

## Retraction

# **Retracted: Utilization of Eco-Friendly Waste Eggshell Catalysts for Enhancing Liquid Product Yields through Pyrolysis of Forestry Residues**

#### Journal of Nanomaterials

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This article has been retracted by Hindawi following an investigation undertaken by the publisher [1]. This investigation has uncovered evidence of one or more of the following indicators of systematic manipulation of the publication process:

- 1. Discrepancies in scope
- 2. Discrepancies in the description of the research reported
- 3. Discrepancies between the availability of data and the research described
- 4. Inappropriate citations
- 5. Incoherent, meaningless and/or irrelevant content included in the article
- 6. Peer-review manipulation

The presence of these indicators undermines our confidence in the integrity of the article's content and we cannot, therefore, vouch for its reliability. Please note that this notice is intended solely to alert readers that the content of this article is unreliable. We have not investigated whether authors were aware of or involved in the systematic manipulation of the publication process.

Wiley and Hindawi regrets that the usual quality checks did not identify these issues before publication and have since put additional measures in place to safeguard research integrity.

We wish to credit our own Research Integrity and Research Publishing teams and anonymous and named external researchers and research integrity experts for contributing to this investigation.

The corresponding author, as the representative of all authors, has been given the opportunity to register their agreement or disagreement to this retraction. We have kept a record of any response received.

#### References

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### Research Article

## Utilization of Eco-Friendly Waste Eggshell Catalysts for Enhancing Liquid Product Yields through Pyrolysis of Forestry Residues

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In this study, catalytic and noncatalytic pyrolysis of *Prosopis juliflora* biomass was carried out in a fluidized bed reactor. This study highlights the potential use of forestry residues with waste eggshells under a nitrogen environment. The experiments were conducted to increase the yield of bio-oil by changing the parameters such as pyrolysis temperature, particle size, and catalyst ratio. Under noncatalytic pyrolysis, a maximum bio-oil yield of 40.9 wt% was obtained when the feedstock was pyrolysed at 500°C. During catalytic pyrolysis, the yield of bio-oil was increased by up to 16.95% compared to the noncatalytic process due to the influence of Ca-rich wastes on devolatilization behavior. In particular, the existence of alkali and alkaline-earth metals present in eggshells might have positive effects on the decomposition of biomass material. The bio-oil obtained through catalytic pyrolysis under maximum yield conditions was analyzed for its physical and chemical characterization by Fourier transform infrared (FT-IR) spectroscopy and gas chromatography mass spectroscopy (GC-MS).

#### 1. Introduction

Due to an increased population and industrialization, the energy consumption of developed and developing countries has increased at a quicker rate in recent years [1]. The world's total power demand reached around 1640 billion units in 2020, and it is predicted to double in the year 2050. India's annual biomass availability is projected to be around 500 million tonnes, with 120-150 million tonnes available for power production [2]. Direct combustion of any lignocellulosic biomass material has advantages since its heating value has been identified for a long time, but it is no longer recommended due to the presence of moisture in the samples, which makes it difficult during burning. Among this variety of techniques, pyrolysis is a simple, low-cost, and pollution-free method of extracting biofuel, especially bio-oil. Pyrolysis is the thermal degradation process of any organic materials to produce energy rich biofuel in the absence of air [3]. Pyrolysis oil is the key element of pyrolysis which has properties nearer to diesel [4]. Investigations carried out on pyrolysis oil obtained from different types of materials such as biomass wastes, tyres, and rubber pyrolysis reported that the chemical composition and other properties were similar to diesel fuel. Hence, pyrolysis oil is considered as a potential alternate to diesel used for heating applications [5].

Pyrolysis oil is generally obtained from different raw materials such as plastics, rubber, and coal. Among these, biomass derived bio-oils are considered a good choice as they are renewable, nontoxic, biodegradable, and easily available. According to Bildirici [6], energy extracted from biomass contributes more to the development of the country than any other source of energy. It also contributes to poverty reduction. In addition to that, biomass is carbonneutral and offers many environmental benefits [7]. Among slow pyrolysis, flash pyrolysis is the advanced method to produce maximum bio-oil yield [8]. However, some unsuitable characteristics such as poor volatility, acidity, and lower heating value significantly limit its application to use as a fuel [9]. Bio-oil is generally a combination of diverse classes of oxygenated components that cause its unfavourable properties. So the removal of oxygen is thus required and essential to transform bio-oil into a liquid fuel [10]. In recent years, many studies have concentrated on various pyrolysis techniques, such as microwave, solar, and stepwise pyrolysis [11–13]. Catalytic pyrolysis is the advanced technology that can convert low-quality pyrolysis vapours into high-quality bio-oils. This has the apparent advantages of a streamlined process and avoidance of condensation and reevaporation of obtained bio-oil [14]. The catalyst is intended to promote heavy molecular cracking processes, to yield maximum biooil [15]. In situ and ex situ are the two types of catalytic pyrolysis processes. This process has been extensively studied by various researchers in order to get higher bio-oil with decreased oxygenating elements [16]. During the in situ catalytic process, both feed materials and catalysts are mixed together while solid and vapour phases are upgraded in a reactor. On the other hand, ex situ requires the addition of feedstocks and catalysts separately, to improve the product yields [17]. The quantity and quality of the biofuel are generally affected by various parameters such as biomass type, catalyst type, operating temperature, amount of catalyst, reaction type, and size of the particles [18-20]. Previously, many researchers have performed pyrolysis processes by utilizing acidic zeolite, alumina, metals, bentonite clay, and red mud [21]. The catalyst used for pyrolysis significantly improves the production rate and number of aromatic hydrocarbons. The olive mill solid wastes were previously pyrolyzed by Christoforou et al. [22] with MgO catalyst. The catalytic process improved the production of bio-oil from 43.96 to 47.03 wt% compared to the noncatalytic process. Stefanidis et al. [23] investigated the outcome of ZSM-5 combined with biomass and showed improved biooil quality because of increased surface area of the catalyst. Hernando et al. [24] investigated pyrolysis reaction with h-ZSM-5 with MgO and ZnO as catalysts and found increased bio-oil production. The addition of catalyst in this study showed a higher degree of deoxygenation with reduced char products.

