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IMPROVEMENT OF PALM KERNEL SHELL PYROLYSIS CONVERSION AND ITS BIO-OIL PRODUCT THROUGH DUAL NATURAL CATALYSTS

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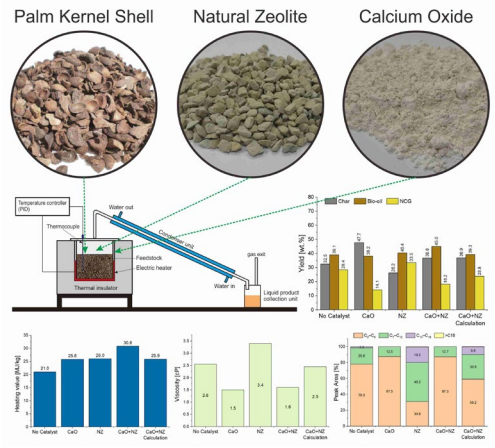
Graphical abstract



Abstract

This study examined the effects of calcium oxide (CaO) and natural zeolite (NZ) catalysts on the pyrolysis of palm kernel shell (PKS) to improve conversion efficiency and bio-oil quality. A 300 g sample of PKS was pyrolyzed in a stainless-steel reactor at 500 °C under four conditions: non-catalytic, CaO-catalyzed, NZ-catalyzed, and dual-catalyst (CaO–NZ). The results showed that both CaO and NZ significantly affected the yields of bio-oil, non-condensable gas (NCG), and char. CaO enhanced cracking to produce lighter bio-oils (C2-C6), whereas NZ acted mainly on heavy intermediates; this upgrading produced both heavier condensed oxygenates and light fragments that remain non-condensable, leading to the highest NCG yield. The catalysts had little effect on bio-oil density but influenced viscosity, pH, and heating value. The dual catalyst produced bio-oil with improved properties: density 980 kg/m^3, viscosity 1.63 cSt, pH 4.1, and heating value 30.76 MJ/kg. Mechanistically, CaO promoted cracking into lighter hydrocarbons (C_2–C_6), whereas NZ favored oligomerization, forming heavier molecules. In combination, CaO suppressed the oligomerization effect of NZ, giving a molecular distribution similar to CaO alone. Although the overall phenolic content changed only slightly, the catalysts significantly altered the ratio of simple to complex phenols. In addition, the dual catalyst facilitated the conversion of esters into ketones, further enhancing bio-oil composition.

Keywords: Bio-oil, Calcium Oxide, Natural Zeolite, Palm Kernel Shell, Pyrolysis

1.0 INTRODUCTION

With the decline of fossil fuel reserves and the growing challenges of global warming and climate change, renewable resources are increasingly explored as alternatives for liquid transportation fuels [1]. Lignocellulosic biomass, the only renewable carbon-rich source, has attracted significant attention in this context. Currently, biomass supplies about 18% of global annual energy demand, and its contribution is expected to reach nearly half of primary energy consumption by 2050 [2]. As a viable substitute for petroleum-based energy, biomass can be upgraded into value-added chemicals and liquid fuels. Among the available methods, pyrolysis is a promising process for converting abundant biomass and other solid fuels into bio-oil with high yields [3]. However, raw bio-oil has limitations, including high viscosity, high oxygen content, acidity, low heating value, poor stability, and the presence of solid impurities [4]. Therefore, upgrading is required before it can be used in conventional petroleum-based engines and systems.

Various catalysts are applied in biomass catalytic pyrolysis and other solid fuels to produce high-quality bio-oil. These include metal oxides (e.g., Fe_2O_3, TiO_2, Al_2O_3, ZrO_2), microporous catalysts (e.g., HZSM-5, ZSM-5, H-Beta, H-USY),

and mesoporous catalysts (e.g., FCC, SBA-15, MCM-41) [5]. Metal oxides are effective in reducing oxygenated compounds such as phenols, acids, and sugars, but their ability to generate hydrocarbons remains limited [6]. Microporous catalysts, particularly ZSM-5, promote catalytic cracking due to their acidity and molecular sieve properties, increasing aromatic hydrocarbon yields while reducing oxygenates. However, rapid deactivation from coke formation is a major drawback [7]. Mesoporous catalysts such as SBA-15 and MCM-41 are widely used to crack larger molecules into smaller ones, enhancing bio-oil quality. Their effectiveness arises from high surface area, moderate acidity, and well-structured mesopores [8]. Despite their effectiveness, these synthetic catalysts are often restricted by high cost, complex synthesis, and limited hydrothermal stability.

In contrast, natural catalysts such as calcium oxide (CaO) and natural zeolites (NZ) have attracted increasing attention due to their low cost, abundance, and environmental friendliness. CaO is particularly effective in improving bio-oil quality through strong deoxygenation and acid-neutralization reactions, leading to reduced acidity and increased heating value [9], [10]. Its high cracking capability also allows large oxygenated molecules to be broken into smaller compounds [11]. Previous studies have shown that CaO significantly suppresses oxygenated compounds such as levoglucosan and organic acids while promoting dehydration reactions during biomass pyrolysis [5].

NZ has also demonstrated favorable catalytic performance in pyrolysis and co-pyrolysis systems. Ahmed et al. [12] demonstrated that NZ in the co-pyrolysis of waste tires and wheat straw increased hydrocarbon content from 72% to 86%, reduced oxygenates from 20.2% to nearly half, and improved the heating value from 40.7 MJ/kg to 42.15 MJ/kg. These results indicate that NZ is effective in enhancing hydrocarbon formation and improving fuel quality through catalytic cracking and deoxygenation.

