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Co-Pyrolysis of EFB and UPCO over Nickel Oxide Loaded HZSM-5: A Comparative Co-Pyrolysis Study via Thermogravimetric Analyser and Fixed-Bed Reactor

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Abstract

The abundance of empty fruit bunches (EFB) in Malaysia, which were once discarded as waste, has recently been recognized as a potential source for biofuel production. The main objective of the present work is to evaluate the impact of nickel oxide-loaded HZSM-5 (NiO/HZSM-5) on the co-pyrolysis of EFB and used palm cooking oil (UPCO) via thermogravimetric analyser (TGA) and fixed-bed reactor separately. The NiO/HZSM-5 was prepared via incipient wetness impregnation method and characterized for physicochemical properties. First, for co-pyrolysis via TGA, the pyrolysis temperature was set at 30 to 700°C. The mass loading was fixed for EFB, EFB-UPCO, EFB-HZSM-5, EFB-UPCO-HZSM-5, EFB-UPCO-(1%)NiO/HZSM-5. Second, for co-pyrolysis via fixed-bed reactor, the temperature was fixed at 600°C. From TGA results, the usage of UPCO for pyrolysis with EFB has generated higher mass loss (99.73%) compared to pyrolysis of EFB and EFB over HZSM-5 at 90.54% and 73.33% respectively. From the fixed-bed reactor, pyrolysis of EFB has generated no hydrocarbons in biofuel. The loading of UPCO has increased the hydrocarbon yield by 64.90%. Catalytic co-pyrolysis over Ni/HZSM-5 had proved to increase oil yield and enhance hydrocarbons. The pyrolysis of EFB with UPCO provides an approach in which UPCO can serve as a hydrogen source to enhance the biofuel quality, and NiO enhances the cracking of the oxygenated vapours into hydrocarbons.

1. Introduction

The global shift towards renewable energy is a crucial response to the growing environmental and economic pressures caused by reliance on fossil fuels. Among various renewable energy sources, biofuels are a sustainable alternative, especially in transportation [1]. Biofuels derived from biomass through pyrolysis show great potential

due to their ability to convert renewable organic materials into energy-dense fuels. Pyrolysis involves the thermal decomposition of biomass in the absence of oxygen, producing biofuel, biochar, and syngas [2].

In Malaysia, empty fruit bunch (EFB), a by-product of the palm oil industry, is a plentiful and inexpensive biomass feedstock. Malaysia's extensive palm oil plantations produce significant amounts of EFB, making it a feasible candidate for biofuel production [3]. However, despite its potential, biofuel produced from EFB pyrolysis is characterized by a high concentration of oxygenated compounds such as phenols, ketones, acids, alcohols, esters, ethers, and aldehydes [4]. These oxygenated compounds present several challenges, including high acidity, low stability, and lower energy content, which limit the direct application of biofuel as a transportation fuel.

The high number of oxygenated compounds in biofuel significantly decreases its quality, making it unsuitable for direct use in internal combustion engines or other fuel systems without further upgrading [5]. For biofuel to replace fossil fuels, its oxygen content must be reduced to improve energy density, stability, and compatibility with existing fuel infrastructure. The presence of oxygenated compounds, especially acids and phenols, contributes to the corrosive nature of the biofuel and hinders its combustibility [6]. To tackle these issues, recent research has focused on developing methods to increase the hydrocarbon content of biofuel while minimizing the presence of oxygenated compounds. An innovative approach called co-pyrolysis involves the thermal decomposition of biomass mixed with other hydrocarbon-rich materials.

Used palm cooking oil (UPCO), a food industry waste product has shown promise for co-pyrolysis with biomass. Malaysia, a major palm oil producer, generates significant amounts of used cooking oil, presenting an opportunity to convert this waste into value-added products such as biofuels [5]. UPCO is rich in triglycerides, which can be cracked during pyrolysis to produce hydrocarbons, improving the overall quality of the resulting biofuel. In this context, UPCO serves as a hydrocarbon enhancer and when added to the pyrolysis process, raises the hydrocarbon content of biofuel. Hydrocarbon enhancers like UPCO contribute additional carbon-rich molecules that can be transformed into hydrocarbons during pyrolysis. This process ultimately improves the energy density and stability of the biofuel.