The use of eco-friendly, inexpensive catalysts for the production of biofuel has been under attention in recent years. Eggshells have no commercial value and are discarded as solid waste. In 2018, global egg production reached 76.7 million metric tonnes [25]. China, US, Indonesia, India, and Mexico are the top five egg-producing countries, accounting for over 63% of world total egg production. In India, eggshell waste produced from poultry firm is huge. India has the 2nd largest poultry market in the world with annual growth of 14%. The majority of it is dumped in landfills without being pretreated. They are porous and contain a significant amount of calcium carbonate [26]. The eggshells are more efficient catalysts due to their higher reaction rates. According to Kim et al. [27], eggshell catalyst utilized for pyrolysis process accelerated various reaction processes such as cracking, deoxygenation, decarboxylation, and alkylation. Valizadeh et al. [28] utilized eggshells for catalytic pyrolysis of food wastes to produce clean and high quality gaseous products. This research suggests that a CO2-assisted process over a Ni-eggshell catalyst might be an environmentally beneficial and long-term solution for food waste disposal. Another study conducted by Rohim et al. [29] showed higher bio-oil production through palm kernel pyrolysis with eggshell. The study showed maximum biooil production of 45.67 wt% compared to the noncatalytic process (19.69 wt%).

India is one of the world's top 10 forest-rich countries. Forestry is a significant rural sector and an important environmental resource in India, despite the fact that natural forests cover 21.34% of the country's total land area [30]. Prosopis juliflora is a spiny plant found in semiarid India. The plant produces about 2.5 tonnes of hard wood per hectare, and around 70% of the wood has hemicellulose [31]. In India, the occupancy of the tree is more in southern zone compared to other part of the country. It covers 79.4% invaded in this zone than western zone (46%). The higher hemicellulose fractions in the wood give a positive approach to produce maximum bio-oils. This plant is a nonfood plant, and it does not pose a risk to food security. Furthermore, the plant is suspected of depleting ground aquifers in its growing area, and the government of Tamil Nadu, India, decided to eradicate the plant completely in a particular region of the state. Chandran et al. [32] utilized the hard wood of the tree for high grade biofuel production. The pyrolysis oil produced in this study was characterized by various physical and chemical analysis and showed 6% water. The chemical analysis showed the presence of more than 20 organic elements in the bio-oil. Microwave pyrolysis of Prosopis juliflora for fuel intermediates was carried out by Suriapparao et al. [33]. The study used five different types of susceptors for the maximum bio-oil production. The study yielded 40 wt% of bio-oil by using fly ash as a susceptor. The produced bio-oil showed a maximum energy value of 26 MJ/ kg with a majority of phenolic and aromatic hydrocarbons.

The current study examines the process and quality of the bio-oil acquired from *Prosopis juliflora* through the flash pyrolysis method. There was no study reported on the use of waste eggshell as a catalyst along with the selected wood biomass for the pyrolysis process. The experiments were carried out through noncatalytic and catalytic environments with the addition of eggshell as a catalyst. The experiments were aimed at producing maximum bio-oil from biomass material combined with powdered eggshell as a catalyst by changing reaction temperature, particle size, and biomass to catalyst ratio. In addition to that, the produced bio-oil was characterized by various spectrochemical analysis in order to find its physical and chemical stability.

#### 2. Materials and Methods

2.1. Material Preparation. Wood samples were collected from a village near Coimbatore, India. Initially, the wood pieces had a moisture content of up to 30%. A chopping machine was utilized to cut the wood into small pieces. After that, the wood pieces were ball milled to get four different particle sizes. The sieved feedstocks were dried in sunlight for 15 days. Furthermore, the materials were dried in a furnace for 2 hours at ±90°C in a controlled environment. The proximate and component analysis of the samples were found according to ASTM standards and are listed in Table 1. The material is having higher volatile mater and lower ash content. The higher amount of volatiles in the biomass is favour for the release for more condensable volatiles. During pyrolysis, the higher ash content in the biomass invariably reduces the production as well as the quality of the biofuel. The fixed carbon of the material was computed using the difference. Eggshells used for the catalytic process were collected from a local restaurant. The collected shells were cleaned well with fresh water to remove the dust particles and then dried in a furnace maintained at 100°C. The dried shells were ground to a homogenised size. In a tube furnace, raw eggshells were calcined for 1 hour under a nitrogen atmosphere at 800°C.

