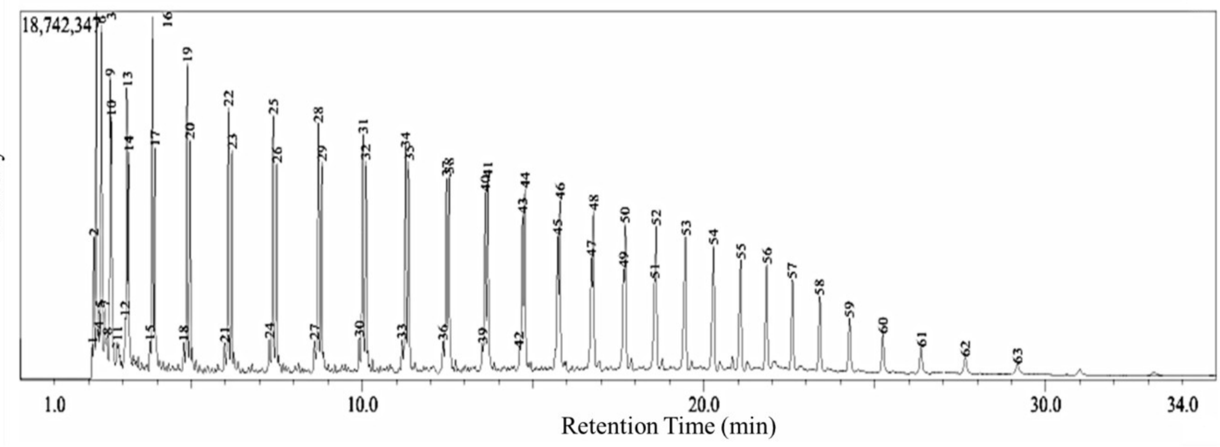

Fig. 9 GC–MS chromatogram of bio-oil from pretreated NFF and HDPE (30:70 wt%) with 5% Ni-Cu/FA catalyst

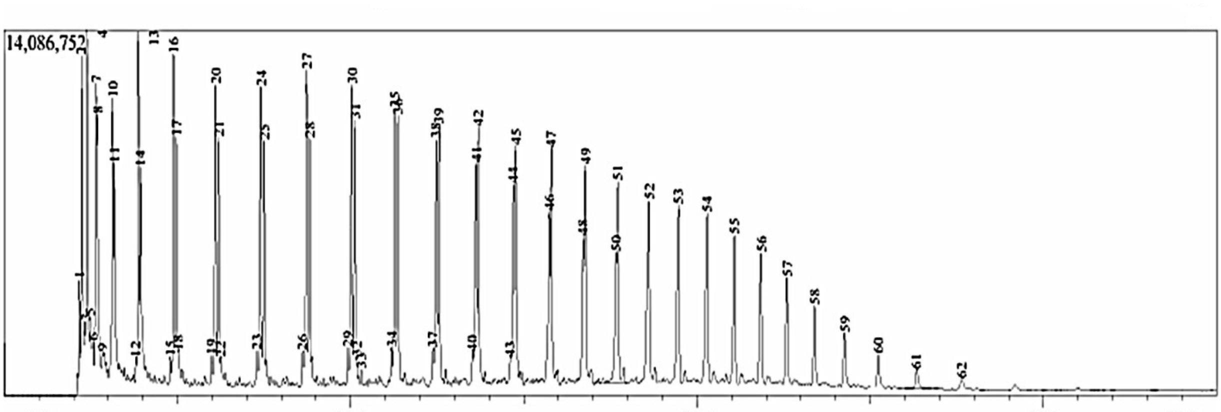

Fig. 10 GC–MS chromatogram of bio-oil from pretreated NFF and HDPE (30:70 wt%) with 15% Ni-Cu/FA catalyst

Table 10 GC–MS analysis of bio-oil obtained from pretreated NFF and co-pyrolysis with HDPE under different catalyst conditions

Compound	Component (%)			
	Pretreated NFF (2.5% AAPW)	Pretreated NFF+HDPE (R = 30:70)	Pretreated NFF+HDPE (R = 30:70) Ni-Cu/FA (5%)	Pretreated NFF+HDPE (R = 30:70) Ni-Cu/FA (15%)
Hyrdocarbons				
Alkanes	-	59.50	63.62	59.46
Alkenes	-	29.01	31.49	36.80
Alkadienes	35.95	2.70	3.34	2.17
Oxygenated compounds				
Alcohol	2.29	4.43	1.33	1.57
Esters	9.46	-	-	-
Ketones	0.33	-	-	-
Others	48.65	1.31	0.23	-

4 Conclusions

This study demonstrates that co-pyrolysis of nypa fronds with HDPE, supported by AAPW pretreatment and catalytic upgrading using a Ni–Cu/FA catalyst, significantly enhances both the yield and quality of the resulting bio-oil. Under the optimal condition of 15% Ni–Cu/FA catalyst, the process produced the highest bio-oil yield (71.87 ± 2.21%), a calorific value of 45.55 MJ/kg, and an energy yield of 89.61%, along with favorable physical properties, including a density of 0.78 g/cm^3, viscosity of 18.476 cSt, pH of 6.82, and a hydrocarbon content of 98.43%. Compared to the untreated sample, the upgraded bio-oil is lighter, less acidic, and more compatible with liquid fuel requirements. Although the upgraded bio-oil falls within the kerosene fuel range, viscosity reduction is still required to meet optimal fuel standards. Overall, the integration of AAPW pretreatment, HDPE co-feeding, and Ni–Cu/FA catalytic co-pyrolysis provides an effective route for producing high-quality, energy-dense bio-oil with strong potential as an alternative liquid fuel.

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