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Catalytic Slow Pyrolysis of Corncob Using Rice Husk-Derived Zeolite-A: The Effect of Temperature and Catalyst-to-Biomass Ratio on Pyrolysis Oil Characteristics

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Abstract
The depletion of fossil fuel reserves and the growing environmental concerns associated with their use have intensified interest in renewable biofuels. Corncob waste, a lignocellulosic biomass composed of approximately 41% cellulose, 36% hemicellulose, and 6% lignin, represents a promising feedstock for pyrolysis oil production. However, conventional pyrolysis processes typically produce pyrolysis oil with low conversion, low density, and poor stability. This study investigated catalytic pyrolysis in a fixed-bed reactor employing Zeolite-A synthesized from rice husk-derived silica to improve pyrolysis oil quality. Catalytic pyrolysis experiments were conducted at various temperatures (300 °C, 350 °C, and 400 °C) and catalyst-to-biomass ratios (1:0 to 1:20 w/w). The highest pyrolysis oil yield of 34% was achieved at 400 °C without a catalyst (1:0 w/w), indicating that while catalyst presence is not essential for maximizing yield, it plays a crucial role in modifying the physicochemical properties of the oil and accelerating the overall reaction. Oil density ranged from 1.24 to 1.35 g/mL, peaking at 400 °C and 1:15 w/w, reflecting enhanced cracking and polymerization. Viscosity varied from 85.28 to 116.00 mm^2/s, increasing with catalyst ratio and influenced by the temperature-dependent cracking and secondary reactions. GC-MS analysis identified hydrocarbons including androstane and spirocyclic compounds, confirming the improvement in fuel quality through catalytic deoxygenation. These findings highlight the potential of Zeolite-A-catalyzed pyrolysis for producing high-quality liquid biofuels.

Keywords
corncob, pyrolysis oil, catalytic pyrolysis, silica synthesis, rice husk, Zeolite-A

1 Introduction

Fossil fuels have long supported the growing global energy demand, especially in transportation and industrial applications. However, the continuous increase in consumption has become a significant concern for long term sustainability [1]. The International Energy Outlook 2018 projects that global energy demand will rise by nearly 28% by 2040, reaching approximately 739 quadrillion British thermal units (Btus) or 7.79×10^{20} J [2]. This trend highlights the urgent need to identify alternative energy sources that can ensure the sustainability of both resources and the environment. In recent years, the development of renewable energy options such as solar, wind, geothermal, and bioenergy has attracted increasing

global attention [3]. Bioenergy has excellent potential to generate energy, fuels, and valuable chemical products.

Biomass can be classified into lignocellulose and non-lignocellulose types. Lignocellulose refers to materials with high lignin content, such as wood, rice husks, bagasse, and wheat straw. In contrast, non-lignocellulose includes sources like inedible oils, algal biomass, and other materials with very low or negligible lignin content. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, lignin, and a small amount of ash. For instance, corncobs, a widely available lignocellulosic biomass, contain 45.88% cellulose, 39.40% hemicellulose, and 11.32% lignin [4]. They make up approximately

40 to 50% of the total mass of the whole corn. Based on data from the Indonesian Central Statistics Agency, the production of dry corn kernels with a moisture content of 14% in 2020 was 12.03 million ton, in 2021 it was 13.41 million ton, in 2022 it was 16.53 million ton, in 2023 it reached 14.77 million ton and in 2024 it increased to 15.14 million ton and the projection in 2025 which experienced an increase of 1.41 million ton to 16.52 million ton [5]. This large, growing corn production volume indicates a substantial supply of corn cobs that can support bioenergy development. To convert biomass into useful energy carriers, thermochemical processes such as combustion, pyrolysis, gasification, and catalytic upgrading are commonly used to break down the complex molecular structures [6].

Pyrolysis is a thermal decomposition process carried out in the absence of oxygen that yields high-energy products. The main outputs of pyrolysis include gaseous products known as synthesis gas, a liquid fraction referred to as biooil, and solid carbon residue known as biochar [7]. Pyrolysis proses are divided into three types, such as fast, flash, and slow pyrolysis. Fast pyrolysis operates at heating rates and high temperature of 200 °C/s and >500 °C, respectively [8]. Flash pyrolysis uses a very rapid heating rate between 1000 and 10000 °C/s [9]. In addition, slow pyrolysis at temperature of 200 °C can achieved biooil production of 48% from corncob waste [10]. Pyrolysis can be carried out in various reactor configurations, among which fixed-bed, fluidized-bed, and microwave-induced reactors are the most widely utilized [11, 12]. Typically constructed from steel, the fixed-bed reactor includes a cavity for holding stationary biomass, an electric heating source, and a steam cooling unit. It offers several advantages, including high conversion efficiency, low tar formation, and compatibility with biomass containing varying ash contents. Nevertheless, this design demands thin feedstock to avoid uneven heating and faces difficulties with scale-up and long heating times [13, 14]. Catalytic pyrolysis is used to improve the quality and characteristics of biooil. This can be achieved through catalytic cracking, hydrocracking, or hydrotreatment. Catalytic pyrolysis typically occurs at temperatures between 400 °C and 500 °C and under pressures at 1.013×10^5 Pa [15]. Reactions involved include dehydration, cracking, polymerization, deoxygenation, and aromatization. Catalysts used in pyrolysis are classified as primary or secondary. Primary catalysts are mixed with the feedstock before the pyrolysis reaction, either through dry or wet preparation. In contrast, secondary catalysts are placed in a separate zone and do not directly interact with the biomass.