2.2. Material Characterization. The analysis of the biomass material and produced pyrolysis oil was done by using an Elementar Vario EL III CHNS analyzer (N2410650, Perkin Elmer Ltd., US). The physical analysis was done with a red-wood viscometer (Swastik Scientific Instruments, MH, India), a Penske Martin closed cup apparatus (Ducom Instruments, India), and a Parr-6772 bomb calorimetric. The FT-IR spectra of the oil sample were recorded with the help of BRUKER Optik GmbH TENSOR-27 (Bruker Corporation) FT-IR spectroscopy. The spectra were recorded in the range of 400–4000 cm<sup>-1</sup>. For this analysis, 1 mg of the samples was mixed with 250 mg of KBr powder to form a pellet. The various chemical elements of bio-oil were analyzed and detected using Thermo GC-TRACE Ultra-5.0, THERMO MS DSQ-II.

2.3. Reactor Setup. A fluidized bed reactor used for this study has diameter of 150 mm and a height of 30 cm, which is operated by keeping the temperature between 350°C and 550°C. The reactor was designed to withstand temperatures of up to 900°C. Generally fluidized bed reactors are well suitable one for pyrolysis process than other type of reactors.

They offer higher efficiency in heat transfer. They are very easy to control and higher gas velocities do not cause any pressure drop. This leads to reduced heat exchange area, simple construction, and lower gas compression costs. Nitrogen was supplied to fluidize the feed material along with the sand particle of 0.5 mm. For all the experiments, the flow rate of the nitrogen was maintained at 1.75 m<sup>3</sup>/hr which is more than the minimum fluidization velocity of the particle. The reactor was heated electrically, and the heat input was controlled by a PID controller. In order to measure the temperature of the reactor, five K-type thermocouples were attached at five different points. The exit of the reactor tube was connected with two cyclone separators and further connected to the condenser. The cooling water circulated to the condenser was maintained at ±5°C. The condensed liquid fractions were collected separately. The char was collected from the cyclone separator. Both the components were weighed using an electronic weighing machine. The weight of the gas components was found by reaming material balance. The following is the formula used for the determination of the desired output products:

Yield of the desired products in wt% = 
$$\frac{\text{Yield of gas or oil or char}}{\text{Amount of biomass}} \times 100.$$
 (1)

2.4. Experimental Scheme. The experimental work for this study was conducted in three different phases. The first two phases of the work were described with a noncatalytic process of biomass material to optimize the operating parameters such as reactor temperature and particle size. The third phase of the work is associated with the effect of eggshell on bio-oil yield. In this phase, the reactor was kept at 500°C and the particle size of 1.0 mm. The readings in this phase were taken by adding eggshell blended with the biomass material at 5, 10, 15, and 20 wt%. The experiments in all these phases were conducted at the heating rate of  $20^{\circ}$ C/min.

#### 3. Results and Discussion

3.1. Thermogravimetric Analysis. The stability of the biomass materials with regard to heat was analyzed from the data acquired from TGA analysis done with the help of TGA701 (LECO Corporation, Michigan, US) thermogravimetric analyzer shown in Figure 1. This analysis can also be used to find the temperature at which pyrolysis can take place. According to this analysis, the breakdown of the biomass material occurred in four different stages. For this analysis, the biomass materials were heated to 600°C at 10°C/ min. In the first zone, the moisture content associated with the biomass was removed from the material between 40°C and 125°C. The second zone of the process was related to the breakdown of hemicellulose between 150°C and 275°C. This process was confirmed with the peak obtained at 275°C. The third zone is the active pyrolysis zone whereas the degradation of hemicelluloses, cellulose, and lignin happen. This process was continued till it reaches to 500°C. The breakdown of hemicellulose and cellulose at this stage is also

Analysis	Parameter	Value in wt%	Standard
	Moisture	5.1	ASTM D3173
D	Volatile matter	69.1	ASTM D3175
Proximate	Fixed carbon <sup>a</sup>	22.7	By difference
	Ash	3.1	ASTM D3174
	С	48.2	ASTM D5373
	Н	5.9	ASTM D5373
	Ν	0.7	ASTM D5373
Ultimate (ash free basis)	S	0.2	ASTM D5373
	O <sup>a</sup>	45.0	By difference
	H/C molar ratio	1.4585	_
	O/C molar ratio	0.7008	_
	Empirical formula	CH <sub>1.458</sub> N <sub>0.012</sub> O <sub>0.7</sub>	_
	Heating value in MJ/kg	17.21	ASTM D240
By difference.			
	100	0	
	80 -	Ê, Î	

TABLE 1: Biomass characterization.