Co-pyrolysis of EFB with UPCO can potentially increase biofuel's hydrocarbon content, making it a more suitable renewable fuel source. UPCO has been successfully used to produce biodiesel through transesterification, but its role as a hydrocarbon enhancer in pyrolysis remains underexplored. To date, no studies have specifically investigated the co-pyrolysis of biomass like EFB with UPCO, making this approach a novel and promising area of research. The motivation for conducting co-pyrolysis of EFB with UPCO is to address the limitations of biomass-derived biofuels, specifically their high oxygen content and low hydrocarbon yield. By combining EFB with UPCO, the process takes advantage of the complementary properties of both materials. EFB serves as a renewable biomass source, while UPCO can add extra hydrocarbons, improving the overall quality of the biofuel. This synergistic effect could enhance the hydrocarbon content and lower the concentration of undesirable oxygenated compounds, making the biofuel more suitable for use in existing fuel systems. Furthermore, co-pyrolysis provides a sustainable solution for managing agricultural and industrial waste, supporting global efforts to reduce environmental pollution and promote circular economy practices.

Catalytic pyrolysis, particularly with catalysts like zeolites, such as hydrogen-exchanged zeolite socony mobil five (HZSM-5), has gained attention for improving biofuel quality. HZSM-5 has demonstrated strong cracking abilities, converting oxygenated compounds into hydrocarbons due to its shape-selective properties and acidity [7]. Recent studies have explored the co-pyrolysis of various biomass feedstocks with hydrocarbon-rich materials in the presence of HZSM-5. For example, Zhang et al. (2022) [8] investigated the co-pyrolysis of pine wood with waste plastics using HZSM-5, reporting a significant increase in aromatic hydrocarbons and a reduction in oxygenated compounds. Similarly, Wang et al. (2021) [9] demonstrated that co-pyrolysis of rice husk with polyethylene over HZSM-5 enhanced the production of mono-aromatics, such as benzene, toluene, and xylene (BTX), which are valuable components of high-quality biofuels. The incorporation of metal oxides like nickel oxide (NiO) into HZSM-5 has been explored to further enhance aromatic hydrocarbon production [10]. Nickel's hydrogenation activity removes oxygen from biofuel, leading to increased hydrocarbon yields. However, studies involving NiO-modified HZSM-5 have not consistently produced biofuel with high hydrocarbon content when only biomass feedstocks are used. For instance, Li et al. (2020) [11] reported that while NiO/HZSM-5 improved the deoxygenation of bio-oil from corn stover pyrolysis, the hydrocarbon yield remained relatively low due to the limited availability of hydrogen donors in the biomass feedstock. Similarly, Chen et al. (2021) [12] observed that NiO/HZSM-5 was effective in reducing oxygenated compounds during the pyrolysis of bamboo, but the overall hydrocarbon yield was insufficient for practical applications. These findings highlight the need for co-pyrolysis strategies that introduce additional hydrogen donors or hydrocarbon-rich materials, such as UPCO, to optimize the performance of NiO/HZSM-5 catalysts.

In this study, the pyrolysis of EFB mixed with UPCO using HZSM-5 and NiO-modified HZSM-5 catalysts was investigated. The main objective of this work is to fill the gap in existing studies by investigating the co-pyrolysis of EFB and UPCO, and assessing the catalytic effects of HZSM-5 and NiO/HZSM-5 on hydrocarbon production. Firstly, the thermal degradation behaviour of the EFB and UPCO mixtures was investigated via thermogravimetric analysis (TGA), and then pyrolysis experiments were conducted via fixed-bed reactor to determine the yield and

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composition of the resulting biofuel (pyrolysis oil). This research also focuses on increasing the hydrocarbon content in biofuel, making it more suitable as a renewable transportation fuel. By utilizing the co-pyrolysis of EFB and UPCO, along with advanced catalytic processes, this study introduces a new approach to overcoming the limitations of biomass-derived biofuel.

2. Methodology

2.1 Preparation of EFB and UPCO

Empty fruit bunch (EFB) was purchased from a local palm mill company in Selangor, Malaysia. The preparation of EFB was reported in our previous work [13]. Next, the used palm cooking oil (UPCO) was collected from nearby restaurants in the Kuala Lumpur area. The UPCO was cooled to room temperature before being filtered to remove any food debris left in the UPCO. Next, the filtered UPCO was heated to 110°C to remove any moisture content. Finally, the UPCO was stored in a tight container to avoid moisture absorption.