Wang et al. [9] combined modified HZSM-5 with CaO for the co-pyrolysis of waste tires and bamboo residue, reporting significant increases in olefins and aromatics through suppression of acid formation. Similarly, Zheng et al. [13] showed that a CaO–HZSM-5 mixture enhanced gas yield and hydrocarbon content in biomass pyrolysis, with a 1:2 ratio of CaO to HZSM-5 yielding bio-oil rich in xylene (35%) and toluene (27%). Chen et al. [14] further demonstrated that Fe-modified CaO and ZSM-5 promoted the conversion of acetic acid to acetone, levoglucosan to furfural, and lignin oligomers to phenolics. The dual CaO–ZSM-5 catalyst also accelerated BTX formation, achieving yields of up to 67.5%.

Previous studies highlight a research gap in the application of combined natural catalysts, such as CaO and NZ, in pyrolysis, despite their effectiveness and low cost. This study, therefore, investigates the role of CaO and NZ in enhancing bio-oil quality during palm kernel shell (PKS) pyrolysis, an abundant agricultural residue in Indonesia, a leading global producer of palm oil [15,16]. PKS is rich in lignin, which yields bio-oil dominated by phenolic compounds—valuable chemical feedstocks with applications as substitutes for fossil-derived phenol, as well as in food flavoring, cosmetics, and resins [17], [18].

2.0 METHODOLOGY

Palm kernel shell (PKS) collected from an oil palm plantation in Pandeglang, Indonesia, was used as the feedstock. Elemental composition (C, H, N) was determined using a Vario EL cube elemental analyzer following ASTM D5291, while oxygen content was analyzed by difference. Proximate analysis was performed by thermogravimetric analysis according to ASTM D7582-15. The characteristics of PKS are presented in Table 1.

To remove impurities, PKS for both catalytic and non-catalytic pyrolysis was rinsed with water, air-dried, and then cut into 3–5 mm pieces. NZ and CaO catalysts were supplied by Brataco Indonesia, Ltd. The catalyst was ground and sieved (<100 mesh) prior to X-ray fluorescence (XRF) analysis, and the results are summarized in Table 2. PKS and catalysts were mixed at a 1:0.75 ratio. NZ was used in its natural granulated form without modification, while CaO was applied in powder form.

Table 1 Physicochemical characteristics of PKS

Proximate analysis (wt. %)	**Value**
Moisture	5.85
Volatiles	76.07
Fixed carbon	16.32
Ash	1.76
Ultimate analysis (wt. %)	**Value**
Carbon	49.62
Hydrogen	5.47
Oxygen	44.53
Nitrogen	0.38
Heating value (MJ/kg)	19.2

Calcium, an alkaline earth element, forms the ionic crystal CaO composed of Ca^{2+} and O^{2-} ions. Ca^{2+} has negligible Lewis acidity due to its low electronegativity, while the surface oxygen anion contributes to the strong alkalinity of CaO. Owing to this property, CaO has been widely applied as a CO_2 absorbent and as a catalyst for tar and bio-oil reforming, cracking, deoxygenation, and deacidification [19].

Zeolites are crystalline inorganic materials characterized by a three-dimensional network of SiO_4^{4-} and AlO_4^{5-} tetrahedral units, which are interconnected through shared oxygen atoms. Their porous, crystalline structure remains stable in water, giving them properties such as low density, high free volume, and strong hydration, which support catalytic activity and molecular sorption [20], [21].

Table 2 Chemical composition of CaO and NZ (wt.%)

Composition	**CaO**	**NZ**
MgO	0.37	0.96
Al_2O_3	0.25	13.05
SiO_2	0.60	76.41
SO_3	0.84	0.09
K_2O	0.06	5.17
CaO	97.65	1.84
Fe_2O_3	0.15	2.36
CuO	0.00	0.02
SrO	0.07	0.09
ZrO_2	0.00	0.02

Pyrolysis experiments were performed using an electrically heated stainless-steel batch reactor measuring 200 mm in both height and diameter. A 2.1 m water-cooled condenser was attached to the outlet to maintain vapor temperatures below 40 °C. Heating was provided by a 3.0 kW electric heater controlled by a proportional–integral–derivative (PID) system. For non-catalytic runs, 300 g of palm kernel shell (PKS) was used, while catalytic runs employed 525 g of PKS mixed with catalyst (a 300 g PKS + 225 g catalyst). Heating of the feedstock was carried out from an initial ambient temperature to a final temperature of 500 °C and maintained until no vapors exited the condenser. To determine the bio-oil yield, a gravimetric approach was employed. The residual mixture consisting of char and catalyst was first weighed, after which the char mass was calculated by subtracting the initial catalyst weight from the total residue. Non-condensable gas (NCG) was calculated by difference. A schematic of the apparatus is shown in Figure 1, and yield calculations are presented in Equations 1–3.

$$Y_{bio-oil} = \frac{m_{bio-oil}}{m_{biomass}} \times 100\% \quad (1)$$

$$Y_{char} = \frac{m_{char}}{m_{biomass}} \times 100\% \quad (2)$$

$$Y_{NCG} = 100\% - (Y_{bio-oil} + Y_{char}) \quad (3)$$

Where $Y_{bio-oil}$, Y_{char}, and Y_{NCG} are the yields of bio-oil, char, and NCG, respectively; meanwhile, $m_{bio-oil}$, m_{char}, and $m_{biomass}$ indicate the mass of bio-oil, char, and biomass, respectively. All experiments were conducted at least twice to ensure repeatability, and the average value for each measured parameter was calculated as the arithmetic mean of the results obtained from the repeated experimental runs; the mean values were analyzed and discussed. The standard deviation for pyrolysis yields, density, viscosity, acidity, and heating value varied as follows: 0.07–2.68 wt.%, 3.25–5.93 kg/m^3, pH 0.07–0.21, 0.0–0.28 cP, and 0.07–0.86 MJ/kg, respectively.