FIGURE 1: TGA and DTG curve of the biomass.

associated with the literature [34, 35]. Due to lower molecular weight, the decomposition of the hemicellulose started more quickly than other components. Here, the decomposition of cellulose began 250°C. Generally, the cellulose in the biomass material started to decompose at 250°C and end around 375°C [36]. The peak of cellulose degradation at 360°C in DTG curve confirmed highly ordered structure of the polymer. The degradation of lignin was stated at 150°C in the fourth zone, but it occurred slowly due to the complex polymeric structure. Lignin is a higher molecular weight component and more thermally stable than hemicellulose and cellulose.

#### 3.2. Pyrolysis Experiment

3.2.1. Effect of Reactor Temperature. Pyrolysis of wood was conducted by changing the reactor temperature as shown in Figure 2. The temperature of pyrolysis has a considerable impact on product yield and properties [37, 38]. The yield of

bio-oil generally reach maximum at the temperatures between 400 and 550°C and then begin to fall with further increment [39, 40]. In this case, the yield of char reached its maximum at 350°C and declined with increased temperature. The production of char is lower at 550°C (30.3 wt%) due to the cracking reaction of the volatile matter. According to Sakhiya et al. [41], thermal cracking is the key factor for the production of light hydrocarbons, resulting in substantial proportions of bio-oil and gas yields. The bio-oil yield increased as the reactor temperature increased from 350 to 500°C, with decreased char and gas products. At 350°C, the bio-oil yield was 27.2 wt%, and at 500°C, it reached to the maximum value of 40.9 wt%. The yield of bio-oil is decreased when the temperature is reached 500°C. The increased bio-oil at 450 C is due to the maximum decomposition of condensable volatile matters. The TGA analysis also confirmed the complete decomposition of the biomass at 500°C with least volatiles remaining. Baghel et al. [35] conducted pyrolysis experiments on Prosopis juliflora and



FIGURE 3: Effect of particle size on pyrolysis yield.

obtained maximum bio-oil at 500°C. The gas yield is steadily improved with increased temperature. The gas yield is changed from 10.7 wt% to 29.4 wt% when the reactor is changed from 350 to 550°C. The increased gas yield can be described by the cracking process and the formation of light hydrocarbons [42].

3.2.2. Effect of Particle Size. Particle size is another factor that influences the yields of biofuels. The yield of pyrolysis oil will be maximum at which the maximum heat transfer and

complete decomposition will occur [43]. Figure 3 depicts the effect of particle size on different biofuel yields. The figure demonstrates that as particle size decreases, liquid yield also decreases. The yield of pyrolysis oil was 36.3 wt% when a 0.5 mm particle was utilized for the experiment. The yield of char increased steadily with increasing particle size. The yield of char was 36.5 wt% at 0.5 mm particle size, and the yield was changed to 42.3 wt% at 1.25 mm. The yield of gas fractions has a tendency to decrease with increasing particle size up to 1.0 mm. The decreased increased pattern of the gas



FIGURE 5: FT-IR analysis of the bio-oil.

yield can be explained by two perspectives. The smaller particles inside the reactor are subjected to maximum heat transfer due to increased surface area. The maximum heat transfer produces light gases and less char [43]. When the particle exceeds 1.0 mm, the residence time of the particle is prolonged, which leads to secondary cracking reactions [44]. With an increased particle size of 1.25 mm, the yield of gas improved from 18.6 wt% to 20.5 wt%. Since the smaller particles produced a maximum gas of 27.2 wt% than the larger particles, it can be concluded that the maximum heat transfer with smaller particles is more pronounced than the secondary cracking reactions.

*3.2.3. Effect of Catalyst.* The effect of eggshell catalysts on the pyrolysis of *Prosopis juliflora* conducted at 500°C is shown in Figure 4. The conversion of biomass into oil increased from 41.3 to 48.3 wt% with the addition of 15% catalyst. With further increase of catalyst, the yield is reduced to 45.2 wt%. The primary aim of using catalysts for the pyrolysis process is to increase the reaction rate at lower temperatures. The