2.2 Preparation of Nickel-modified HZSM-5

Zeolite Socony Mobil -5 (ZSM-5) and Nickel (II) Nitrate Hexahydrate [$Ni(NO_3)_2.6H2O$, Purity = 99%] was acquired from ACROS Organics. First, the ZSM-5 in ammonium form was converted into hydrogen-exchanged Zeolite Socony Mobil-5 (HZSM-5) via calcination at 650°C for four hours (ramp rate: 5°C/min). Next, nickel oxide (NiO) from Nickel (II) Nitrate Hexahydrate was impregnated into HZSM-5 via the incipient wetness impregnation (IWI) technique. For the preparation of 1 wt% of NiO into HZSM-5, first, the chemicals were combined with 80 mL of deionized water in a beaker and swirled over a hot plate magnetic stirrer for four hours at 80°C. After that, the paste was dried for 12 hours at 110°C in a microwave oven. The generated solid catalyst was then calcined at 650 °C for four hours (ramp rate: 5 °C/min) in a furnace. Finally, the synthetic catalyst was labelled as (1%)NiO/HZSM-5. The physicochemical properties of (1%)NiO/HZSM-5 were reported in our previous work [14].

2.3 Co-Pyrolysis of EFB and UPCO

2.3.1 Thermogravimetric Analyzer (TGA)

Thermogravimetric analyser (TGA) (TGA/SDTA851, METTLER TOLEDO, USA) was used to investigate the thermal degradation behaviour of catalytic co-pyrolysis of EFB and UCO over catalysts. Total of five samples as follows: EFB, EFB-UPCO, EFB-HZSM-5, EFB-UPCO-HZSM-5, EFB-UPCO-(1%)NiO/HZSM-5 were individually heated to a maximum temperature of 700°C in an inert (N_2) atmosphere flowing at 150 mL/min at a fixed heating rate of 20 °C/min. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were obtained from the TGA to observe the degradation pattern of the samples.

2.3.2 Fixed-bed Reactor

The co-pyrolysis of EFB and UPCO over NiO/HZSM-5 was investigated via fixed bed reactor. Firstly, the EFB and UPCO were well-mixed at an equal mass ratio of 1:1 by mass. Next, mixed EFB and UPCO samples were loaded separately, followed by NiO/HZSM-5 onto the fixed bed, maintaining a catalyst-to-feedstock ratio of 1:1 by mass. Nitrogen (N_2) gas purges the reactor to achieve an inert environment with a 100 mL/min flow rate. The experiments were conducted at fixed pressure and temperature at 1 atm and 600°C, respectively. The condenser is an ice bath (10°C to 15°C), condensing gaseous products into pyrolysis oil. This oil was subsequently analyzed via gas chromatography/ mass spectrometry (GC/MS) to determine its chemical composition. The standard operating procedures for oil analysis were reported in our previous work [14]. Meanwhile, the non-condensable vapours were collected in the gas bag. After each experiment, the reactor was disassembled, and its contents were separated and calculated for mass balance. To ensure accuracy, each test was repeated at least twice.

3. Results and Discussions

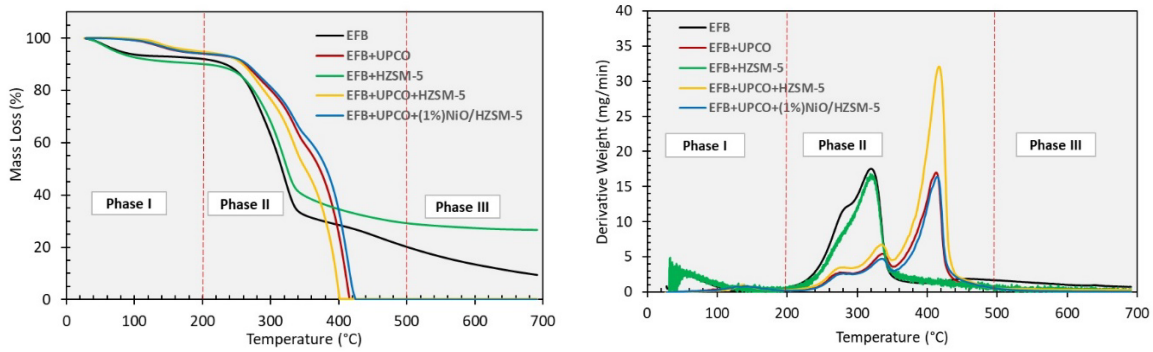
3.1 Catalytic Pyrolysis of EFB and UPCO via TGA

Fig. 1 (a) displays the thermogravimetric (TG) curve depicting the mass loss of the samples against the temperature profile. The derivative thermogravimetric (DTG) curve representing differential mass loss over time was plotted against temperature and presented in Fig. 1 (b). Based on the TG-DTG curves obtained, the degradation of feedstock was divided into three phases, where phase I (drying phase) involves the evaporation of moisture and impurities from 30°C to 200°C. Phase II (devolatilization phase) includes the rapid deterioration of the volatile components of feedstock, from 200°C to 500°C. Next, phase III involves further decomposition, mainly

