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Catalytic Cracking of Pyrolytic Oil Derived from Arabica Coffee Parchment Using Ni-NZ Catalysts

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Abstract

The potential of bio-oil derived from biomass has garnered significant attention among researchers for its prospects as an environmentally friendly fuel alternative. This study aims to produce biofuel from bio-oil extracted from Arabica coffee parchment collected from Bener Meriah Regency, Aceh, Indonesia, via catalytic cracking using a nickel-based catalyst supported on natural zeolite. The goal is to improve fuel quality while utilizing cost-effective agricultural residue and environmentally friendly catalytic materials. Nickel metal was used as a catalyst impregnated into natural zeolites to accelerate the reaction rate of the catalytic cracking method. The catalyst was prepared following the wet impregnation method, with activation of natural zeolite using 1 N HCl solution. During the impregnation process, stirring was conducted for 6 hours at 25°C, followed by drying in an oven at 115°C for 12 hours, and calcination at 500°C for 4 hours. The resulting catalyst was then characterized using TGA, XRD, and SEM analyses to determine the catalyst properties. Based on the XRD analysis, diffractogram curves were observed at angles 2θ of 37° and 44°, which can be assigned to be the peaks of nickel catalysts on the zeolite surface. In this study, the Ni-NZ catalyst concentration varied to 15%, 20%, and 25% wt. GC-MS chromatogram results indicated that the highest formation of bio-benzene occurred at a 25% catalyst concentration with a residence time of 2 hours, yielding 9.28%. The findings suggest that Ni-NZ catalysts are technically capable of producing aromatic hydrocarbons from the pyrolytic oil of coffee parchment, which can be utilized as a biofuel component.

Keywords: catalytic cracking, pyrolytic oil, biofuel, coffee parchment, natural zeolite

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INTRODUCTION

The dependence on fossil fuels by the transportation and industrial sectors continues to rise over the year, leading to inevitable depletion of fossil fuel reserves (Mona *et al*., 2020). The massive use of fossil-based fuels has caused significant increase in air pollution, negatively impacting the environment. Thus, more environmentally friendly and readily available alternative fuels are urgently required (Ganesan *et al*., 2021; Ibrahim *et al*., 2021).

Biomass-based fuel is one of the potential solutions to replace fossil fuels. Among the methods for producing fuel from biomass, pyrolysis is an effective technique that processes various types of biomasses to obtain products, such as biochar, bio-oil, and syngas. This method often utilizes agricultural and forestry waste as feedstock (Setiawan *et al*., 2020).

Statistical data indicates that the annual coffee plantation waste has been increasing, with Indonesia emerging as the fourth-largest coffee producer in the world (Nurmalita & Nur, 2022). Bener Meriah Regency in Aceh, Indonesia, is one of the major regions for Indonesia's Arabica coffee plantations, with a cultivation area of 48.163 hectares and a total production of 30.138 tons per year (Statistik, 2024). As coffee production increases, so does the generation of coffee processing waste. If left untreated, this waste can cause complicated environmental problems, especially for the soil. This is because coffee residues contain various compounds, such as phenolics, caffeine, tannins, and chlorogenic acids, that potentially inhibit the growth of plant roots (Nurmalita & Nur, 2022). To address the abundantly generated coffee waste, this study employs coffee parchment as feedstock for the pyrolysis method to produce bio-oil, which will then be upgraded to enhance its quality.

The process of converting coffee parchment oil into biogasoline involves the breaking of oxygen bonds (deoxygenation) in the oxygenated compounds present in the oil (da Costa *et al*., 2022). By reducing the oxygen content, the final product comprises hydrocarbons with chemical structures more similar to conventional gasoline. Several deoxygenation methods are commonly employed in this process, such as catalytic cracking, hydrodeoxygenation, and decarboxylation (Jęczmionek & Porzycka-Semczuk, 2014). Each method has a unique mechanism for removing oxygen atoms, resulting in products with varying fuel characteristics. One approach involves the addition of catalysts that can accelerate reactions and enhance product selectivity. In this context, nickel-based catalysts and natural zeolites offer advantages in the deoxygenation process.