The density of the collected bio-oil was calculated from its mass and volume, while viscosity was measured using an NDJ 8 S Viscometer (WANT Balance Instrument Co., Ltd., Changchun, China) with 75 mL of oil maintained at 40 °C. Viscosity measurements were adjusted according to rotor type and rotational speed. Acidity was measured with a calibrated digital pH meter. The heating value of raw material and bio-oil was analyzed using a Parr 6050 Bomb Calorimeter (Parr Instrument Company, Moline, IL, USA), where 0.70–0.72 mL oil samples were combusted in an oxygen-saturated chamber.

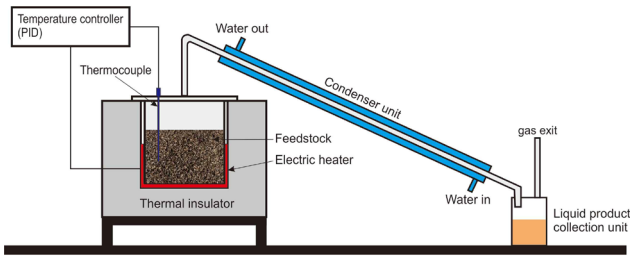


Figure 1 Schematic configuration of pyrolysis reactor system

The characterization of the bio-oil's chemical composition was performed using a GC/MS QP2010 system manufactured by SHIMADZU with an Agilent HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm) and ultra-pure helium as the carrier gas (split ratio 32.3:1). Compounds were identified by comparing peak areas and retention times with the NIST library. The identified compounds—including furans, alcohols, phenolics, acids, ketones, and esters—were further classified into functional groups and carbon chain length categories.

To evaluate the synergistic effect of the catalyst, theoretical calculations were conducted. The pyrolysis results obtained using single catalysts (CaO and NZ) were averaged; this averaged value (denoted as CaO+NZ calculation) represents the expected performance assuming purely additive behavior with no interaction between the two catalysts. The theoretical value was then compared with the experimental pyrolysis results obtained using the dual-catalyst system (CaO/NZ). The magnitude of the deviation between the prediction and the dual-catalyst experiment was used to assess synergy; a larger deviation indicates a stronger synergistic effect of the dual catalyst, whereas a smaller deviation suggests a weaker or negligible synergistic effect.

3.0 RESULTS AND DISCUSSION

Figure 2 illustrates the distribution of pyrolysis products obtained from PKS under different catalyst configurations, including the effects of CaO, NZ, and their combined application on char, bio-oil, and NCG yields. The pyrolysis of PKS produced char (32.5%), bio-oil (39.1%), and NCG (28.4%), in agreement with earlier studies [22], [23]. The introduction of CaO as a catalyst increased the char yield to 47.7% while markedly reducing NCG to 14.1%. Conversely, the addition of NZ decreased char formation but promoted NCG production. Notably, the combined application of CaO and NZ enhanced the bio-oil yield while suppressing NCG generation. Relative to theoretical calculations (CaO+NZ Calculation), the dual-catalyst system demonstrated a synergistic effect by simultaneously increasing bio-oil yield (45.0%) and decreasing NCG yield (18.2%).

Pyrolysis in the presence of CaO as a catalyst produced the highest char yield while simultaneously minimizing the generation of NCGs. The NCG fraction primarily consists of CO_2 and CO [24], yet the gas yield was substantially reduced because CaO actively absorbed CO_2 released during the process. This absorption not only suppressed gas formation but also facilitated the conversion of CO_2 into $CaCO_3$. These findings suggest that the catalytic role of CaO promotes carbon retention in the solid phase, thereby enhancing solid residue yield and altering the distribution of pyrolysis products [25].

In contrast, pyrolysis with NZ resulted in the lowest char yield and the highest non-condensable gas (NCG) fraction. This behavior originates from the strong acidic properties of NZ, where Brønsted and Lewis acid sites actively catalyze secondary reactions of heavy pyrolytic intermediates, such as tars and oligomeric species. While these intermediates are the primary substrates for NZ-driven vapor upgrading, their extensive cracking generates smaller molecular fragments, a significant portion of which fall below the condensation range and are therefore detected as NCG. As a result, although NZ primarily interacts with heavy intermediates, its strong cracking activity

favors gas formation rather than char stabilization. In addition, the microporous structure of NZ limits aromatic polymerization and condensation, further suppressing char formation and directing reaction pathways toward gaseous products through dehydration and decarboxylation reactions [26].