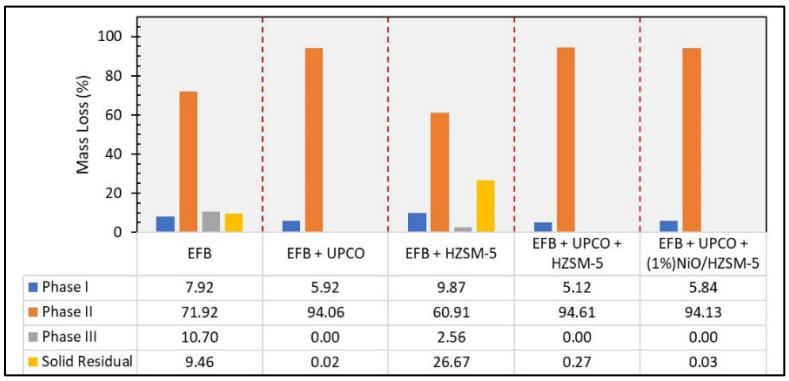
lignin components in EFB at 500°C to 700°C. Lastly, solid residual left after 700°C which could be biomass char and/or coke due to the presence of catalyst.

As shown in Fig. 1 (a), the potential of using UPCO as a secondary feedstock for pyrolysis is evident in the rapid decomposition of EFB when compared to using EFB as a single feedstock, as shown in Fig. 1 (a). There is a rapid mass loss observed between the temperatures of 200°C to 500°C in phase II before the degradation levels off. Specifically, as seen in Fig. 1 (c), the EFB sample experiences a lower mass loss of 71.92% compared to the mixed EFB and UPCO sample, which shows a mass loss of 94.06%. Additionally, the EFB sample gradually degrades in phase III, leaving behind 10.70% as solid residual, as shown in Fig. 1 (c). Interestingly, the addition of UPCO as a co-feedstock for the pyrolysis of EFB has resulted in complete degradation in phase III (0%) and left a negligible amount of solid residual at 0.02%. Therefore, it can be concluded that the addition of UPCO significantly improved the degradation of EFB into volatile matter and left no solid residual.

The study also investigated the impact of HZSM-5 on the pyrolysis of EFB compared to the co-pyrolysis of EFB and UPCO. As shown in Fig. 1 (a) and (c), using HZSM-5 catalyst in the pyrolysis of EFB resulted in less significant mass loss than the co-pyrolysis of EFB and UPCO. Specifically, the HZSM-5 catalyst reduced the degradation of EFB at phase II to 60.91% compared to the EFB and EFB + UPCO samples. This could be attributed to rapid coking during the pyrolysis process, which quickly deactivated the HZSM-5 catalyst, as evidenced by the highest solid residual at 26.67% compared to other samples (see Fig. 1 (c)).



(a) **(b)**



	EFB	EFB + UPCO	EFB + HZSM-5	EFB + UPCO + HZSM-5	EFB + UPCO + (1%)NiO/HZSM-5
Phase I	7.92	5.92	9.87	5.12	5.84
Phase II	71.92	94.06	60.91	94.61	94.13
Phase III	10.70	0.00	2.56	0.00	0.00
Solid Residual	9.46	0.02	26.67	0.27	0.03

(c)

Fig. 1 *(a) TG curves of mass loss (%); (b) DTG curves; and (c) Mass loss of volatile matter at phase I, II and II*

The combination of EFB, UPCO, and HZSM-5 resulted in a more thorough degradation process. Fig. 1 (c) shows that the mass loss in Phase I was the lowest among all the samples, at 5.12%. This demonstrates that the presence of both UPCO and HZSM-5 inhibited the initial volatile release. Interestingly, in phase II, the mass loss remained high at 94.61%, consistent with the previous sample that included UPCO. This indicates that HZSM-5 did not significantly alter the main degradation phase. For the EFB + UPCO sample, no mass loss occurred in Phase III, and the solid residual was minimal at 0.27%. This suggests that the combination of UPCO and HZSM-5 was highly effective in promoting near-complete degradation.