RT/min	Compound name	Molecular formula	Area %
3.41	2-Cyclopenten-1-one	C <sub>5</sub> H <sub>6</sub> O	2.24
3.78	Pyrogallol 1,3-dimethyl ether	$C_8H_{10}O_3$	2.97
4.04	Formic acid	$CH_2O_2$	3.33
6.12	4-Hydroxy-3-methoxy benzaldehyde	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	2.47
9.44	1,2-Cyclopentanedione, 3-methyl	$C_6H_8O_2$	4.04
9.52	Acetic acid	CH <sub>3</sub> COOH	3.11
10.01	Butyrolactone	$C_4H_6O_2$	3.97
12.22	Phenol	C <sub>6</sub> H <sub>5</sub> OH	8.76
14.52	Dibenzo[a,e]cyclooctene	$C_{16}H_{12}$	0.84
14.69	1,4-Dimethoxybenzene	$C_8H_{10}O_2$	2.67
16.87	Butyholachone	$C_4H_8O_4$	4.38
16.91	4-Methyl phenol (p-cresol)	C <sub>7</sub> H <sub>8</sub> O	0.91
18.08	Phenol, 2-methoxy-	$C_7H_8O_2$	12.33
18.83	Phenol, 3,4-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	3.41
20.15	Benzenemethanol, 4-hydroxy	$C_7H_8O_2$	1.72
20.26	9-Octadecenoic acid (Z)-,methyl ester	$C_{19}H_{36}O_{2}$	7.55
20.84	4-Ethyl-2-methoxy phenol	$C_9H_{12}O_2$	2.74
22.51	1-Propyne, 3-iodo-	C <sub>3</sub> H <sub>3</sub> I	1.42
22.89	2-Methoxyphenol	$C_7H_8O_2$	5.11
23.58	Cyclohexanol,3,3,5-trimethyl	C <sub>9</sub> H <sub>18</sub> O	4.12
23.80	Triamcinolone	C <sub>21</sub> H <sub>27</sub> FO <sub>6</sub>	0.95
24.04	9-Octadecenamide	C <sub>18</sub> H <sub>35</sub> NO	1.14
24.15	Phenol, 3-amino	C <sub>6</sub> H <sub>7</sub> NO	5.07
24.58	2H-Pyran, 2-(2 heptadecynyloxy)tetrahydro-	$C_{22}H_{40}O_2$	4.74
24.99	1-Methyl-1,3,3-triphenylindan-2-one	C <sub>28</sub> H <sub>22</sub> O	1.52
25.04	4-(2'-Methyl-3'-butenyl)azulene	$C_{15}H_{16}$	0.21
26.57	Pyridine, 2-propyl-	$C_8H_{11}N$	2.74
26.91	2,4-Methanoproline	$C_6H_9NO_2$	0.62
27.09	Methyl 4-T-butyl-2-furoate	$C_{10}H_{14}O_3$	3.98

TABLE 2: GC-MS analysis of the bio-oil.

yield of bio-oil was higher at 15% addition of catalyst than other percentages due to catalytic contact of the higher vapours produced during the pyrolysis reaction [45]. Considering char and gas yield, both decreased with the addition of the catalyst. The char and gas yields were 40.1 wt% and 18.6 wt% at noncatalytic pyrolysis, respectively. But the yield was decreased to 35.6 wt% and 16.1 wt% with 15% addition of eggshell. In this case, the yield of gas fractions was not affected much due to catalytic reaction. Rohim et al. [19] conducted pyrolysis experiments on palm kernel shells using eggshell catalyst and found maximum bio-oil production of 45.67 wt% by adding 20% catalyst with the biomass. In another study conducted by Ahmad et al. [46] 65.67 wt% of bio-oil was produced by utilizing 20% of eggshell and palm shell under 450°C.

#### 3.3. Characterization

3.3.1. Analysis of Functional Groups. The FT-IR spectra displayed in Figure 5 help to detect the various functional groups of the catalytic pyrolysis oil. The test was carried out on the sample obtained at maximum yield conditions. The existence of broad -OH stretching vibrations indicates the occurrence of phenols and alcohols. The presence of the water components in the oil sample is indicated by the peak that appears at 3200-3600 cm<sup>-1</sup> [47]. The C  $\equiv$  C stretch at 2000-2200 cm<sup>-1</sup> shows the appearance of alkynes. The C-H stretching vibrations of alkenes and aromatics match the peak found at 1650-1750 cm<sup>-1</sup>. The peak obtained at 1400-1600 cm<sup>-1</sup> confirms the presence of mono, polycyclic, and aromatic components. The C-H stretching vibration that appeared at 1350-1450 cm<sup>-1</sup> shows the existence of alkanes. The existence of alcohols and phenols is confirmed by peaks that appear between 800 and 1250 cm<sup>-1</sup> [48].

3.3.2. Composition of Bio-oil. The various chemical components present in the bio-oil derived from the catalytic process were analyzed using GC-MS. Bio-oil is a complex mixture of several elements. Around 30 compounds were identified through mass spectra and are listed in Table 2. The oil has large quantities of acids, phenols, ketones, furfural, and alcohols. Similar components have been found in bio-oil derived from wood chips, pressed oil cake, and red pine [49–51]. Phenols and their constituents are the key elements of bio-oil, which are ascribed to the oxidation of cellulose and lignin [52]. The breakdown of carbohydrates in the biomass material may result in the formation of acids and alkanes. The presence of furfural suggests that it has a possible potential for usage as a biofuel for burners and biomedical applications. The total percentage of phenol and its derivatives is greater than the other components. These components are important industrial feedstock used for the production of plastics and other products. In addition to that, pharmaceutical medications require phenol and its chemical derivatives.