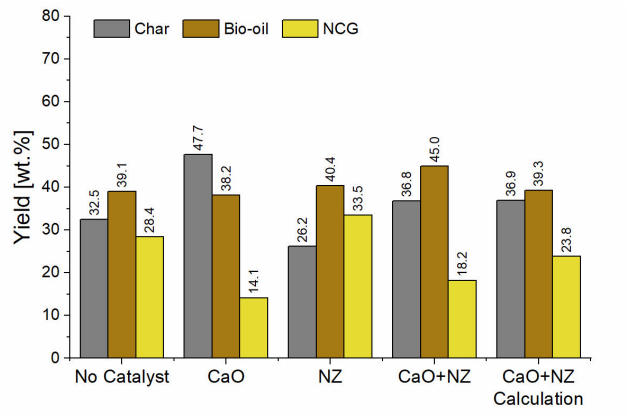


Figure 2 PKS pyrolysis product yield

The combined application of CaO and NZ exhibits a synergistic catalytic effect during the pyrolysis process. CaO functions primarily to suppress excessive gas formation by neutralizing acidic intermediates and capturing carbon dioxide, thereby limiting secondary decarboxylation and decarbonylation reactions that typically lead to NCG production. Meanwhile, NZ enhances vapor upgrading by cracking heavy molecular fragments into liquid-range compounds, effectively promoting the generation of condensable vapors rather than gaseous products. The interplay between these two mechanisms establishes a balance between cracking and stabilization, which ultimately increases the proportion of condensable vapors (bio-oil) while simultaneously reducing the yield of NCG, thus improving the overall efficiency of the catalytic pyrolysis process.

Figures 3 and 4 show the density and viscosity of bio-oil from PKS pyrolysis. Overall, the densities of catalytic and non-catalytic oils were similar, ranging from 953.3 to 980.0 kg/m³. The lowest density was observed with NZ, while the highest occurred with the CaO–NZ mixture. Density was influenced by liquid composition: long-chain acids such as dodecanoic acid (883 kg/m^3) and hexadecanoic acid (852 kg/m^3) lowered density, as seen in NZ-derived oil, whereas phenols (1071 kg/m^3) and short-chain acids or esters such as formic acid methyl ester (974 kg/m^3) and propanoic acid (993 kg/m^3) increased density, as in the CaO–NZ mixture [27], [28], [29], [30], [31]. These findings align with earlier studies reporting PKS bio-oil densities of 905–1015.17 kg/m^3 [32].

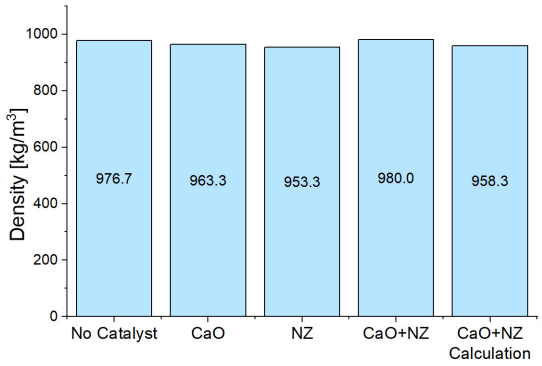


Figure 3 Density of bio-oil

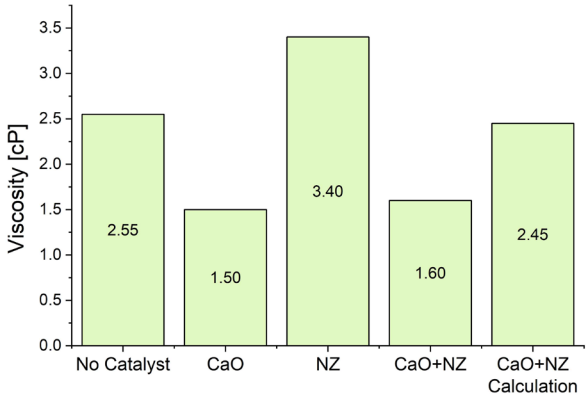


Figure 4 Viscosity of bio-oil

Catalysts had a stronger impact on viscosity. CaO reduced the viscosity from 2.55 cP (non-catalytic) to 1.50 cP, while NZ increased it to 3.40 cP. The CaO–NZ mixture produced 1.6 cP, close to CaO alone, suggesting CaO was more influential. Viscosity correlated with carbon chain length. Non-catalytic oil contained 78.0% C_2–C_6 and 20.6% C_7–C_{12}, whereas CaO further increased short chains (87.5%) and reduced C_7–C_{12}. NZ reduced C_2–C_6 (30.9%) while increasing C_7–C_{12} (49.2%) and C_{13}–C_{18} (19.2%), raising viscosity. The CaO–NZ mixture resembled CaO in chain distribution, explaining the similar viscosities. This phenomenon demonstrated that CaO had a greater impact than NZ on the viscosity of bio-oil. Our non-catalytic oil viscosity (2.61 cSt, converted from 2.55 cP) was slightly higher than that reported by Utarina et al. [32] (1.21–1.5 cSt), likely due to their acid pretreatment, which lowered viscosity to values comparable with our catalytic oils (1.56–1.63 cSt).

CaO significantly reduced the acidity of PKS bio-oil during pyrolysis (Figure 5). The pH increased by 24.7% with CaO compared to non-catalytic pyrolysis (from 3.7 to 4.6). In contrast, NZ slightly lowered the pH to 3.6, while the CaO–NZ mixture gave an intermediate value of 4.1. The acidity of bio-oil is influenced by its organic composition: acids, esters, and complex phenols generally have pH values below 6.0, while simple phenols exceed 6.0. Non-catalytic pyrolysis produced more esters and fewer simple phenols, explaining its lower pH. NZ-derived oil contained more acids and fewer simple phenols, leading to an even lower pH. The dual catalyst yielded an average pH between the single catalysts, confirming that CaO alone was most effective in reducing acidity. These results are consistent with the PKS bio-oil pH reported by Kim et al. [33] (3.27).