Finally, the EFB + UPCO + 1%NiO/HZSM-5 sample showed the most efficient results. In Phase I, the mass loss was 5.84%, similar to other UPCO-containing samples, indicating consistent behaviour in the initial stages, as shown in Fig. 1 (a) and (c). In Phase II, the mass loss remained high at 94.13%, comparable to the other UPCO

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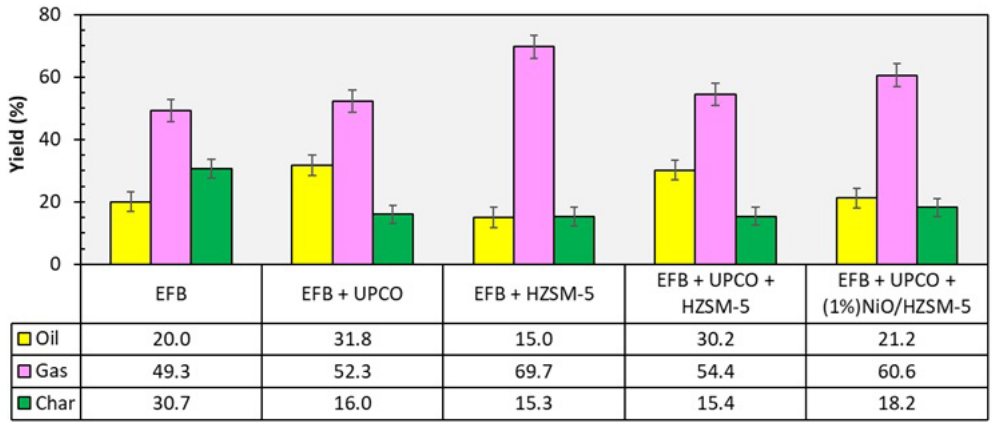
samples. No mass loss was recorded in Phase III, confirming that almost all degradation occurred during Phase II. The solid residual was the lowest of all samples, at just 0.03%, demonstrating that the nickel oxide-modified HZSM-5 catalyst was the most effective in promoting complete pyrolysis. The addition of NiO/HZSM-5 as a catalyst facilitated a more thorough breakdown of the material, leaving behind minimal solid residue.

In summary, the study shows that the thermal breakdown of EFB and UPCO depends significantly on the catalyst chosen. While EFB alone loses a significant amount of mass in Phase II, it leaves a substantial solid residue behind. The addition of UPCO improves the breakdown process, reducing the solid residue to almost zero. HZSM-5 catalysis moderates the breakdown process, but combining UPCO and HZSM-5 results in nearly complete pyrolysis. The most effective catalyst was the nickel oxide-modified HZSM-5, which produced the lowest solid residue and the most efficient overall breakdown. These findings highlight the potential of using advanced catalysts like NiO/HZSM-5 to enhance biomass and waste oil conversion processes.

3.2 Catalytic Pyrolysis of EFB and UPCO via Fixed-Bed Reactor

3.2.1 Pyrolysis Product Yield

Fig. 2 shows the pyrolysis product yield, such as pyrolysis oil, gas and char from pyrolysis of EFB and EFB over HZSM-5 and co-pyrolysis of EFB and UPCO over catalyst. In this study, the primary focus is maximizing pyrolysis oil yield. It can be observed that the highest oil yield (31.8%) was obtained when EFB was mixed with UPCO in the absence of catalysts, as depicted in Fig. 2. This suggests that UPCO, rich in fatty acids, contributes significantly to oil formation during pyrolysis. This is consistent with other studies by Gollakota et al. (2023) [16], which found that liquid biomass feedstocks tend to favour oil production due to their high hydrogen-to-carbon ratios and lower oxygen content than lignocellulosic materials like EFB.



	EFB	EFB + UPCO	EFB + HZSM-5	EFB + UPCO + HZSM-5	EFB + UPCO + (1%)NiO/HZSM-5
Oil	20.0	31.8	15.0	30.2	21.2
Gas	49.3	52.3	69.7	54.4	60.6
Char	30.7	16.0	15.3	15.4	18.2

Fig. 2 *Pyrolysis product yield (%)*

However, when the catalytic effect of HZSM-5 was introduced, the oil yield dropped to 15%. HZSM-5 is well-known for its acidic sites and microporous structure, which promote the cracking of more significant hydrocarbons into lighter gases. As a result, the reduction in oil yield when using HZSM-5 can be attributed to secondary cracking reactions that convert the liquid oil fractions into non-condensable gases. Previous research supports this, indicating that HZSM-5 is particularly effective in producing light hydrocarbons such as ethane, propane, and butane through catalytic cracking [2].

Interestingly, when nickel oxide was incorporated into HZSM-5 (NiO/HZSM-5), the oil yield improved to 21.2%. This improvement can be explained by the role of nickel oxide in enhancing deoxygenation and hydrogenation reactions, which are critical for upgrading pyrolysis oil. Nickel oxide helps reduce the oxygen content of the pyrolysis oil, thereby improving its stability and energy content. Studies have shown that NiO-modified catalysts can improve the oil yield by facilitating the conversion of oxygenated compounds into hydrocarbons [8]. Therefore, NiO/HZSM-5 holds the potential as a more effective catalyst for pyrolysis oil production compared to pure HZSM-5.