Zeolites are crystalline porous aluminosilicate minerals with a three-dimensional framework composed of silicon and aluminum tetrahedra [15]. The framework contains open channels and cavities that accommodate exchangeable cations to balance the negative charge of the lattice. Zeolites release water upon heating and are available in natural and synthetic forms. Natural zeolites are derived from volcanic activity and sedimentation, while synthetic zeolites are made from materials such as soda ash and feldspar. Common types of zeolites include types A, X, Y, and P. Zeolite-A is rich in aluminum, highly porous, and has a low silicon to aluminum ratio between 1 and 1.5 [16]. Zeolite catalysts enhanced pyrolysis oil quality through deoxygenation, aromatization, cracking, and shape-selective effects [17]. During deoxygenation, zeolites remove oxygen from pyrolysis oil compounds via dehydration, decarboxylation, and decarbonylation, which lowers acidity and increases the calorific value. In aromatization, zeolites convert oxygenated intermediates into valuable aromatic hydrocarbons, improving energy density and overall fuel quality [18]. Through cracking, zeolites break down larger molecules into smaller ones, reducing viscosity and enhancing the flow properties of pyrolysis oil. Zeolite-based catalysts are widely used for polymer cracking and dehydration due to their high selectivity for hydrocarbon production and their ability to reduce unwanted byproducts such as carboxylic acids and oxygenated compounds. Catalyst application in pyrolysis significantly improves the hydrocarbon content of the biooil. A recent study Kumar et al. [19] showed that the choice of catalyst can influence the yields of gas, char, and pyrolysis oil. Without a catalyst, the process produced 6.31, 22.0, and 71.6 wt% of gas, char, and pyrolysis oil, respectively. In comparison, using the CuNiZ-1 catalyst resulted in yields of 8.98, 21.0, and 70.0 wt%, respectively. In addition, corncob liquid smoke produced via catalytic pyrolysis at 350 °C for 2 h with 6% (w/w) zeolite exhibited optimal properties, including a yield of 6.5%, pH 2, density 1.132 g/mL, acid content 24%, and viscosity 1.309 cP, suitable for food preservation applications [20]. Furthermore, catalytic treatment reduces the presence of undesirable compounds such as water and organic acids while enhancing the content of aromatic hydrocarbons [21]. Despite increasing interest in utilizing zeolite catalysts for biomass pyrolysis, including corncob and other lignocellulosic residues, previous studies have inadequately and superficially addressed the research gap related to catalytic slow pyrolysis of corncob using rice husk-derived zeolite catalysts. Many existing works on catalytic pyrolysis focus on fast pyrolysis or different catalyst systems (e.g., HZSM-5, activated carbon,

metal-impregnated catalysts), but do not critically analyze the fundamental mechanisms, catalyst effectiveness, optimal catalyst-to-biomass ratios, or the interactions between process temperature and catalyst properties in slow pyrolysis conditions. For example, investigations into catalytic pyrolysis of corncob with zeolite mixtures have shown improved aromatic yields but lack detailed discussion of catalyst structural influence and process parameter optimization in slow pyrolysis systems [22]. Likewise, while zeolite catalysts have been employed in biomass pyrolysis broadly, comprehensive explanation of why rice husk-derived Zeolite-A specifically improves corncob oil characteristics under slow pyrolysis remains limited and poorly articulated in the literature.

This study aims to investigate the potential of corncob biomass as a raw materiaZ to produce high-quality biooil through catalytic pyrolysis using a fixed bed reactor from conventional pyrolysis. Specifically, the research focuses on enhancing the properties of the resulting biooil by utilizing Zeolite-A as a catalyst synthesized from rice husk-derived silica. The catalytic pyrolysis process is carried out under varying temperature (i.e. 300 °C, 350 °C and 400 °C) and catalyst-to-biomass ratio (i.e. 1:0, 1:5, 1:10, 1:15, and 1:20 w/w) conditions to evaluate their effects on pyrolysis oil yield, physicochemical properties (e.g. density and viscosity), and calorific value. The catalyst used in this pyrolysis is classified as a primary catalyst, where the catalyst is mixed with the raw material before the pyrolysis reaction, either through dry preparation. The novelty of this study lies in exploring the catalytic effects at temperatures below 400 °C, a range that remains less studied, to better understand the combined impact of reaction temperature and catalyst loading on pyrolysis oil yield, composition, and fuel properties. The performance of the produced liquid fuel is assessed through combustion capability tests to determine its suitability as an alternative energy source. The overall objective is to improve the efficiency and quality of bio-energy technologies from corncob waste, thereby contributing to the advancement of sustainable bioenergy technologies. Despite numerous studies on pyrolysis of lignocellulosic biomass, few have systematically investigated the catalytic effects of rice husk-derived Zeolite-A on corncob pyrolysis oil at temperatures below 400 °C. This study addresses this research gap by evaluating the combined influence of catalyst-to-biomass ratio and sub-400 °C pyrolysis conditions on oil yield, composition, and fuel properties, providing insights for optimized catalytic pyrolysis strategies.

2 Materials and methods
2.1 Materials
The primary raw materials utilized in this study consisted of corncobs and rice husks. The corncobs were obtained from local corn farmers in Bangil District, Pasuruan Regency, East Java, while the rice husks were obtained from farmer cooperatives in Kepohbaru District, Bojonegoro Regency, East Java. The chemical reagents employed throughout the experiment procedures, include sodium hydroxide (Merck), nitric acid (Merck), silica gel (Sigma-Aldrich), aluminum powder (Merck), and distilled water. All chemicals were used at the highest commercially available purity to ensure consistency and reproducibility of the results.

2.2 Rice husk silica extraction
Rice husk silica was prepared using the alkali extraction method [23]. A total of 50 g of dry husk was mixed with 500 mL of 1.5% NaOH solution. The mixture was boiled for 30 min, to extract the silica content. The resulting mixture was then cooled to room temperature and left to stand for 24 h. Subsequently, the mixture was filtered to obtain the filtrate containing soluble silica (silica sol). To precipitate solid silica, the sol was acidified by the gradual addition of 10% HNO_3 solution until gel formation was observed. The resulting gel was aged for three days, thoroughly washed with deionized water to remove residual acid, oven-dried at 110 °C for 8 h, and finally ground into a fine powder.