#### 4. Conclusion

In this study, the flash pyrolysis characteristics of Prosopis juliflora biomass with Ca-rich eggshell wastes were investigated. Eggshell waste collected from restaurants can be repurposed as a catalytic material for this study. According to the experimental findings, a maximum of 48.3 wt% biooil was achieved at 500°C, 1.0 mm particle size, with the addition of 15% waste eggshell. The reuse of waste based environmental friendly eggshell components can reduce the risk of microbiological activities and the disposal cost into the environment as well as provide raw materials. Compared to thermal pyrolysis processes, the catalytic pyrolysis improved the bio-oil output by 16.95% due to higher lignin decomposition influenced by the calcium-based catalyst. The addition of eggshell potentially reduces the production costs due to the increased reaction rate. The analysis of bio-oil with FT-IR and GC-MS analysis showed the existence of acids, phenols, ketones, furfural, and alcohols. The chromatographic study showed that the bio-oil can be used as a potential source for industrial chemicals. The current research can be expanded in the future to include blending bio-oil with diesel to make biodiesel and testing its efficiency in IC engines.

#### **Data Availability**

The data used to support the findings of this study are included within the article.

#### **Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this article.

#### References

- K. V. Shivaprasad, R. Rajesh, W. A. Wogasso, B. Nigatu, and F. Addisu, "Usage of hydrogen as a fuel in spark ignition engine," *IOP Conference Series: Materials Science and Engineering*, vol. 376, article 012037, 2018.
- [2] R. Prakash, R. K. Singh, and S. Murugan, "Experimental studies on combustion, performance and emission characteristics of diesel engine using different biodiesel bio oil emulsions," *Journal of the Energy Institute*, vol. 88, no. 1, pp. 64–75, 2015.

- [3] C. S. Dhanalakshmi and P. Madhu, "Recycling of wood bark of Azadirachta indica for bio-oil and chemicals by flash pyrolysis," *Indian Journal of Ecology*, vol. 46, no. 2, pp. 347–353, 2019.
- [4] P. Das and A. Ganesh, "Bio-oil from pyrolysis of cashew nut shell-a near fuel," *Biomass and Bioenergy*, vol. 25, no. 1, pp. 113–117, 2003.
- [5] P. Madhu, M. Sasireka, R. Samikannu et al., "Production and characterization of maximum liquid oil products through individual and copyrolysis of pressed neem oil cake and waste thermocol mixture," *Advances in Polymer Technology*, vol. 2022, 11 pages, 2022.
- [6] M. E. Bildirici, "Economic growth and biomass energy," *Biomass and Bioenergy*, vol. 50, pp. 19–24, 2013.
- [7] F. Abnisa and W. M. A. W. Daud, "A review on co-pyrolysis of biomass: an optional technique to obtain a high- grade pyrolysis oil," *Energy Conversion and Management*, vol. 87, pp. 71– 85, 2014.
- [8] R. O. Arazo, D. A. D. Genuino, M. D. G. de Luna, and S. C. Capareda, "Bio-oil production from dry sewage sludge by fast pyrolysis in an electrically-heated fluidized bed reactor," *Sustainable Environment Research*, vol. 27, no. 1, pp. 7–14, 2017.
- [9] M. Parthasarathy, S. Ramkumar, and J. I. J. R. Lalvani, "Influence of various flow rates of CNG in CI engine with blend of tamanu methyl ether and ethanol," *International Journal of Vehicle Structures & Systems*, vol. 11, no. 2, pp. 144–148, 2019.
- [10] J. I. J. Lalvani, M. Parthasarathy, B. Dhinesh, and K. Annamalai, "Pooled effect of injection pressure and turbulence inducer piston on performance, combustion, and emission characteristics of a DI diesel engine powered with biodiesel blend," *Ecotoxicology and Environmental Safety*, vol. 134, Part 2, pp. 336–343, 2016.
- [11] S. Jiang, X. Hu, X. Shao, Y. Song, D. Xia, and C. Z. Li, "Effects of thermal pretreatment and ex-situ grinding on the pyrolysis of mallee wood cylinders," *Fuel Processing Technology*, vol. 159, pp. 211–221, 2017.
- [12] J. Asomaning, S. Haupt, M. Chae, and D. C. Bressler, "Recent developments in microwave-assisted thermal conversion of biomass for fuels and chemicals," *Renewable and Sustainable Energy Reviews*, vol. 92, pp. 642–657, 2018.
- [13] X. Chen, Q. Che, S. Li et al., "Recent developments in lignocellulosic biomass catalytic fast pyrolysis: strategies for the optimization of bio-oil quality and yield," *Fuel Processing Technology*, vol. 196, article 106180, 2019.
- [14] B. Valle, A. Remiro, N. García-Gómez, A. G. Gayubo, and J. Bilbao, "Recent research progress on bio-oil conversion into bio-fuels and raw chemicals: a review," *Journal of Chemical Technology & Biotechnology*, vol. 94, no. 3, pp. 670–689, 2019.
- [15] A. V. L. N. Sujith, R. Swathi, R. Venkatasubramanian et al., "Integrating nanomaterial and high-performance fuzzy-based machine learning approach for green energy conversion," *Journal of Nanomaterials*, vol. 2022, Article ID 5793978, 2022.
- [16] Y. Wang, A. Akbarzadeh, L. Chong, J. Du, N. Tahir, and M. K. Awasthi, "Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: a review," *Chemosphere*, vol. 297, p. 134181, 2022.
- [17] R. Liu, M. Sarker, M. M. Rahman et al., "Multi-scale complexities of solid acid catalysts in the catalytic fast pyrolysis of biomass for bio-oil production - a review," *Progress in Energy and Combustion Science*, vol. 80, article 100852, 2020.