Several studies have successfully converted biomass into biofuels. For instance, Li *et al.* reported biofuel production from cottonseed oil using a fixed-fluidized bed reactor under ambient pressure through a catalytic cracking method. The study revealed that the optimal cracking reaction temperature was 426.2°C, yielding 65.6% light fuel, 33.7% gasoline fraction, and 11.6% gas (Li *et al*., 2009). Similarly, Husin *et al.* produced gasoline fractions using pyrolytic oil derived from plastic waste as feedstock and natural Ni-zeolites from Aceh as catalysts through catalytic cracking. The highest yield was achieved with a nickel catalyst concentration of 15 % *wt.*, resulting in a gasoline fraction conversion (C5-C12) of 96.71% at 450°C over 3 hours (Husin *et al*., 2023).

Nickel is one of the most widely used heterogeneous catalysts by researchers due to its ability to produce hydrocarbons from bio-oil. Among transition metals, nickel is also the most cost-effective compared to other alternatives, such as platinum (Pt) and palladium (Pd). Previous studies have also highlighted that natural Ni-zeolite catalysts exhibit high selectivity in cracking reactions and effectively prevent coke formation on the catalyst surface. Additionally, the acidic properties of zeolites enhances their efficiency and effectiveness in hydrocarbon production (Husin et al., 2022)

Previous research has shown that natural nickel-zeolite can effectively be used as a catalyst in catalytic cracking reactions. For that reason, this study employs the catalytic cracking method to produce biofuel. This method is considered to be a more energy efficient process because it requires less thermal energy to break carbon chain bonds in bio-oil (Widyastuti *et al*., 2024). Natural zeolites serve as a suitable catalyst to support the cracking reactions. Additionally, natural zeolites are readily available and offer several advantages, such as diverse pore structures, large surface areas, high acidity, excellent thermal and chemical stability, shape selectivity, environmental friendliness, and easy separation, as they are heterogeneous catalysts (Wijaya *et al*., 2021).

To enhance the catalytic performance of natural zeolites, their properties can be improved through activation processes, such as acid treatment, base treatment, thermal treatment, and impregnation (Philia *et al*., 2023). However, zeolite activation is typically conducted using acid and base solutions, with HCl and NaOH solutions being the most commonly used reagents. Acid activation, known as dealumination, removes aluminum (Al) atoms from the zeolite framework, thereby increasing the silica-to-alumina (Si/Al) ratio. Acid treatment also removes impurities and enhances the strength of Brønsted acid sites, improving catalytic activity for acid-catalyzed reactions, such as isomerization, cracking, and alkylation [18]. On the other hand, base activation, referred to as desilication, removes silicon (Si) atoms from the zeolite framework, aiming to increase the porosity, surface area, and accessibility to active sites within the zeolite (Aziz *et al*., 2023). However, an excessive use of base solutions can damage the zeolite framework, causing a reduced thermal stability of the catalyst (Bahmanzadegan & Ghaemi, 2024).

This study aims to produce biofuel through catalytic cracking using a nickel-based catalyst supported on natural zeolite, focusing on bio-oil derived from Arabica coffee husk as the primary feedstock. The novelty of this research lies in the utilization of coffee husk-derived bio-oil, which has never been previously investigated for biofuel production. Considering its chemical composition, bio-oil is regarded a promising potential renewable feedstock, offering a new pathway for valorizing agricultural waste into sustainable liquid fuels. To realize this idea, natural zeolites were activated using the acid treatment and subsequently impregnated in a nickel salt solution to form catalyst, which was then employed in the catalytic cracking of the coffee parchment bio-oil. The physical and chemical properties of both the catalyst and the resulting biofuel were analyzed to evaluate the effectiveness of the pyrolytic oil conversion process.

MATERIAL AND METHOD

Materials

The raw material used in this study was coffee parchment sourced from coffee plantations in Bener Meriah, located in Central Aceh, Aceh Province, Indonesia. The coffee parchment was washed to remove impurities and then sun-dried for 2–3 days. The dried coffee parchment was subsequently introduced into a pyrolysis reactor and heated at a temperature of 400–500°C for three hours (Raihan *et al.*, 2020). The pyrolysis product, bio-oil, was collected and used as the feedstock for biofuel production.

Natural zeolites were obtained from CV. Rudang Jaya, Medan, Indonesia. The acid solution used was 1 M HCl (37%, Merck). Nickel ($Ni(NO_3)2.6H_2O$) was supplied by PT. Smart Lab Indonesia (99%, Smart Lab), and distilled water were used as the solvent.