2.3 Zeolite-A synthesis
Zeolite-A was synthesized from an aluminosilicate gel. Initially, 0.723 g NaOH was dissolved in 80 mL deionized water, and the resulting solution was divided into two equal portions. A silicate solution was prepared by adding 15.480 g of silica to one portion, while an aluminate solution was obtained by adding 8.258 g of aluminum powder to the second portion of the NaOH solution. The two solutions were then combined and stirred thoroughly until a homogeneous aluminosilicate gel formed. The gel was aged at 60 °C for 3 h, followed by transfer into a sealed Teflon-lined autoclave for hydrothermal crystallization at 100 °C for 20 h. After crystallization, the solid product was filtered, repeatedly washed with deionized water until the pH reached neutral (pH 7), and finally dried at 200 °C for 3 h [24–26]. A schematic overview of the rice husk silica extraction, Zeolite-A synthesis, and pyrolysis processes is presented in Fig. 1.
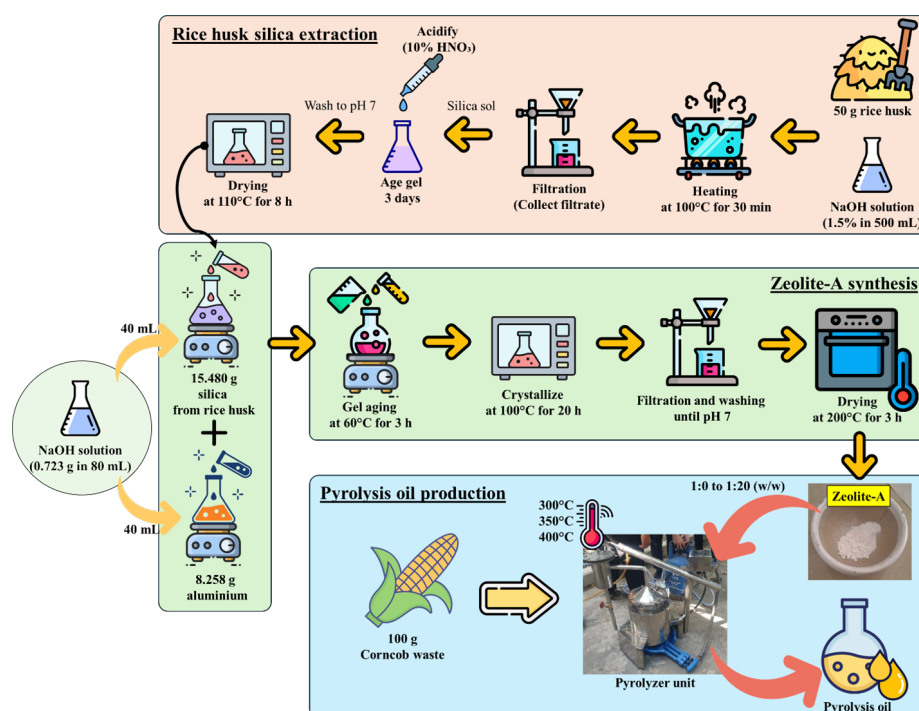
Fig. 1 Process flow diagram of rice husk silica extraction, Zeolite-A synthesis, and pyrolysis oil production. Silica from rice husk was extracted and used as a precursor for Zeolite-A synthesis, which was then applied as a catalyst (1:0 to 1:20 w/w) in the pyrolysis of corncob biomass at 300 °C, 350 °C, and 400 °C to produce pyrolysis oil.

2.4 Pyrolysis oil production using catalytic pyrolysis

Corncob biomass was used as the raw material, prior to pyrolysis, the physicochemical properties of the biomass were determined through proximate and ultimate analyses, as shown in Table 1. The relatively high moisture content (23.64 wt%) is expected to promote the formation of an aqueous phase during condensation, while the ash content may contribute to enhanced char formation. The high oxygen content of the biomass explains the abundance of oxygenated compounds observed in the pyrolysis oil.

A total 100 g biomass was placed into the pyrolysis tube, and varying amounts of catalyst were added according to catalyst-to-biomass ratios (w/w) of 1:0, 1:5, 1:10, 1:15, and 1:20. The solid zeolite catalyst was thoroughly mixed

with the corncob biomass using a glass mortar and spatula to ensure uniform distribution, and the mixture was gently pressed prior to loading into the reactor. The prepared samples were transferred to a fixed-bed stainless steel reactor, consisting of a closed cylindrical vessel with inlets and outlets for gas or steam and a condensation line leading to a secondary container for collecting pyrolysis oil and water. The reactor was custom-designed and fabricated in-house (Malang, Indonesia) and operated under controlled pyrolysis conditions with maximum temperature 500 °C. The reactor was heated externally using a temperature-controlled furnace, with a controlled heating rate to ensure uniform temperature ramping to the target pyrolysis temperatures (300 °C, 350 °C, and 400 °C), which were maintained for 60 min. As the pyrolysis proceeded, the volatile vapors were transported through horizontal metal pipes to a vertical condenser containing an internal oil cooler with circulating cooling water, condensing the vapors into pyrolysis oil and aqueous fractions. The organic fraction (pyrolysis oil) was collected and subsequently analyzed using gas chromatography-mass spectrometry (GC-MS) (Shimadzu GCMS-QP2010 SE) to determine its chemical composition [27, 28]. No carrier gas was used in this procedure.

Table 1 Proximate and ultimate analyses of corncob biomass used as feedstock for catalytic pyrolysis

Parameter	Method	Value (wt%)
Moisture content	ASTM D3173	23.64
Ash content	ASTM D3174	1.56
Carbon	ASTM D5373	43.32
Hydrogen	ASTM D5373	6.42
Nitrogen	ASTM D5373	0.50
Sulfur	ASTM D4239	0.056
Oxygen	ASTM D3176	48.14

2.5 Determination of yield, density, viscosity, and calorific value

2.5.1 Pyrolysis oil, char and gas yield determination

The yield of pyrolysis oil was calculated based on the mass of pyrolysis oil products obtained after pyrolysis proses, as shown in Eq. (1).

$$\text{Yield}\left(\%\right) = \frac{\text{Mass product}\left(\text{g}\right)}{\text{Mass raw materials}\left(\text{g}\right)} \times 100 \qquad (1)$$

After pyrolysis process, the pyrolysis oil product was collected in a pre-weighed container.