- [18] C. Vibhakar, R. S. Sabeenian, S. Kaliappan et al., "Production and optimization of energy rich biofuel through co-pyrolysis by utilizing mixed agricultural residues and mixed waste plastics," *Advances in Materials Science and Engineering*, vol. 2022, 9 pages, 2022.
- [19] M. Sharifzadeh, M. Sadeqzadeh, M. Guo et al., "The multiscale challenges of biomass fast pyrolysis and bio-oil upgrading: review of the state of art and future research directions," *Progress in Energy and Combustion Science*, vol. 71, pp. 1–80, 2019.
- [20] D. Raguraman, A. Kumar, S. Prasanna Raj Yadav et al., "Performance and emission characteristics of pyrolysis oil obtained from neem de Oiled cake and waste polystyrene in a compression ignition engine," *Advances in Materials Science and Engineering*, vol. 2021, pp. 1–10, 2021.
- [21] R. Liu, M. M. Rahman, M. Sarker, M. Chai, C. Li, and J. Cai, "A review on the catalytic pyrolysis of biomass for the bio-oil production with ZSM-5: focus on structure," *Fuel Processing Technology*, vol. 199, article 106301, 2020.
- [22] E. A. Christoforou, P. A. Fokaides, S. W. Banks et al., "Comparative study on catalytic and non-catalytic pyrolysis of olive mill solid wastes," *Waste and Biomass Valorization*, vol. 9, no. 2, pp. 301–313, 2018.
- [23] S. D. Stefanidis, K. G. Kalogiannis, E. F. Iliopoulou, A. A. Lappas, and P. A. Pilavachi, "In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor," *Bioresource Technology*, vol. 102, no. 17, pp. 8261–8267, 2011.
- [24] H. Hernando, I. Moreno, J. Fermoso et al., "Biomass catalytic fast pyrolysis over hierarchical ZSM-5 and beta zeolites modified with Mg and Zn oxides," *Biomass Conversion and Biorefinery*, vol. 7, no. 3, pp. 289–304, 2017.
- [25] T. A. Ahmed, L. Wu, M. Younes, and M. Hincke, "Biotechnological applications of eggshell: recent advances," *Frontiers in Bioengineering and Biotechnology*, vol. 9, p. 548, 2021.
- [26] Y. Gao and C. Xu, "Synthesis of dimethyl carbonate over waste eggshell catalyst," *Catalysis Today*, vol. 190, no. 1, pp. 107–111, 2012.
- [27] S. Kim, C. G. Lee, Y. T. Kim, K. H. Kim, and J. Lee, "Effect of Pt catalyst on the condensable hydrocarbon content generated via food waste pyrolysis," *Chemosphere*, vol. 248, article 126043, 2020.
- [28] S. Valizadeh, C. H. Ko, J. Lee et al., "Effect of eggshell- and homo-type Ni/Al<sub>2</sub>O<sub>3</sub> catalysts on the pyrolysis of food waste under CO<sub>2</sub> atmosphere," *Journal of Environmental Management*, vol. 294, article 112959, 2021.
- [29] R. O. H. A. Rohim, R. Ahmad, N. Ibrahim, N. Hamidin, and C. Z. A. Abidin, "Potential of eggshell waste for pyrolysis process," *Advanced Materials Research*, vol. 1087, pp. 77–80, 2015.
- [30] D. K. Davis and P. Robbins, "Ecologies of the colonial present: pathological forestry from the taux de boisement to civilized plantations," *Environment and Planning E: Nature and Space*, vol. 1, no. 4, pp. 447–469, 2018.
- [31] A. Demirbas, "Biofuels securing the planet's future energy needs," *Energy Conversion and Management*, vol. 50, no. 9, pp. 2239–2249, 2009.
- [32] R. Chandran, R. Kaliaperumal, S. Balakrishnan, A. J. Britten, J. MacInnis, and M. Mkandawire, "Characteristics of bio-oil from continuous fast pyrolysis of Prosopis juliflora," *Energy*, vol. 190, article 116387, 2020.