Gas production is another important consideration in pyrolysis, especially regarding energy recovery. The highest gas yield of 69.7% was observed when HZSM-5 was used as the catalyst. This finding aligns with the knowledge that HZSM-5 is highly effective in breaking down large molecules into smaller gaseous compounds, thanks to its strong Brønsted acid sites [15]. HZSM-5 promotes cracking reactions that convert pyrolysis oil into light gases such as methane, hydrogen, and carbon monoxide. As such, gasification and cracking are favoured over oil formation when HZSM-5 is present.

The addition of nickel oxide slightly reduced the gas yield to 60.6%. This reduction is likely because NiO promotes oil production rather than gas by facilitating hydrogenation reactions. Nickel is known to catalyze the formation of valuable liquid hydrocarbons by reducing the oxygen content of pyrolysis oil precursors and preventing over-cracking into gases [16]. Therefore, the slightly lower gas yield with NiO/HZSM-5 suggests that nickel modification helps shift the product distribution more favourably towards oil production.

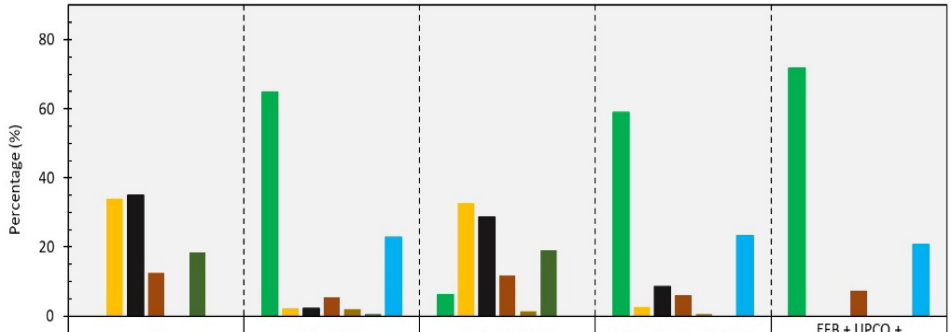
Finally, the solid residue also known as char left after pyrolysis, is typically considered the least desirable product due to its low economic value compared to oil and gas. The data indicate that the highest char yield (30.67%) was obtained from the pyrolysis of EFB alone. This result aligns with other studies, which have found that lignocellulosic materials such as EFB contain high amounts of fixed carbon and ash, leading to significant char production [4]. Meanwhile, when UPCO was co-pyrolyzed with EFB, the char yield dropped to 16%, suggesting that the liquid components of UPCO help improve conversion efficiency and reduce solid residue formation.

Fig. 2 shows that char yields remained relatively consistent, ranging between 15.3% and 18.2% when catalysts were introduced. The slight increase in char yield with NiO/HZSM-5 compared to HZSM-5 alone (18.2% vs. 15.3%) could be attributed to partial catalyst deactivation or incomplete cracking of biomass components. This minor variation in char yield is consistent with a study by Xu et al. (2024) [1] on catalytic pyrolysis, where metal oxides can sometimes lead to coke formation, contributing to solid residues.

In conclusion, the pyrolysis of EFB and UPCO over HZSM-5 and NiO/HZSM-5 demonstrates the importance of catalyst selection in determining product yields. UPCO enhances oil production, particularly when no catalyst is used, while HZSM-5 favours gas production through cracking reactions. NiO/HZSM-5 is a promising catalyst for maximizing pyrolysis oil yield, making it a more suitable choice for biofuel applications. This research emphasizes the significance of waste reduction and the promotion of a circular economy within the environmental framework. By utilizing EFB and UPCO in co-pyrolysis, agricultural and food waste can be converted into valuable biofuels. This process not only reduces landfill waste but also supports zero-waste principles. This approach enhances the sustainability of biofuel production and aligns with global efforts to develop renewable energy from waste sources.

3.2.2 Organic Compositions in Pyrolysis Oil

The organic composition of pyrolysis oil provides valuable insights into the potential of pyrolysis oil as a renewable fuel source and the role of catalysts in enhancing the quality of the resulting oil. The key organic compounds present in pyrolysis oils are hydrocarbons, phenols, acids, ketones, aldehydes, alcohols, and esters as shown in Fig. 3. This discussion focuses on these compounds, particularly hydrocarbons, as they are the main target for biofuel production, followed by phenols and other minor compounds.