The biochar yield was determined by weighing the solid residue remaining in the reactor after cooling to room temperature and applying the same equation. The yield of non-condensable gas was calculated indirectly by the mass balance, assuming that the total mass of products equals the initial mass of raw material, as expressed in Eq. (2).

$$\text{Gas yield}\left(\%\right) = 100 - \left(\text{Pyrolysis oil}\% + \text{Char}\%\right) \qquad (2)$$

2.5.2 Density and viscosity measurement

The density of the pyrolysis oil was measured using a 25 mL pycnometer (Iwaki, Japan). The density was calculated using the Eq. (3).

$$\text{Density}\left(\text{g}/\text{mL}\right) = \frac{\text{Mass product in pycometer}\left(\text{g}\right)}{\text{Volume of product}\left(\text{mL}\right)} \qquad (3)$$

All measurements were performed at room temperature (25 ± 1 °C). In addition, viscosity was determined using a Brookfield digital viscometer (Iwaki, Japan) at 25 °C. Approximately 20 mL of pyrolysis oil was placed in a sample adapter, and the appropriate spindle was selected according to the expected viscosity range. The measurements were recorded after the spindle achieved a steady rotational speed.

2.5.3 Calorific value determination

The calorific value of the pyrolysis oil was measured using a Parr 6100 bomb calorimeter. Approximately 1 g of pyrolysis oil was placed in a metal crucible and combusted under a high-pressure oxygen environment at 3.04 MPa. The higher heating value (HHV) was calculated based on the temperature rise in the water jacket surrounding the combustion chamber, as shown in Eq. (4).

$$\text{Calorific value}\left(\text{kJ}/\text{kg}\right) = \frac{C \times \Delta T}{m} \times 1000 \,, \qquad (4)$$

where C is the heat capacity of the calorimeter system (kJ/°C), ΔT is temperature (°C), m is mass of the pyrolysis oil sample (g).

3 Results and discussion

3.1 Zeolite-A characterization

In this study, rice husk was used as a silica source for the synthesis of Zeolite-A. The rice husk was obtained as agricultural waste from rice harvesting in East Java. In this study, 100 g of rice husk produced approximately 7–10 g silica, depending on the extraction conditions. The characterization tests indicated that the silica content in the rice husk ranged from 90% to 98% [29]. This is comparable to previous studies reporting silica synthesis from palm oil mill slag, which achieved a high silica content of 85.68% [30]. X-ray diffraction (XRD) (Bruker D2 Phaser, Germany) analysis was performed to investigate the crystalline structure of the synthesized silica, providing detailed insights into the materials phase composition and crystallinity, as illustrated in Fig. 2.

In this study, the zeolite sample exhibits relatively low crystallinity, which is typical for porous materials with fine particle size. The zeolite is formed through the reaction of several precursor compounds that result in a solid structure composed primarily of aluminum, silicon, oxygen, and sodium elements. The XRD pattern confirms the presence of these elements within the zeolite framework. When compared to standard patterns reported in previous studies, some differences in peak positions and intensities are observed. These differences may result from several factors during the synthesis process, such as incomplete or uneven mixing and very low concentration of NaOH used (0.2 M), which was insufficient to fully dissolve the silica and form the aluminosilicate gel necessary for Zeolite-A crystallization. To evaluate the effect of catalyst structure
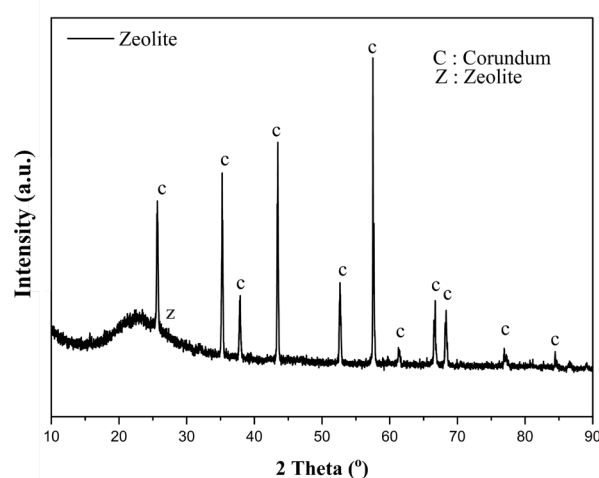

Fig. 2 X-ray diffraction (XRD) pattern of the synthesized Zeolite-A. The sharp diffraction peaks indicate the presence of crystalline phases, while the broad background suggests an amorphous component. Peaks are consistent with typical Zeolite-A structure.

on pyrolysis performance, corundum and Zeolite-A were compared. Corundum, being chemically inert, served as a baseline, showing minimal influence on pyrolysis reactions. In contrast, Zeolite-A, despite its relatively low crystallinity, exhibited a porous structure and active sites that facilitated enhanced cracking and deoxygenation reactions. This led to pyrolysis oil with higher hydrocarbon content, increased density, and modified viscosity compared to inert supports. These results indicate that the improvement in oil quality was primarily due to the structural characteristics and active sites of the zeolite rather than the inert support or reactor surface. Optimizing the synthesis conditions, such as NaOH concentration and precursor mixing, could further enhance the crystallinity and catalytic efficiency, potentially leading to even better fuel properties. A recent study by Gougazeh and Buhl [31] showed that Zeolite-A forms as the dominant phase at low NaOH concentrations (1.5-3.5 M), while higher concentrations (>3.5 M) favor conversion to hydroxysodalite with minor quartz consistently present. Therefore, the relatively low alkalinity applied in this study likely hindered the complete zeolite crystallization, leading to peak variations compared to the reference XRD data. In addition, the limited contact among particles, both in terms of quantity and mixing duration, can affect the consistency of the crystal growth and the development of well-defined phases, leading to variations in the diffraction pattern.