- [33] D. V. Suriapparao, N. Pradeep, and R. Vinu, "Bio-oil production from Prosopisjuliflora via microwave pyrolysis," *Energy* & Fuels, vol. 29, no. 4, pp. 2571–2581, 2015.
- [34] A. Sahoo, S. Kumar, J. Kumar, and T. Bhaskar, "A detailed assessment of pyrolysis kinetics of invasive lignocellulosic biomasses (Prosopisjuliflora and Lantana camara) by thermogravimetric analysis," *Bioresource Technology*, vol. 319, article 124060, 2021.
- [35] P. Baghel, A. K. Sakhiya, and P. Kaushal, "Influence of temperature on slow pyrolysis of Prosopis Juliflora: an experimental and thermodynamic approach," *Renewable Energy*, vol. 185, pp. 538–551, 2022.
- [36] A. Chandrasekaran, S. Subbiah, S. Ramachandran, S. Narayanasamy, P. Bartocci, and F. Fantozzi, "Natural draft-improved carbonization retort system for biocarbon production from Prosopis juliflora biomass," *Energy & Fuels*, vol. 33, no. 11, pp. 11113–11124, 2019.
- [37] P. Madhu, L. Vidhya, S. Vinodha et al., "Co-pyrolysis of Hardwood Combined with Industrial Pressed Oil Cake and Agricultural Residues for Enhanced Bio-Oil Production," *Journal* of Chemistry, vol. 2022, pp. 1–12, 2022.
- [38] P. Madhu, M. M. Matheswaran, and G. Periyanayagi, "Optimization and characterization of bio-oil produced from cotton shell by flash pyrolysis using artificial neural network," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 39, no. 23, pp. 2173–2180, 2017.
- [39] I. Kathir, K. Haribabu, A. Kumar et al., "Utilization of tea industrial waste for low-grade energy recovery: optimization of liquid oil production and its characterization," Advances in Materials Science and Engineering, vol. 2022, 9 pages, 2022.
- [40] Y. K. Park, M. L. Yoo, H. W. Lee et al., "Effects of operation conditions on pyrolysis characteristics of agricultural residues," *Renewable Energy*, vol. 42, pp. 125–130, 2012.
- [41] A. K. Sakhiya, I. Aier, S. Pathak et al., "Copper (II) removal from aqua solution using rice straw derived biochar," *Materials Today: Proceedings*, vol. 43, pp. 740–745, 2021.
- [42] J. Park, Y. Lee, C. Ryu, and Y. K. Park, "Slow pyrolysis of rice straw: analysis of products properties, carbon and energy yields," *Bioresource Technology*, vol. 155, pp. 63–70, 2014.
- [43] L. J. Cui, W. G. Lin, and J. Z. Yao, "Influences of temperature and coal particle size on the flash pyrolysis of coal in a fastentrained bed<sup>1</sup>," *Chemical Research in Chinese Universities*, vol. 22, no. 1, pp. 103–110, 2006.
- [44] S. Luo, B. Xiao, Z. Hu, and S. Liu, "Effect of particle size on pyrolysis of single-component municipal solid waste in fixed bed reactor," *International Journal of Hydrogen Energy*, vol. 35, no. 1, pp. 93–97, 2010.
- [45] B. B. Krishna, R. Singh, and T. Bhaskar, "Effect of catalyst contact on the pyrolysis of wheat straw and wheat husk," *Fuel*, vol. 160, pp. 64–70, 2015.
- [46] R. Ahmad, N. Kasmuri, S. Ramasamy, R. Santiagoo, and N. A. Mahadi, "Catalytic pyrolysis of agricultural waste using waste egg shell," *AIP Conference Proceedings*, vol. 2347, no. 1, article 020013, 2021AIP Publishing LLC.
- [47] E. R. Kenawy, A. A. Ghfar, S. M. Wabaidur et al., "Cetyltrimethylammonium bromide intercalated and branchedpolyhydroxystyrene functionalized montmorillonite clay to sequester cationic dyes," *Journal of Environmental Management*, vol. 219, pp. 285–293, 2018.
- [48] A. Aboulkas, H. Hammani, M. El Achaby, E. Bilal, and A. Barakat, "Valorization of algal waste via pyrolysis in a

fixed-bed reactor: production and characterization of bio-oil and bio-char," *Bioresource Technology*, vol. 243, pp. 400–408, 2017.

- [49] Y. K. Rao, C. S. Dhanalakshmi, D. K. Vairavel et al., "Investigation on forestry wood wastes: pyrolysis and thermal characteristics of Ficus religiosa for energy recovery system," *Advances in Materials Science and Engineering*, vol. 2022, Article ID 3314606, 9 pages, 2022.
- [50] V. Sugumaran, S. Prakash, E. Ramu et al., "Detailed characterization of bio-oil from pyrolysis of non-edible seed-cakes by Fourier transform infrared spectroscopy (FTIR) and gas chromatography mass spectrometry (GC-MS) techniques," *Journal of Chromatography B*, vol. 1058, pp. 47–56, 2017.
- [51] T. Cheng, Y. Han, Y. Zhang, and C. Xu, "Molecular composition of oxygenated compounds in fast pyrolysis bio-oil and its supercritical fluid extracts," *Fuel*, vol. 172, pp. 49–57, 2016.
- [52] R. D. J. Subagyono, Y. Qi, W. R. Jackson, and A. L. Chaffee, "Pyrolysis-G3C/MS analysis of biomass and the bio-oils produced from CO/H<sub>2</sub>O reactions," *Journal of Analytical and Applied Pyrolysis*, vol. 120, pp. 154–164, 2016.