As illustrated in Figure 6, the calorific value of the non-catalytic PKS bio-oil was determined to be 21.0 MJ/kg, slightly lower than values reported by Asadullah et al. [34] (23.13–24.10 MJ/kg) but higher than those of Kim et al. [33] (17.9 MJ/kg). Both CaO and NZ individually improved heating values to 25.8 and 26.0 MJ/kg, while the CaO–NZ mixture further increased it to 30.8 MJ/kg. Heating value correlates with elemental composition, particularly lower oxygen content [35]. CaO-derived oil contained a high proportion of phenol (HHV phenol=32.5 MJ/kg) [36], [37], while NZ-derived oil contained fewer phenols (25.5%) but higher amounts of long-chain acids with relatively low oxygen content, giving similar heating values. The CaO–NZ mixture produced bio-oil rich in phenol (48.05%) and ketones (e.g., 2-butanone, cyclopentanone, and 3-pentanone) with lower oxygen fractions, while reducing oxygen-rich compounds such as formic acid methyl ester. This resulted in the highest caloric value (30.8 MJ/kg), exceeding the theoretical estimate of 25.9 MJ/kg, indicating a synergistic effect of the combined catalysts.

Catalytic pyrolysis enhances deoxygenation by removing oxygen through decarboxylation and decarbonylation, releasing CO_2 and CO. The CaO–NZ dual catalyst intensified deoxygenation, as reflected by the significantly improved heating value of the bio-oil.

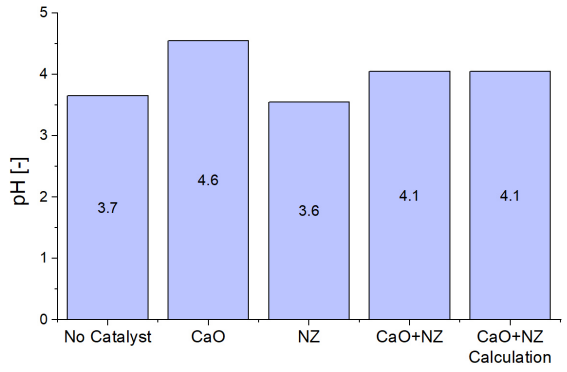


Figure 5 Acidity of bio-oil

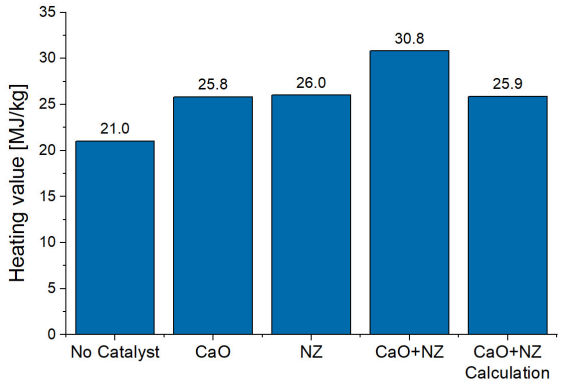


Figure 6 Heating value of bio-oil

Bio-oil is characterized as a multifaceted blend of organic constituents. In this study, 14 species were identified in bio-oil from both non-catalytic and CaO-catalyzed PKS pyrolysis, while the use of NZ increased the number of compounds to 30. The CaO–NZ mixture produced 15 species, slightly more than non-catalytic pyrolysis, indicating that NZ promotes greater molecular diversity. Organic compounds with proportions above 1% are listed in Table 3.

Non-catalytic pyrolysis yielded the highest proportion of formic acid methyl ester (24.56%), a short-chain ester. With CaO, this fraction decreased by 17.95%, while propanoic acid increased from 2.7% to 8.71%, reflecting CaO's role in deoxygenation. CaO also promoted simple phenol formation by reducing complex phenols. In contrast, NZ strongly enhanced deoxygenation, suppressing high-oxygen esters and producing long-chain, low-oxygen acids such as dodecanoic, tetradecanoic, and hexadecanoic acids. Unlike CaO, NZ inhibited simple phenols and favored complex phenol formation, including methyl and methoxy phenols.

The CaO–NZ dual catalyst reduced formic acid methyl ester to levels similar to CaO alone, while increasing ketones such as cyclopentanone and 3-pentanone, indicating enhanced ketonization. The dual catalyst also increased simple phenols and suppressed complex phenols, resembling CaO's effect, while limiting long-chain acids and phenols. Overall, CaO exerted stronger control over bio-oil composition, whereas NZ in combination promoted additional formation of simple phenols and ketones.

The organic compounds were classified by carbon chain length (Figure 7). PKS pyrolysis without a catalyst, with CaO, or with the CaO–NZ mixture predominantly produced short chains (C_2–C_6). In contrast, NZ shifted the distribution toward medium (C_7–C_{12}) and long chains (C_{13}–C_{18}), resulting in a more diverse composition. This indicates that CaO promotes the cracking of molecules into lighter compounds, while NZ induces oligomerization, increasing long-chain fractions. Similar behavior was reported by Khan et al. [2], where NZ caused overcracking and oligomerization, enhancing NCG and coke formation.