Catalyst Preparation and Characterization

The initial washing of the zeolite was performed using distilled water and repeated three times to remove impurities from the zeolite surface. After washing, the zeolite was dried in an oven at 105°C for three hours. The zeolite was then activated using a 1 M HCl solution by soaking it in the solution for 24 hours. After soaking, the zeolite was washed to achieve a neutral pH and dried in an oven at 120°C for four hours. The zeolite was subsequently ground using a grinding mill and sieved using a 120-mesh sieve. The final zeolite product was labeled as NZ.

The preparation of the nickel-NZ catalyst by impregnation method followed a procedure previously reported by Husin *et al.* (2023). First, 7.5 g of $Ni(NO_3)2.6H_2O$ was dissolved in 100 mL of distilled water. Then, 50 g of NZ was added and stirred at room temperature for six hours. The mixture was then filtered and subsequently dried in an oven at 115°C for 12 hours. The dried catalyst powder was eventually calcined at 500°C for four hours (Aziz *et al.*, 2023). The variation of the $Ni(NO_3)_2.6H_2O$ weight in the impregnation solution concentrations was as followings: 7.5 g at 15% (w/w), 10 g at 20% (w/w), and 12.5 g at 25% (w/w). The resulting catalyst products are labeled as 15Ni-NZ, 20Ni-NZ, and 25Ni-NZ, respectively.

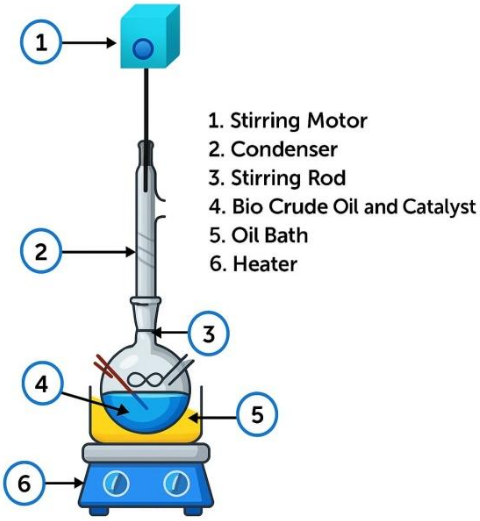


Figure 1. Catalytic cracking experimental set-up

Catalytic Cracking Experiments

A carefully prepared 100 mL bio-oil obtained from the pyrolysis of coffee parchment was mixed with 1 g of Ni-NZ catalyst and introduced into a boiling flask equipped with a vertical ball condenser. Figure 1 illustrates the experimental setup used for the catalytic cracking process. The reaction was carried out at a temperature of 200°C, with the reaction times for each sample varying from 1 hour, 1.5 hours, and 2 hours. Upon the completion of the catalytic cracking process, the reaction mixture was then filtered to separate the catalyst from the bio-oil. Subsequently, the catalyst-free bio-oil was distilled for three hours.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

To evaluate the thermal stability of the support material made from natural zeolite, a thermogravimetric analysis (TGA) was conducted in a nitrogen atmosphere with a flow rate of 20 mL/min. Figure 2 displays the thermogram curves for the three types of Ni-NZ catalyst samples, with the temperature ramp rate set at 40°C/min during the test. Figure 2 shows the TGA analysis curves for the three sample variations, with each catalyst sample heated from 25.21°C to 1000°C. During the initial heating phase, a mass loss of 13.3 % occurred from 25.21°C to 200°C, indicating the evaporation of weakly bound physical water on the surface of the zeolite and nickel. From 200°C to 600°C, a slower mass loss was observed. This mass loss according to (Brockner *et al.*, 2007), during thermal decomposition, nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) undergoes sequential dehydration and partial decomposition, leading to the formation of basic nickel salt. Additionally, in this temperature range, chemically bound water is released due to dehydroxylation of both the zeolite structure and nickel compounds.

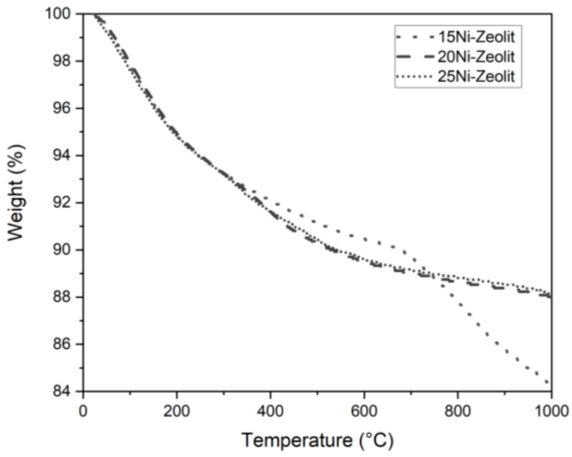


Figure 2. TGA curves of Ni-NZ with varying concentrations

This step includes the loss of hydroxyl (-OH) groups and nitrate decomposition, which aligns with the TG analysis curve shown in this study. nickel compounds are expected to undergo thermal decomposition, transitioning from $Ni(NO_3)_2$ to NiO.