3.2 Effect of catalyst-to-biomass ratios on yield production

The application of catalysts in biomass pyrolysis has been widely reported to influence not only the product composition but also the physical and chemical properties of the resulting pyrolysis oil. In the present study, this trend was also observed, where catalytic pyrolysis using Zeolite-A reduced the overall liquid yield compared to non-catalytic runs. It should be noted that "pyrolysis oil" here refers only to the organic fraction separated from the aqueous phase, not to the total liquid collected. The pyrolysis oil yield was effected by both the pyrolysis temperature and the catalyst-to-biomass ratios, as presented in Fig. 3.

As shown in Fig. 3, the catalytic pyrolysis generally resulted in a reduction of pyrolysis oil yield compared to non-catalytic runs, particularly at higher catalyst loadings. At 300 °C increasing the catalyst-to-biomass ratio from 1:0 to 1:20 resulted in a gradual decrease in pyrolytic oil yield from approximately 30% to 21%, a corresponding increase in char from 35% to 40% and gas yields from 35% to 40%. This trend suggests that an excessive
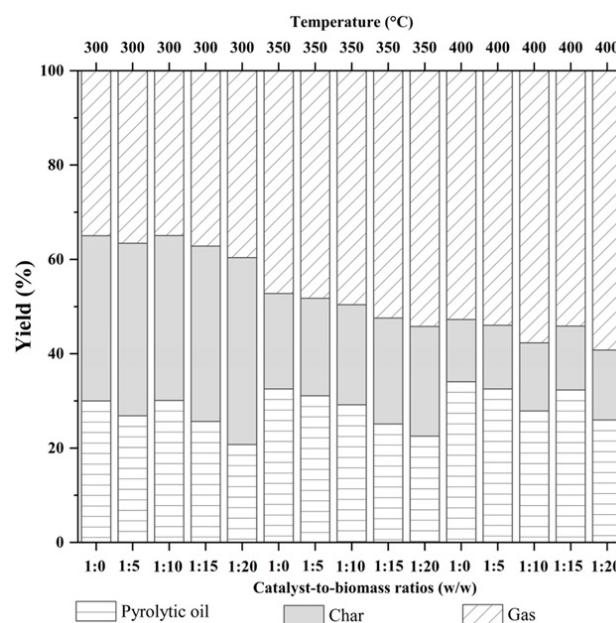

Fig. 3 Effect of catalyst-to-biomass ratio on pyrolysis oil yield at different pyrolysis temperatures (300 °C, 350 °C, and 400 °C) using Zeolite-A catalyst.

catalyst loading at relatively low temperatures promotes the incomplete volatilization of the biomass and enhances solid residue formation due to catalytic condensation and polymerization reactions.

At 350 °C a different behavior was observed. The pyrolysis oil yield decreased moderately from approximately 33% in the non-catalytic experiment to 23% at a catalyst ratio of 1:20, while the biochar yield remained relatively stable within a narrow range from 20% to 23%. In contrast, the gas yield increased markedly from 47% to 54% with increasing catalyst ratio. This indicates that at intermediate temperatures Zeolite-A primarily facilitates secondary cracking and deoxygenation reactions, converting condensable vapors into permanent gases rather than solid char.

At 400 °C the highest pyrolytic oil yield of approximately 34% was achieved under non-catalytic conditions, while the catalytic runs showed a more complex trend. A moderate catalyst ratio 1:5 produced a comparable pyrolytic oil yield about 33% whereas higher catalyst loadings generally favored gas formation. The gas yield increased substantially from 53% at 1:0 to 59% at 1:20 while the char yield remained relatively low from 13% to 15% reflecting enhanced thermal cracking and gasification reactions at elevated temperatures. The slight increase in char at higher catalyst ratios may be attributed to coke formation on the catalyst surface, a common phenomenon in zeolite-catalyzed pyrolysis.

This contrast illustrates that while moderate temperature and lower catalyst ratios enhance pyrolysis

oil production, temperatures beyond the optimal range or high catalyst loading can be detrimental to liquid yield. These observations align with previous studies by Zhang et al. [32] which reported that pyrolysis oil yield increases with temperature until reaching an optimum, after which further heating favors gas formation. Similarly, the synergistic interaction between desulfurization ash and corncob observed in a previous study by An et al. [33] showed a comparable trend, where the pyrolysis oil yield reached a maximum of 30.48 wt% at a ratio of 80:100, representing a 30.9% increase compared to corncob pyrolysis alone [27]. Futuremore, in a recent study Bello et al. [34] also reported that catalytic pyrolysis of corncob using 10% urea at 400 °C increased the pyrolysis oil yield from 49.33% to 54.66% and improved the chemical composition, highlighting the critical influence of both temperature and catalyst concentration on pyrolysis oil production and quality [34].

In this study, the application of Zeolite-A from rice husk exhibited a similar catalytic principle, where moderate catalyst loading and temperature favored pyrolysis oil formation. However, excessive Zeolite-A addition led to decreased liquid yield due to intensified secondary cracking and gasification reactions. Overall, Zeolite-A proved to be an effective catalyst for enhancing pyrolysis oil yield under optimized conditions, confirming its potential for biomass pyrolysis applications.

3.3 Effect of catalyst ratio on density and viscosity

The density and viscosity of pyrolysis oil are important physical properties that determine its flow behavior, storage stability, and compatibility with existing fuel infrastructure. These properties are closely related to the molecular mass distribution and oxygenated compounds present in the pyrolysis oil. In this study, varying catalyst-to-biomass ratios were applied during pyrolysis at different temperatures (300 °C, 350 °C, and 400 °C) to investigate their effects on the resulting pyrolysis oil density and viscosity, as presented in Figs. 4(a) and 4(b).