The bio-oil contained esters, acids, ketones, phenolics, furans, and alcohols (Figure 8). Phenolics, mainly simple and complex phenols, were the dominant fraction due to the lignin-rich nature of PKS. Non-catalytic pyrolysis yielded 58.8% phenolics, while catalytic pyrolysis produced 58.1%–61.3%, suggesting that catalysts altered the balance between simple and complex phenols without changing total phenolic content.

In non-catalytic pyrolysis, esters were the second most abundant group. CaO reduced esters while increasing acids and furans. NZ completely removed esters and sharply increased acids. The CaO–NZ mixture inhibited ester and furan formation but promoted ketones, indicating a synergistic effect where CaO counteracted NZ's tendency to convert esters into acids while enhancing ketonization.

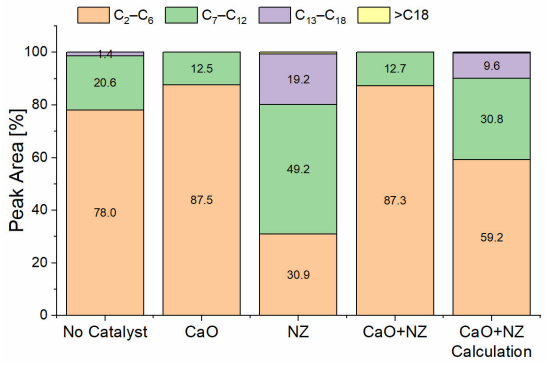


Figure 7 GC-MS characteristic of bio-oil contents categorized by carbon chain length

CaO reacts with acids and carboxyl compounds to form calcium carboxylates and water (Eq. 4), reducing total acids. These intermediates decompose into ketones and $CaCO_3$ (Eq. 5), explaining the rise in ketones with CaO [1], [38]. Reaction 4 occurs at moderate temperatures, while reaction 5 begins at 430 °C [13]. Since experiments were conducted at 500 °C, both neutralization and ketonization were active. CaO also reacts with esters to form calcium carboxylates [39], further supporting these pathways

Table 3 Bio-oil composition from the GC-MS analysis

Compounds	Formula	O/C	No Catalyst	CaO	NZ	CaO–NZ	CaO–NZ Calculation
Formic acid methyl ester	$C_2H_4O_2$	1.0	24.56	17.95	–	16.58	8.98
Propanoic acid	$C_3H_6O_2$	0.67	2.77	8.71	–	4.83	4.36
2-Butanone	C_4H_8O	0.25	–	–	–	2.07	–
Butanoic acid	$C_4H_8O_2$	0.5	–	–	0.99	–	0.50
Furancarboxaldehyde	$C_5H_4O_2$	0.4	–	–	2.18	–	1.09
Propanoic acid, 2,2-dimethyl-	$C_5H_{10}O_2$	0.4	1.95	1.97	–	–	0.99
2-Furancarboxaldehyde	$C_5H_4O_2$	0.4	5.37	–	–	–	–
2-Furanmethanol	$C_5H_6O_2$	0.4	1.39	3.57	–	3.8	1.79
Cyclopentanone	C_5H_8O	0.2	–	2.66	–	7.48	1.33
3-Pentanone	$C_5H_{10}O$	0.2	–	–	–	2.38	–
Furan, 2,5-dimethyl-	C_6H_8O	0.167	–	3.57	–	–	1.79
2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	0.167	2.01	–	–	2.11	–
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	0.33	3.11	–	–	–	–
Phenol	C_6H_6O	0.167	39.59	46.06	25.5	48.05	35.78
Phenol, 2-methyl-	C_7H_8O	0.143	–	1.47	1.72	1.38	1.6
Phenol, 3-methyl-	C_7H_8O	0.143	–	–	2.17	1.35	1.09
Phenol, 4-methyl-	C_7H_8O	0.143	–	1.41	–	–	0.71
Phenol, 2-methoxy-	$C_7H_8O_2$	0.286	6.58	4.95	5.84	5.12	5.4
3-Methoxy-pyrocatechol	$C_7H_8O_3$	0.429	2.8	–	–	–	–
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	0.375	–	2.23	–	–	1.12
2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	0.25	3.83	–	5.26	1.38	2.63
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	0.375	4.89	–	5.17	2.28	2.59
2,5-Cyclooctadienol	$C_8H_{12}O$	0.125	–	1.96	–	1.19	0.98
Octanoic acid	$C_8H_{16}O_2$	0.25	–	–	2.42	–	1.21
Ethanone, 1-(2,6-dihydroxy-4-4methoxyphenyl)-	$C_9H_{10}O_4$	0.444	–	–	1.98	–	0.99
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0.222	1.4	–	4.06	–	2.03
Benzene, 1,2,3-trimethoxy-	$C_9H_{12}O_3$	0.333	1.78	–	2.5	–	1.25
Phenol, 2-Methoxy-3-(2-propenyl)-	$C_{10}H_{12}O_2$	0.2	–	–	2.36	–	1.18
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	0.273	–	–	1.97	–	0.99
Dodecanoic acid	$C_{12}H_{24}O_2$	0.167	–	–	10.27	–	5.14
2-Pentadecynyl alcohol	$C_{15}H_{28}O$	0.067	1.44	–	–	–	–
Tetradecanoic acid	$C_{14}H_{28}O_2$	0.143	–	–	3.2	–	1.6
Hexadecanoic acid	$C_{16}H_{32}O_2$	0.125	–	–	5.89	–	2.95
Heptadecene-(8)-Carbonic acid	$C_{18}H_{34}O_2$	0.111	–	–	7.66	–	3.83
Octadecanoic acid	$C_{18}H_{36}O_2$	0.111	–	–	1.06	–	0.53