A significant mass loss was observed at temperatures within the range of 600°C and 800°C. In this temperature range, it is estimated that decomposition of the nickel material occurs. At high temperatures, the mass loss is attributed to the decomposition of several nickel oxide phases (NiO), involving the loss of oxygen from the material, resulting in the formation of Ni (Brockner *et al.*, 2007). Furthermore, during this temperature range, a structural transformation of the zeolite was also identified as shown in Figure 3. Based on the presented XRD patterns, it is evident that the crystalline structure of natural zeolite (NZ) undergoes transformation following modification into 15Ni-NZ, 20Ni-NZ, and 25Ni-NZ. This transformation is indicated by changes in the intensity and position of the main diffraction peaks, particularly in the 2θ regions around 9.8°, 22.5°, and 27°, which are characteristic of the clinoptilolite-type natural zeolite structure (de Lima *et al.*, 2021). In the modified samples, the intensities at these positions decrease or shift, suggesting alterations in crystal ordering or the possible formation of new zeolite phases through interzeolitic transformation (M. Król *et al.*, 2024). This phenomenon is consistent with previous studies reporting that chemical or hydrothermal treatments on natural zeolites can lead to partial degradation of the original crystalline structure and the emergence of new phases, as evidenced by the changes in diffraction peak profiles (Alver *et al.*, 2010). Although zeolite is known to be thermally stable, temperatures above 600°C can affect the zeolite framework structure, potentially leading to the release of material from the zeolite structure. From 900°C to 1000°C, the mass loss in this range is identified as the complete decomposition of the zeolite structure, resulting in the loss of most of the material in the zeolite. At this temperature, it is also likely that the nickel oxide (NiO) undergoes further thermal transformation, leading to its vaporization into a lighter form (Brockner *et al.*, 2007; Król & Jeleń, 2021).

From Figure 2, it is evident that the 15Ni-NZ catalyst experiences greater mass loss compared to the 20Ni-NZ and 25Ni-NZ catalysts. This is attributed to the lower nickel concentration, which results in reduced thermal stability, making the zeolite structure more prone to decomposition. In contrast, the 20Ni-NZ and 25Ni-NZ catalysts exhibit good thermal stability, likely due to the nickel metal occupying nearly the entire zeolite surface. This observation is supported by the XRD analysis results, as shown in Figure 3. The presence of nickel metal on the zeolite surface is believed to enhance thermal stability and reinforce the zeolite framework, preventing decomposition at high temperatures (Yao *et al.*, 2015).

X-Ray Diffractions (XRD)

X-ray diffraction (XRD) analysis was performed to investigate the crystallographic structure and phase composition of the Ni-natural zeolite catalyst. This characterization aims to confirm the successful incorporation of nickel into the natural zeolite framework, evaluate the structural integrity of the zeolite after modification, and identify potential phase changes that could affect the catalytic performance.

In Figure 3, three Ni-NZ catalyst samples and one natural zeolite (NZ) sample without nickel are displayed. As shown in Figure 3, the NZ sample exhibits a black pattern, with peaks observed at 2θ angles of approximately 10° to 30°. The peaks formed are identified as the structure of natural zeolite crystals.

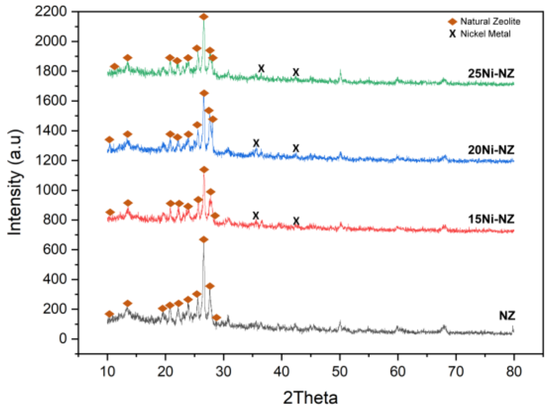


Figure 3. XRD graph of NZ and Ni-NZ with varying concentrations

Zeolites generally have an ordered pore structure, resulting in a characteristic diffraction pattern. The natural zeolite in this study belongs to the modernite (PDF no. 049-0924) and klinoptilolite (JCPDS No. 00–025–1349) types (Sudiyarmanto *et al.*, 2017; Wijaya *et al.*, 2021). This is evidenced by the appearance of main diffraction peaks at 2θ values of approximately 9.8°, 22.5°, and 27°, which are characteristic of the crystalline structure of clinoptilolite, along with an additional peak near 26.6° that is commonly associated with the presence of mordenite.