As shown in Fig. 4(a), the pyrolysis oil density increased with catalyst ratio (w/w) at all pyrolysis temperatures. At 300 °C, the density ranged from 1.28 g/cm^3 (1:0 w/w) to 1.34 g/cm^3 (1:20 w/w). A similar trend was observed at 350 °C, increasing from 1.24 g/cm^3 to 1.33 g/cm^3. At 400 °C, the highest density (1.35 g/cm^3) occurred at 1:15 w/w, highlighting enhanced catalytic effects at elevated temperatures. The increasing density can be attributed to cracking and polymerization reactions promoted by the catalyst, which favor the formation of heavier molecular compounds. These results are quite similar to the findings of Abatyough et al. [35] who reported that the application of zeolite prepared from wastepaper sludge effectively catalyzed the thermal cracking of corncob-derived crude pyrolysis oil. Their study also showed that the upgraded pyrolysis oil exhibited a density of 0.852 g/cm^3 [35]. In this study, the use of Zeolite-A promoted secondary

Fig. 4 (a) Density and (b) viscosity of pyrolysis oil produced at 300 °C, 350 °C, and 400 °C under various catalyst-to-biomass ratios (w/w) of 1:0, 1:5, 1:10, 1:15, and 1:20. The results show that catalyst presence influences the molecular composition of the pyrolysis oil, affecting its density. Higher catalyst ratios generally lead to lower density values, indicating improved fuel characteristics closer to conventional liquid fuels.

reactions that increased the density of pyrolysis oil with increasing catalyst ratio, suggesting similar catalytic behavior in improving the quality and stability of the produced liquid fuel. These reactions promote the formation of heavier molecular compounds in the pyrolysis oil. High-density fuel generally implies higher energy content per unit volume, which is beneficial for energy efficiency. However, excessively high density may hinder fuel atomization and combustion efficiency, as denser fuels are harder to vaporize and may lead to incomplete combustion.

The pyrolysis oil viscosity also depended on both temperature and catalyst ratio (Fig. 4(b)). At 300 °C, viscosity increased from 111.24 mm²/s (1:0 w/w) to 116.00 mm²/s (1:20 w/w). For all catalyst-to-biomass ratios (1:0–1:20 w/w), the viscosity decreased markedly at 350 °C (85.28-88.22 mm²/s) compared to 300 °C (111.24-116.00 mm²/s), indicating extensive thermal cracking of heavier compounds into lighter fractions. At 400 °C, a slight increase in viscosity (93.36-97.09 mm²/s) was observed, attributed to the formation of larger aromatic structures through condensation processes enhanced by higher catalyst loadings. These results indicate that temperature and catalyst ratio jointly control the molecular structure and flow behavior of pyrolysis oil. In this study, pyrolysis oil produced through pyrolysis generally exhibits moderate to high viscosity and a density higher than that of conventional fossil fuels. A previously study by Feng et al. [36] has reported that the biooil from corncob at 500 °C achived viscosity and density of 67 mPa·s and 1.18 g/cm³, respectively. For improved handling and performance, lower viscosity and density are preferred.

However, the inherent chemical composition of pyrolysis oil restricts the extent to which these properties can be reduced without additional treatment [37]. This research trend indicates that moderate catalyst addition enhances molecular cracking and reduces viscosity, thus improving pyrolysis oil fluidity. However, after a certain point, excessive catalyst addition can lead to secondary polymerization of lighter organic molecules on the catalyst, forming heavier, more viscous compounds [38, 39]. This study shows that catalyst addition affects density and viscosity nonlinearly. The moderate point of catalyst addition is at 1:15 or 0.0486 where the balance between cracking and recombination reactions maximizes the desired pyrolysis oil properties. Lower viscosity favors easier pumping and spraying in combustion systems, while the appropriate density enhances energy content per unit mass. These findings indicate that proper control of catalyst ratio and temperature

is crucial to tailoring pyrolysis oil characteristics for practical fuel applications. The results aligned with the previous studies emphasize that catalyst-promoted thermal degradation pathways govern the molecular structure of resulting pyrolysis oils and, consequently, their physical properties.

3.4 Effect of catalyst ratio on calorific value at 400 °C

The calorific value of pyrolysis oil is a key indicator of its energy content and suitability as a fuel. In this study, the pyrolysis oil samples produced at 400 °C under varying catalyst ratios exhibited significant differences in their heating values, as presented in Table 2.

The calorific value of pyrolysis oil reached a maximum of 27769 kJ/kg at a catalyst-to-biomass ratio of 1:15 (w/w), indicating the optimal catalyst loading for energy enhancement. Moderate catalyst concentrations likely promote efficient deoxygenation and cracking, whereas both lower (1:20 w/w) and higher (1:0–1:5 w/w) ratios were less effective, either due to insufficient activation or excessive secondary reactions. This is supported by the results of research conducted by Liu et al. [40] showing that the increase in catalyst concentration affects the decrease in water content and the increase in calorific value of pyrolysis oil. However, in the current study, an overly high catalyst ratio (1:5) did not result in further improvement and instead showed a slight drop in calorific value, indicating an optimal threshold at 1:10. When the catalyst loading is high or the contact time is extended, lighter fragments can experience secondary reactions, leading to the formation of heavier compounds or further gasification. This reduces the proportion of desirable liquid pyrolysis oil, even though the calorific value per kilogram may increase. At the same time, the rise in gas production lowers the overall liquid yield, so although the calorific value of the remaining liquid may be higher, the total energy captured in the liquid fraction decreases, potentially producing more unwanted heavy compounds [41]. Thus, while both studies support the positive role of catalysts in enhancing calorific value, the present findings emphasize the existence of an optimal ratio specific to the feedstock and catalyst used.

Table 2 Heating value of pyrolysis oil at 400 °C

Catalyst-to-biomass ratios (w/w)	Calorific value (kJ/kg)
1:0	27047
1:5	27511
1:10	26775
1:15	27769
1:20	26829

3.5 GC-MS analysis on pyrolysis oil with different catalyst ratio

GC-MS analysis of pyrolysis oil at catalyst-to-biomass ratios of 1:0, 1:5, 1:10, 1:15, and 1:20 (w/w) showed that, all of them have acetic acid, propionic acid, furan and phenol (Fig. 5 and Table 3). GC-MS was used to identify and characterize the individual chemical compounds present in the pyrolysis oil, based on their retention times and mass spectra, rather than to determine a single compound.