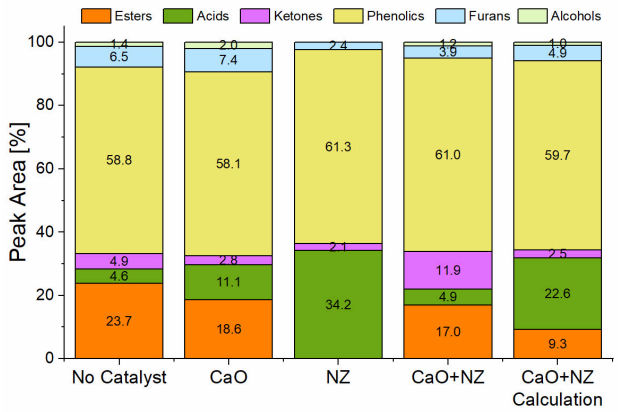


Figure 8 GC-MS characteristic of bio-oil contents categorized by compound group

$$2R-COOH+CaO \rightarrow H_2O+(R-COO)_2Ca \quad (4)$$

$$(R-COO)_2Ca \rightarrow R-COR+CaCO_3 \quad (5)$$

As shown in Figure 8, the addition of CaO promoted acid formation while reducing the production of esters and ketones. In principle, acid yield should decrease with an increase in ketones, since CaO reacts with acids to form calcium carboxylates, which subsequently decompose via ketonization to produce ketones. However, in this study, ketone yield was reduced in the presence of CaO, suggesting that CaO may also facilitate the hydrolysis of esters into acids and the catalytic decarbonylation of ketones to release carbon monoxide. This behavior deviates from the conventional reaction pathways described in Equations 4 and 5, where CaO is expected to suppress acid formation and enhance ketone production. A plausible explanation is that esters, being more reactive toward CaO than acids, underwent hydrolysis in the presence of abundant water vapor during pyrolysis, producing additional acids and alcohols. PKS pyrolysis oil is known to contain a high water fraction, up to 53% [40], which would favor such hydrolysis reactions. Consequently, CaO-catalyzed pyrolysis increased the concentrations of acids and alcohols. This interpretation is consistent with previous findings [41], [42]. An illustration of the hydrolysis reaction is presented in Figure 9.

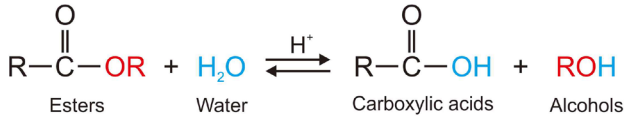


Figure 9 Hydrolysis reaction during pyrolysis with CaO and NZ

The Si:Al ratio of NZ generally ranges from 1.00 to 6.14 [43], which is significantly lower than that of synthetic zeolite HZSM-5 (32.2) [2]. This low Si:Al ratio imparts strong acidity, leading to extensive oil cracking and oligomerization. It is well established that catalysts with higher acidity enhance deoxygenation reactions by facilitating the cleavage of C—O and C—C bonds through their acidic sites [44].

In this study, NZ effectively eliminated esters and converted them into acids. This suggests that NZ catalyzes ester hydrolysis into carboxylic acids while simultaneously promoting deoxygenation, as illustrated in Figure 9. Hydrolysis also produces alcohols; however, these alcohols are rapidly dehydrated, releasing water vapor. The resulting dehydrated alcohols, together with newly formed acids, undergo oligomerization to generate long-chain carboxylic acids [45], [46]. Consequently, NZ-catalyzed PKS pyrolysis yielded substantial amounts of long-chain acids without detectable alcohols (Figure 8). In contrast, the combined CaO–NZ catalyst accelerated ester hydrolysis while further converting acids into ketones via neutralization and ketonization. As a result, ester fractions decreased while ketone fractions increased.

The application of catalytic pyrolysis employing a CaO–NZ catalyst has been demonstrated to significantly improve the physicochemical properties of bio-oil derived from palm kernel shells (PKS). Notable enhancements are observed in viscosity, density, acidity, and heating value—parameters that critically determine the viability of bio-oil as an alternative to conventional liquid fuels. Typically, bio-oil obtained from lignocellulosic biomass such as wood exhibits relatively high density and viscosity (Table 4). This phenomenon is attributed to the dominance of the cellulose fraction in woody biomass, which during pyrolysis predominantly forms levoglucosan—a compound characterized by a density of approximately 1690 kg/m^3 and a notably viscous nature. In contrast, PKS contains a higher proportion of lignin relative to cellulose. The pyrolysis of lignin primarily produces phenolic compounds, which exhibit lower viscosity and density compared to levoglucosan. Consequently, even prior to catalytic upgrading, PKS-derived bio-oil generally possesses superior flow characteristics compared with bio-oil obtained from cellulose-rich feedstocks.