	EFB	EFB + UPCO	EFB + HZSM-5	EFB + UPCO + HZSM-5	EFB + UPCO + (1%)NiO/HZSM-5
Hydrocarbons	0	64.89	6.27	59.07	71.86
Phenol	33.97	2.23	32.71	2.61	0
Acid	35.12	2.18	28.80	8.50	0
Ketones	12.48	5.30	11.77	6.01	7.38
Aldehydes	0	2.05	1.47	0.58	0
Alcohols	18.43	0.55	18.98	0	0
Ester	0	22.80	0	23.23	20.76

Fig. 3 *Organic compositions (%) in pyrolysis oil*

Hydrocarbons are important compounds in pyrolysis oil because they directly impact fuel quality and calorific value. According to Figure 2, the co-pyrolysis of EFB and UPCO over a NiO/HZSM-5 catalyst resulted in the highest hydrocarbon yield of 71.86%. This suggests that effective deoxygenation occurred, leading to a biofuel with lower oxygen content and higher energy density. The presence of fewer oxygenated compounds reduces corrosiveness and improves stability, making these biofuels more compatible with the existing petroleum infrastructure. Additionally, compared to fossil fuels, biofuels derived from biomass pyrolysis produce fewer net carbon

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emissions due to the carbon neutrality of biomass. On the other hand, nickel is known to facilitate hydrogenation reactions, which reduce oxygenated compounds and improve the overall quality of oil [8]. The high hydrocarbon yield obtained with NiO/HZSM-5 suggests that it is a more effective catalyst for biofuel production than pure HZSM-5. Additionally, catalyst regeneration and reusability are key factors for long-term economic sustainability.

The use of HZSM-5 alone resulted in significantly lower hydrocarbon yields (6.27%) due to its strong cracking activity (see Fig. 3). Cai et al. (2023) [15] reported that HZSM-5 is known for its strong acidity, which causes large hydrocarbon molecules to break down into smaller gaseous compounds. However, this excessive cracking reduces the liquid hydrocarbon content, making it less suitable for applications targeting oil production. When UPCO was co-pyrolyzed with EFB without any catalyst, the hydrocarbon yield was still relatively high (64.89%), highlighting the potential of UPCO as a valuable feedstock for oil production due to its high lipid content.

Based on Fig. 3, it is evident that phenolic compounds form during the pyrolysis of lignocellulosic materials like EFB, originating from the decomposition of lignin. In this study, the highest phenol content (33.97%) was observed in the pyrolysis of EFB alone. This aligns with literature findings that lignin-derived feedstocks produce significant amounts of phenols, which have value as chemical precursors for industrial applications [8]. However, phenolic compounds in pyrolysis oil are generally undesirable for fuel applications due to their corrosive nature and high oxygen content. On the other hand, the addition of UPCO into the feedstock mixture significantly reduced phenol formation to 2.23% and 2.61% in the cases of uncatalyzed and catalyzed reactions with HZSM-5, respectively. This reduction can be attributed to the higher hydrogen-to-carbon ratio in UPCO, which favours the formation of hydrocarbons over oxygenated compounds like phenols. Notably, no phenols were detected when NiO/HZSM-5 was used as a catalyst, further demonstrating its effectiveness in promoting deoxygenation and improving the quality of pyrolysis oil by minimizing oxygenated compounds.

Acids are a type of oxygenated compound often found in pyrolysis oils. They are undesirable because of their corrosiveness and high oxygen content. When empty fruit bunches (EFB) are subjected to pyrolysis, a significant amount of acid (35.12%) is produced. Zhong et al. (2024) [17] addressed the production of acids that are typically formed from the cellulose and hemicellulose components of lignocellulosic biomass. However, when EFB is co-pyrolyzed with upgraded pyrolysis oil (UPCO), the acid content is significantly reduced to 2.18%. This reduction is attributed to the higher lipid content in UPCO, which promotes the formation of hydrocarbons over oxygenated compounds. On the other hand, using HZSM-5 as a catalyst resulted in a relatively high acid content of 28.8%, likely due to the cracking of larger molecules into smaller oxygenated species. This is consistent with previous studies by Zhang et al. (2022) [8], which have shown that HZSM-5 tends to favour the formation of light-oxygenated compounds, including acids. However, when NiO/HZSM-5 was used as a catalyst, the formation of acids was eliminated, further demonstrating the superior deoxygenation ability of nickel-modified catalysts.