Based on the concept, GC-MS separates components based on the volatility of a substance. It can be seen in the table that the real time on acetic acid, propionic acid, furan and phenol have relatively the same value. Table 3 shows sample testing from processes with the same temperature, this is one reason why the components in it are almost the same. Based on these samples there are some differences in the components where at a catalyst-to-biomass ratio of 1:0 (w/w) there is benzene acetamide and
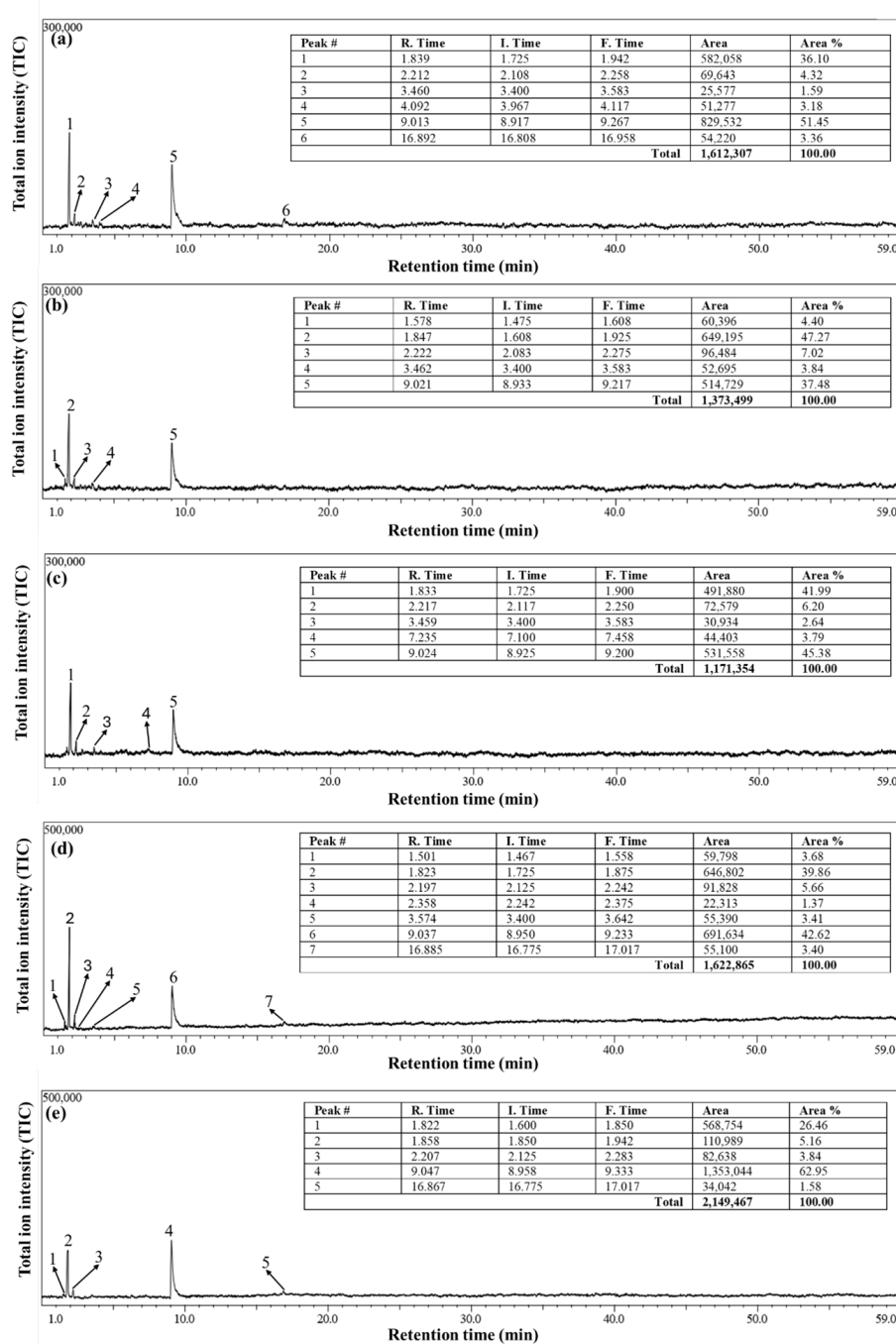

(a)

Peak #	R. Time	I. Time	F. Time	Area	Area %
1	1.839	1.725	1.942	582,058	36.10
2	2.212	2.108	2.258	69,643	4.32
3	3.460	3.400	3.583	25,577	1.59
4	4.092	3.967	4.117	51,277	3.18
5	9.013	8.917	9.267	829,532	51.45
6	16.892	16.808	16.958	54,220	3.36
Total				1,612,307	100.00

(b)

Peak #	R. Time	I. Time	F. Time	Area	Area %
1	1.578	1.475	1.608	60,396	4.40
2	1.847	1.608	1.925	649,195	47.27
3	2.222	2.083	2.275	96,484	7.02
4	3.462	3.400	3.583	52,695	3.84
5	9.021	8.933	9.217	514,729	37.48
Total				1,373,499	100.00

(c)

Peak #	R. Time	I. Time	F. Time	Area	Area %
1	1.833	1.725	1.900	491,880	41.99
2	2.217	2.117	2.250	72,579	6.20
3	3.459	3.400	3.583	30,934	2.64
4	7.235	7.100	7.458	44,403	3.79
5	9.024	8.925	9.200	531,558	45.38
Total				1,171,354	100.00

(d)

Peak #	R. Time	I. Time	F. Time	Area	Area %
1	1.501	1.467	1.558	59,798	3.68
2	1.823	1.725	1.875	646,802	39.86
3	2.197	2.125	2.242	91,828	5.66
4	2.358	2.242	2.375	22,313	1.37
5	3.574	3.400	3.642	55,390	3.41
6	9.037	8.950	9.233	691,634	42.62
7	16.885	16.775	17.017	55,100	3.40
Total				1,622,865	100.00