The incorporation of a CaO–NZ catalyst further enhances the physicochemical properties of PKS-derived bio-oil. Conventional bio-oil is typically limited by its high acidity and relatively low heating value, both of which hinder its direct application as a transportation fuel. The CaO–NZ catalyst facilitates deoxygenation reactions and neutralizes acidic compounds, thereby improving the chemical stability of the fuel while simultaneously increasing its calorific value. This catalytic process effectively mitigates two of the most significant drawbacks associated with untreated bio-oil.

In terms of density, PKS bio-oil produced under catalytic conditions exhibited a value of 980 kg/m3, which was slightly higher than that of heavy oil (953.3 kg/m3) and substantially higher than diesel fuel (850 kg/m3). However, this value was lower than the density of conventional bio-oil reported in the literature (1180 kg/m3), indicating improved fuel properties after catalytic upgrading. This indicates that catalytic PKS bio-oil aligns more closely with the density range of petroleum-derived fuels, an advantageous attribute for both storage and combustion performance.

Furthermore, the viscosity of catalytic PKS bio-oil (1.63 cSt) represented a substantial improvement. This value approximates those of gasoline (1.17 cSt) and kerosene (2.2 cSt) and comfortably falls within the operational range of diesel fuel (2.3–5 cSt). By contrast, heavy oil possesses a markedly high viscosity of 130 cSt, rendering it unsuitable for direct utilization without extensive upgrading. The reduced viscosity of catalytic PKS bio-oil enhances its handling and transport properties while promoting efficient atomization and combustion in conventional fuel injection systems.

Acidity constitutes another critical limitation of conventional bio-oil, as its pronounced corrosiveness and limited storage stability significantly restrict direct utilization. The measured pH of untreated bio-oil was 2.55, reflecting a highly acidic character. Following catalytic upgrading, the pH increased to

4.1, indicating a substantial reduction in acidity. Although this value remains slightly below that of diesel fuel (pH ≈ 5), the improvement signifies enhanced chemical stability and a lower risk of corrosion—key factors for long-term storage and practical fuel application.

Table 4 Liquid fuel comparison

Properties	Density (kg/m^3)	Viscosity (cSt)	pH	Heating value (MJ/kg)
PKS bio-oil with CaO–NZ catalyst	980	1.63	4.1	30.76
Bio-oil [47]	1180	11.85	2.55	18.79
Heavy oil [47]	953.3	130	n.a	42.93
Diesel oil [48]	850	2.3–5	5	42.75
Gasoline [2]	720–780	1.17	n.a	42–46
Kerosene [49]	780–810	2.2	n.a	43–46

The heating value likewise exhibited a marked enhancement following catalytic treatment. Conventional bio-oil typically possesses a relatively low calorific value of 18.79 MJ/kg, which is considerably lower than that of fossil fuels such as diesel, gasoline, and kerosene (42–46 MJ/kg). In contrast, PKS-derived bio-oil produced using the CaO–NZ catalyst attained a heating value of 30.76 MJ/kg. Although still approximately 28% lower than that of diesel fuel, this represents a significant improvement that narrows the energy density disparity between renewable and petroleum-based fuels. The increase in heating value can be attributed to the reduced oxygen content in the upgraded bio-oil, consistent with the deoxygenation function facilitated by the CaO–NZ catalyst.

Taken together, these findings indicate that catalytic PKS bio-oil occupies an intermediate position between untreated bio-oil and conventional petroleum-based fuels. While its energy density has yet to reach parity with fossil fuels, its viscosity, density, and acidity already fall within—or are approaching—the acceptable ranges for liquid fuel applications. This suggests that catalytic PKS bio-oil holds considerable promise as a blending component with petroleum fuels or for direct use in existing combustion systems with minimal modification.

In summary, the catalytic pyrolysis of PKS employing a CaO–NZ catalyst constitutes an effective upgrading strategy that significantly enhances the physicochemical and energetic attributes of bio-oil. The upgraded product demonstrates improved flow characteristics, reduced acidity, and a markedly higher heating value compared to untreated bio-oil, thereby improving its technical feasibility for practical applications. Collectively, these advancements underscore the potential of PKS-derived catalytic bio-oil to support sustainable energy transitions and to function as a viable partial substitute for conventional liquid hydrocarbons.

4.0 CONCLUSION

This study demonstrated that the application of natural catalysts, specifically CaO and NZ, significantly influences the pyrolysis behavior of palm kernel shell (PKS) and the resulting bio-oil characteristics. Individually, CaO enhanced deoxygenation, reduced viscosity, and increased the heating value of bio-oil, while NZ promoted cracking and oligomerization, leading to higher gaseous products and long-chain acids. When combined, CaO and NZ exhibited a synergistic catalytic effect, simultaneously increasing bio-oil yield (up to 45.0%), improving viscosity (1.63 cSt), moderating acidity (pH 4.1), and achieving the highest heating value (30.8 MJ/kg). The dual catalyst system was particularly effective in enhancing bio-oil composition by suppressing ester formation, promoting ketonization, and increasing the proportion of simple phenols and ketones, which are valuable for downstream applications. These improvements suggest that inexpensive and abundant natural catalysts such as CaO and NZ can provide a sustainable and efficient route for upgrading biomass-derived bio-oil. Although its energy density remains below that of petroleum fuels, the improved characteristics position catalytic PKS bio-oil as a promising renewable alternative suitable for blending or partial substitution. Future research should focus on optimizing catalyst ratios, exploring regeneration and reusability of the catalysts, and evaluating the performance of upgraded bio-oil in combustion systems to further validate its potential for large-scale bioenergy applications.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper

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