This identification is further supported by the study conducted by (Costafreda & Martín, 2021), which reported similar XRD patterns in natural zeolite from Cuba containing a mixture of mordenite and clinoptilolite, as well as by (Wahono *et al.*, 2019), who observed a high-intensity peak at around 22°, indicating the dominant presence of the clinoptilolite phase.

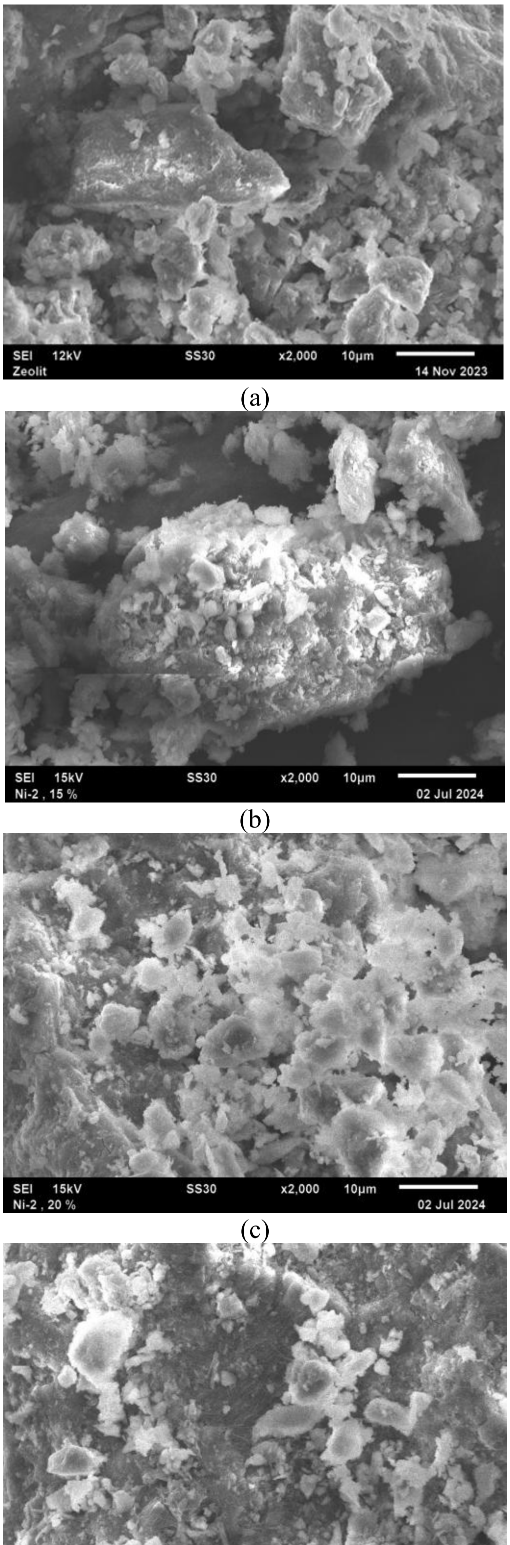
In the three Ni-NZ catalyst samples shown in Figure 3, the diffraction patterns in the 10° to 30° range closely resemble the diffraction pattern of NZ. This indicates that the basic structure of natural zeolite is retained after the addition of nickel, suggesting that natural zeolite exhibits greater thermal stability. Furthermore, the nickel peaks are expected to appear at 2θ angles around 37° and 44°, in accordance with the powder diffraction standard (JCPDS 04–0850), as previously reported *(Aziz et al.*, 2023; Prihadiyono *et al.*, 2022). In the 25Ni-NZ catalyst, the diffraction peaks at approximately 37° and 44° are more pronounced compared to those in the 15Ni-NZ and 20Ni-NZ catalysts. This suggests that with higher nickel content, the amount of nickel deposited on the zeolite surface increases. This is consistent with the TGA analysis in Figure 2, which shows that the 25Ni-NZ catalyst exhibits good thermal stability, as nickel is well-impregnated into the pores of the natural zeolite.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis was conducted to study the surface morphology and microstructure of the Ni-NZ catalyst. The SEM observations aimed to evaluate the distribution of nickel particles on the zeolite surface, as well as to examine the morphological changes in the zeolite after the nickel impregnation process, as shown in Figure 4.