(e)

Peak #	R. Time	I. Time	F. Time	Area	Area %
1	1.822	1.600	1.850	568,754	26.46
2	1.858	1.850	1.942	110,989	5.16
3	2.207	2.125	2.283	82,638	3.84
4	9.047	8.958	9.333	1,353,044	62.95
5	16.867	16.775	17.017	34,042	1.58
Total				2,149,467	100.00

Fig. 5 GC-MS and relative compositions of pyrolysis oil with catalyst-to-biomass ratio (a) 1:0; (b) 1:5; (c) 1:10; (d) 1:15; and (e) 1:20 w/w

Table 3 Chemical composition of pyrolysis oil at 400 °C with varying catalyst-to-biomass ratios, as identified by GC-MS analysis

Catalyst-to-biomass ratio (w/w)	Peak	Retention time (min)	Percentage (%)	Component	Formula
1:0	1	1.725	36.1	Acetic acid	$C_2H_4O_2$
	2	2.212	4.32	Propanoic acid	$C_3H_6O_2$
	3	3.46	1.59	Furan	C_4H_4O
	4	4.092	3.18	Benzene acetamide	C_8H_9NO
	5	9.013	51.45	Hydroxybenzene	C_6H_6O
	6	16.892	3.36	Phenol	C_6H_6O
1:5	1	1.578	4.4	2-Propanone	C_3H_6O
	2	1.847	47.27	Acetic acid	$C_2H_4O_2$
	3	2.222	7.02	Propanoic acid	$C_3H_6O_2$
	4	3.462	3.84	Furan	C_4H_4O
	5	9.021	37.48	Phenol	C_6H_6O
1:10	1	1.833	41.99	Acetic acid	$C_2H_4O_2$
	2	2.217	6.2	Propanoic acid	$C_3H_6O_2$
	3	3.459	2.64	Furan	C_4H_4O
	4	7.235	3.79	2-Cyclopenten-1-one	C_5H_6O
	5	9.024	45.38	Phenol	C_6H_6O
1:15	1	1.501	3.68	2,5-Cyclooctadien-1-ol	$C_8H_{12}O$
	2	1.823	39.86	Acetic Acid	$C_2H_4O_2$
	3	2.197	5.66	Propanoic acid	$C_3H_6O_2$
	4	2.358	1.37	Androstane	$C_{19}H_{32}$
	5	3.574	3.41	Spiro[4.6]undecane	$C_{11}H_{20}$
	6	9.037	42.62	Phenol	C_6H_6O
	7	16.885	3.4	2-Methoxyphenol (guaiacol)	$C_7H_8O_2$
1:20	1	1.822	26.46	Butanoic acid	$C_4H_8O_2$
	2	1.858	5.16	Hexanoic acid	$C_6H_{12}O_2$
	3	2.283	3.84	Propanoic acid	$C_3H_6O_2$
	4	8.958	62.95	Phenol	C_6H_6O
	5	16.775	1.58	2-Methoxyphenol (guaiacol)	$C_7H_8O_2$

2-methoxyphenol (guaiacol) which is a derivative compound of phenol. At a catalyst-to-biomass ratio 1:20 2-propanone was detected, whereas 2-cyclopenten-1-one was identified at a ratio 1:15. At a ratio 1:10, 2,5-cyclooctadien-1-ol was observed together with two hydrocarbon compounds, namely androstane and spiro[4,6]undecane. In contrast, at a ratio 1:05, hexanoic acid was detected. The sample with a catalyst-to-biomass ratio 1:10 showed the best performance, because hydrocarbons were clearly detected in the product.

The data shows the presence of phenolic groups, which are aromatic compounds containing a hydroxyl group attached to a benzene ring. This sample also contain acids (acetic and formic), as well as aldehydes and ketones, which are oxygenated compounds derived mainly from the thermal decomposition of the cellulose and hemicellulose in the biomass. Aldehydes and ketones have lower heating values than phenolics or hydrocarbons due to their high oxygen content. Oxygen reduces the net energy released during combustion. Due to their strong aromatic bonds, phenolics have high calorific value compared to other oxygenated compounds. Their calorific value exceeds those of most aldehydes, ketones, and organic acids in pyrolysis oil, which generally range from 10–15 MJ/kg. Aromatic phenolics also combust more cleanly and steadily than reactive aldehydes, enhancing effective heat recovery. Additionally, a lower proportion of low-molecular-weight oxygenates reduces incomplete combustion, thereby improving the overall energy efficiency [42].

4 Conclusion

This study demonstrates that rice husk-derived Zeolite-A effectively modulates the properties of corncob pyrolysis oil through catalytic fast pyrolysis. Characterization of the synthesized Zeolite-A confirmed the formation of

a primarily amorphous structure with low crystallinity, typical of fine porous materials, indicating successful utilization of rice husk-derived silica as a catalyst precursor. The overall optimal conditions were identified at 400 °C with a 1:15 w/w catalyst ratio, where pyrolysis oil exhibited a balanced combination of high density (1.35 g/mL), suitable viscosity (97.09 mm^2/s), and enhanced fuel stability. GC-MS analysis confirmed the presence of hydrocarbons such as androstane and spirocyclic compounds, demonstrating effective deoxygenation and fuel stabilization. These results suggest that by carefully adjusting catalyst ratio and pyrolysis temperature, pyrolysis oil characteristics can be tailored for high-quality, energy-efficient fuel production, offering a sustainable strategy for valorizing agricultural residues. Future research should focus on optimizing catalyst types and loading, exploring alternative biomass-derived catalysts, and investigating continuous or scaled-up pyrolysis systems to enhance industrial feasibility. Further studies on fuel performance, emission characteristics, and techno-economic evaluation will provide practical insights for commercial biofuel applications.

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