During the thermal degradation of cellulose and hemicellulose, ketones are typically formed. The highest ketone content (12.48%) was observed in the pyrolysis of EFB alone, as shown in Fig. 3. The use of catalysts generally reduced ketone formation. For example, HZSM-5 promoted the formation of 11.77% ketones, a reduction compared to uncatalyzed pyrolysis but still significant. A similar observation was reported by Chong et al. (2019) [6] and stated that the reduction is due to the strong cracking ability of HZSM-5, which breaks down larger molecules, forming light-oxygenated compounds. The use of NiO/HZSM-5 further reduced the ketone content to 7.38%, suggesting that nickel oxide plays a role in suppressing the formation of oxygenated compounds through deoxygenation reactions. Similarly, Bari et al. (2024) [7] reviewed that nickel oxides are the most promising metal oxides in cracking oxygenated compounds into hydrocarbons. In general, ketones are less corrosive than acids. However, their presence still contributes to the overall oxygen content of the pyrolysis oil, which lowers its fuel quality.

Aldehydes are typically present in small amounts in pyrolysis oils. As shown in Fig. 3, the highest aldehyde content (2.05%) was observed in the co-pyrolysis of EFB and UPCO, while catalytic pyrolysis resulted in lower aldehyde yields. For example, the use of HZSM-5 produced 1.47% aldehydes, while NiO/HZSM-5 further reduced this to 0.58%. This reduction is consistent with Mbeugang et al. (2024) [18] and they stated that the deoxygenation role of nickel oxide helps eliminate oxygenated compounds. Alcohols were found in significant amounts in some of the pyrolysis oils. The highest alcohol content (18.98%) was obtained from the pyrolysis of EFB over HZSM-5, as shown in Fig. 3. Alcohols are typically formed from the breakdown of lignin and cellulose components in biomass, and their presence can indicate incomplete deoxygenation. The use of UPCO in the feedstock mixture significantly reduced the alcohol content to 0.55%, highlighting its potential to improve the quality of the pyrolysis oil. Additionally, the use of NiO/HZSM-5 further reduced alcohol formation to 0%, demonstrating the catalyst's effectiveness in promoting hydrocarbon production while minimizing oxygenated compounds.

The esters are valuable compounds in pyrolysis oil upgrading, as they are typically formed from the reaction between acids and alcohols. The highest ester content (22.8%) was obtained from the co-pyrolysis of EFB and UPCO, as shown in Fig. 3, indicating the formation of oxygenated compounds from the lipid-rich feedstock. Interestingly, esters were not detected in the presence of HZSM-5, likely due to the strong cracking activity of the catalyst, which breaks down larger molecules into smaller compounds. This aligns with the discussion by

Gollakota et al. (2023) [16]. However, using NiO/HZSM-5 resulted in an ester content of 20.76%, suggesting that nickel oxide facilitates the formation of esters, possibly through hydrogenation and esterification reactions.

To sum up, the organic composition of pyrolysis oil resulting from the co-pyrolysis of EFB and UPCO varies significantly based on the catalyst used. NiO/HZSM-5 was identified as the most effective catalyst for hydrocarbon production, with the highest hydrocarbon yield (71.86%) and eliminating undesirable oxygenated compounds such as acids, phenols, and alcohols. In contrast, using HZSM-5 alone resulted in lower hydrocarbon yields and higher amounts of oxygenated compounds. These findings highlight the potential of NiO/HZSM-5 as a superior catalyst for enhancing pyrolysis oil by promoting deoxygenation and enhancing the overall quality of the oil.

4. Conclusion

The influence of used palm cooking oil and nickel oxide modified HZSM-5 catalyst in pyrolysis of EFB was successfully investigated via thermogravimetric analyser (TGA) and fixed bed reactor. The co-pyrolysis of EFB and UPCO with HZSM-5 and NiO/HZSM-5 catalysts highlights the importance of catalyst selection in pyrolysis outcomes. Meanwhile, the HZSM-5 increases gas production but lowers oil yield due to excessive cracking, while NiO/HZSM-5 improves oil yield by enhancing deoxygenation and hydrogenation. UPCO addition reduces char formation, improving conversion efficiency. NiO/HZSM-5 is the best catalyst for maximizing oil production and hydrocarbon yields while minimizing undesirable compounds like acids and phenols, making it ideal for biofuel applications. In the future, the study should focus on optimizing catalyst formulations and exploring methods for maintaining catalytic performance over time.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Vekes Balasundram, Norazana Ibrahim;* ***data collection:*** *Vekes Balasundram, Norhuda Abdul Manaf;* ***analysis and interpretation of results:*** *Vekes Balasundram, Ruzinah Isha, Suchithra Thangalazhy Gopakumar;* ***draft manuscript preparation:*** *Le Kim Hoang Pham. All authors reviewed the results and approved the final version of the manuscript.*

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