Figure 4 shows the surface morphology of natural zeolite and Ni-NZ catalysts with varying nickel concentrations. The surface of natural zeolite at 2000× magnification displayed in Figure 4 (a) appears to be randomly arranged, stacked and tends to be rough, with a denser surface texture.

Figures 4(b), 4(c), and 4(d) show the morphology of the 15Ni-NZ, 20Ni-NZ, and 25Ni-NZ catalysts, respectively. The surfaces of these catalysts appear looser, and the particles deposited on the catalyst surfaces form aggregates of varying sizes, predominantly with rounded shapes. These aggregates are likely formed by nickel metal particles adhering to the zeolite surface (Sihombing *et al.*, 2023; Suhendi *et al.*, 2020).



(a)

(b)

(c)

(d)

Figure 4. SEM images of (a) NZ; (b) 15Ni-NZ; (c) 20Ni-NZ; (d) 25Ni-NZ

Table 1. Chemical composition of coffee parchment pyrolytic oil

No.	Retention time (min)	Relative area (%)	Compound content
1	1.664	8.21	Methyl Alcohol
2	1.847	2.84	Acetone
3	1.970	0.77	Acetic acid, methyl ester
4	2.306	0.94	2-Butanone
5	4.180	51.75	Ammonium acetate
6	4.847	0.58	1.2:5.6-Dianhydrogalactitol
7	5.126	1.85	Pyridine
8	5.354	0.56	1-Hydroxy-2-butanone
9	5.517	1.76	Pyridine, 2-methyl-
10	6.235	1.55	Pyridine, 2-methyl-
11	6.616	1.69	N,N'-Isophthaloylbis(3-aminobenzoic acid)
12	7.173	1.47	Pyridine, 4-methyl-
13	7.612	1.47	2.6-Lutidine
14	7.830	0.81	Tricyclo[2.2.1.0(2.6)] heptan-3-ol, 4.5.5- trimethyl-
15	8.354	1.59	Butanoic acid. 4-hydroxy-
16	8.755	1.76	Pyridine, 2.5-dimethyl-
17	9.116	0.64	Pyridine, 2.5-dimethyl-
18	10.129	2.74	Phosphonic acid, (p-hydroxyphenyl)-
19	10.326	3.44	Phenol
20	11.489	1.40	Spiro[2.4]heptan-4-one
21	12.156	2.11	Phenol, 3-methyl-
22	12.993	1.38	Phenol, 3-methyl-
23	14.659	1.11	Paromomycin
24	14.853	1.85	4-(2.5-Dihydro-3-methoxyphenyl)butylamine
25	16.027	0.55	3.6-Dimethyl-3.6-dihydro-pyran-2-one oxime
26	17.952	0.96	4.5.6.7-Tetrahydro-1H-indazol-3-amine
27	20.329	0.57	2.4-Dimethoxyphenol
28	31.866	3.63	Caffeine

GC-MS Analysis of Raw Material

Coffee parchment, as agro-industrial waste, holds significant potential for conversion into high-value products through pyrolysis technology. The pyrolysis process of coffee parchment produces products such as bio-oil, biochar, and syngas.

One of the key components of bio-oil is complex organic compounds, including lipids, lignin, and decomposed carbohydrates. To evaluate the potential compounds in coffee parchment bio-oil that can be utilized as an alternative fuel, GC-MS testing was conducted. Table 1 presents the chemical composition of coffee parchment bio-oil.

The most abundant compound in coffee parchment bio-oil is ammonium acetate, comprising 51.75% of the total content. During coffee cultivation, farmers typically use fertilizers and chemicals to nourish coffee plants and protect them from pests. These fertilizers and chemicals are absorbed into the plant, including the coffee parchment. As shown in Table 1, compounds such as ammonium acetate, phosphonic acid, and paromomycin are likely residues from fertilizer and chemical usage. Other detected compounds include tar, with a total percentage of 9.03%, while the least abundant detected compound is caffeine, at 3.63%.

Table 1 shows that the analysis of coffee parchment bio-oil reveals a high concentration of oxygenated compounds, which possess favorable combustion properties and can serve as an alternative fuel (Stelmach *et al.*, 2023). Utilizing coffee parchment bio-oil as an alternative fuel not only reduces agricultural waste but also provides a clean and sustainable energy source. The oxygenated compounds in bio-oil enhance combustion efficiency and fuel quality (Amrullah *et al.*, 2024), making coffee parchment bio-oil a viable option for various energy applications. In Table 1, oxygenated compounds are the second most abundant component, accounting for 37.11% of the bio-oil.

Based on the composition of compounds in Table 1, two main components show potential for utilization in biogasoline production. Methyl Alcohol (8.21%) can be processed through the methanol-to-gasoline (MTG) method to produce short-chain hydrocarbons suitable as fuel (Galadima & Muraza, 2015).

Table 2. GC-MS results for distillate obtained from catalytic cracking using 25Ni-NZ catalyst

Compound content	Area %		
	1h	1.5 h	2h
2-Furanmethanol	7.47	7.65	-
Pyridine, 3-methyl-	1.8	-	-
2(3H)-Furanone, dihydro-(CAS) Butyrolactone	1.72	-	2.05
2-Cyclopenten-1-(2-furanyl)-(CAS) 2-Acetylfuran	3.35	2.82	-
Ethanone, 1-(2-furanyl)- (CAS) 2-Acetylfuran	2.56	1.7	-
Pyridine, 2-ethyl-	1.74	-	-
Pyrazine, 2.6-dimethyl-	2.74	1.65	-
2-Cyclopenten-1-one,3-methyl-(CAS) 3-methyl-2cyclopentenone	2.33	3.11	1.52
Glycerin	2.15	4.93	5.15
Phenol (CAS) Izal	9.96	44.83	56.76
2.3-Dimethyl-2-Cyclopenten-1-one	2.52	2.45	-
Phenol,2- methyl-(CAS) o-cresol	7.79	4.88	2.09
Phenol, 4-methyl-	4.88	4.94	3.35
Phenol,3- methyl-(CAS) m-cresol	5.7	4.04	4.88
Phenol, 2-methoxy-	5.55	6.42	-
Phenol, 2.4-dimethyl-	0.89	-	-
Phenol, 4-ethyl-	0.91	-	-
Phenol, 2.3-dimethyl-	1.17	-	-
1.2-Benzenediol	3.4	4.95	9.28
Phenol, 2.6-dimethoxy- (CAS) 2.6-Dimethoxyphenol	1.36	1.95	-
Butanoic acid, 3-methyl-	-	1.23	-
Butanoic acid, 4-chloro-	-	1.25	-
Hydroquinone	-	1.21	2.2
2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS) Corylon	-	-	2.28
2-Furanmethanol, tetrahydro- (CAS) Tetrahydrofurfuryl alcohol	-	-	2.07
Pentanal (CAS) n-Pentanal	-	-	1.53
1.2.3-Propanetriol, monoacetate	-	-	1.57
1.4:3.6-Dianhydro-.alpha.-d-glucopyranose	-	-	1.25
Phenol, 2.6-dimethoxy-	-	-	4.04

Additionally, phenol and its derivatives (a total of approximately 7.37%, including phenol at 3.44%, phenol, 3-methyl- at 2.11%, and phenol, 3-methyl- at 1.38%) possess aromatic groups that can be converted into aromatic hydrocarbons via the hydrodeoxygenation process. These compounds provide a strong foundation for the development of biogasoline with the appropriate conversion processes.

GC-MS Analysis Results of the Product and Yield

The catalytic cracking process of coffee parchment bio-oil was carried out in a stirred reactor, where Ni-NZ catalyst was added to accelerate the reaction and facilitate the formation of lighter hydrocarbon compounds. The operating conditions included a temperature of 200°C at 1 atm pressure, with varying reaction times. After the cracking process was completed, the reaction mixture was fed into a distillation column to efficiently separate the resulting compounds based on their boiling points. The GC-MS analysis results of the obtained distillate are presented in Table 2.

Table 2 presents the compound composition formed at different reaction times detected by the GC-MS analysis. The results indicate that reaction time significantly influences the composition of the resulting compounds. At a reaction time of 1 hour, 1,2-benzenediol was detected at a concentration of 3.4%, which increased to 4.95% after 1.5 hours and reached 9.28% after 2 hours. This increase suggests that a longer reaction time allows advanced lignin decomposition, resulting in a higher phenolic compound yield, namely 1,2-benzenediol. It is well-recognized that benzene compounds are aromatic hydrocarbons that can help improve combustion efficiency in engines due to their flammability and high-octane number.

Moreover, phenol was detected as the primary component at all reaction durations, indicating that phenol is a dominant product of coffee parchment pyrolysis and has yet to be fully transformed into more valuable compounds. Tar compounds, such as 3-methylpyridine were also identified, with a concentration of 6.28% at 1 hour,

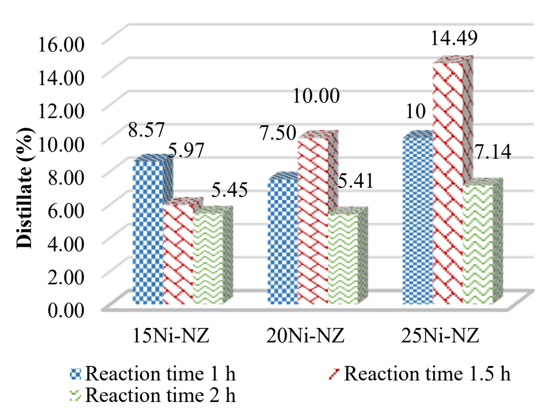


Figure 5. Comparison of distillates by reaction time

which decreased to 1.65% after 1.5 hours, and became undetectable at 2 hours.This decline implies that tar compounds underwent decomposition or conversion into other compounds at a longer reaction time.

Based on the findings, several compounds with potential as liquid fuel precursors were identified: 1,2-benzenediol, which functions as a high-energy aromatic precursor, octane enhancer, and a hydrogen and oxygen donor in fuel reformulation (Ouellette & Rawn, 2018);
phenol, which can be converted into derivatives, such as alkylated and ether compounds, important components in liquid fuels (Nenkova *et al*., 2008); 2-methylphenol (o-cresol) and 3-methylphenol (m-cresol), phenolic derivatives with potential for conversion into aromatic-based fuels via catalytic deoxygenation (Zhu *et al*., 2014); hydroquinone, an oxygen-rich aromatic precursor used in synthesizing high-energy fuel compounds (Naranov *et al*., 2024); 2-furanmethanol (furfuryl alcohol), a furan-based compound used in the production of biofuels like dimethylfuran (DMF), known for high calorific value and combustion stability (Hoang *et al*., 2022); 2-acetylfuran, which can be catalytically converted into furanic biofuels, such as DMF, a gasoline substitute with high specific energy; and pyrazine, 2,6-dimethyl-, a nitrogen-containing aromatic compound that can serve as a combustion-enhancing fuel additive (He *et al*., 2022).

Figure 5 displays the relationship between the variation of Ni-Natural Zeolite (NZ) catalyst samples with different nickel contents (15Ni-NZ, 20Ni-NZ, and 25Ni-NZ) and the percentage of distillate produced at three different reaction times, namely 1 hour, 1.5 hours, and 2 hours. For all catalyst samples, an interesting phenomenon can be observed that the distillate percentage increases as the reaction time progresses, with the 25Ni-NZ sample producing the highest distillate percentage at each tested time interval. The 15Ni-NZ catalyst shows a relatively lower increase in distillate compared to both 20Ni-NZ and 25Ni-NZ samples, although a clear upward trend is seen at the 1.5-hour reaction time.

The 25Ni-NZ catalyst, with a 1.5-hour reaction time, achieved 14.49% distillate, which resembles the highest distillate yield observed in this study. The lowest distillate yield was obtained from catalytic cracking using 20Ni-NZ catalyst employing 2 hours of reaction, at 5.41%. Overall, catalysts with a higher nickel content (25Ni-NZ) exhibit better performance in distillate production, particularly after 1.5 hours of reaction. These findings suggest that increasing the nickel content in the catalyst can enhance reaction conversion, leading to higher distillate yields as the reaction time is extended to 1.5 hours.

CONCLUSION

The use of Ni-NZ catalysts with varying nickel concentrations successfully breaks the complex bonds present in the carbon chains of coffee parchment bio-oil. This bio-oil contains oxygenated compound fractions with favorable combustion properties, making it a potential alternative fuel. The bio-oil also produces 1.2-benzenediol, as seen from the results where the reaction time significantly affects the amount of 1.2-benzenediol produced. The longer the reaction time, the greater the formation of 1.2-benzenediol.

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