

Research Article

Green Catalytic Pyrolysis: An Eco-Friendly Route for the Production of Fuels and Chemicals by Blending Oil Industry Wastes and Waste Furniture Wood

M. D. Mohan Gift,¹ Savita Verma,² Kalapala Prasad,³ K. Kathiresan,⁴ Rohi Prasad,⁵ T. Logeswaran,⁶ Suresh Ghotekar,⁷ D. V. Thao,⁸ and J. Isaac JoshuaRamesh Lalvani ⁹

¹Department of Mechanical Engineering, Panimalar Engineering College, Chennai, 600123 Tamil Nadu, India

²Department of Applied Sciences, Galgotias College of Engineering and Technology, Greater Noida, 201306 Uttar Pradesh, India

³Department of Mechanical Engineering, University College of Engineering, Kakinada, Jawaharlal Nehru Technological University, Kakinada, Kakinada, 533003 Andhra Pradesh, India

⁴Department of Physics, PSNA College of Engineering and Technology, Dindigul, 624622 Tamil Nadu, India

⁵Department of Mechanical Engineering, Guru Gobind Singh Educational Society's Technical Campus, Chas, 827013 Jharkhand, India

⁶Department of Electrical and Electronics Engineering, Kongu Engineering College, Perundurai, Erode, 638060 Tamil Nadu, India

⁷Department of Chemistry, Smt. Devkiba Mohansinhji Chauhan College of Commerce and Science, University of Mumbai, Dadra and Nagar Haveli (UT), Silvassa 396230, India

⁸Technology and International Cooperation Department, Thai Nguyen University of Agriculture and Forestry, Thai Nguyen, Vietnam

⁹Faculty of Mechanical Engineering, Arba Minch Institute of Technology, Arba Minch University, P.O. Box 21, Arba Minch, Ethiopia

Correspondence should be addressed to J. Isaac JoshuaRamesh Lalvani; isaac.jrl@amu.edu.et

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Lignocellulosic biomass is converted into liquid products through pyrolysis, which can be used as an alternative fuel for heating applications and industrial chemicals. Pyrolysis liquid is a mixture of many oxygenated fractions which deteriorates its burning properties. Through specific bond cleavage reactions like deoxygenation, cracking, and decarbonylation, catalysts in the pyrolysis process can be used to improve the quality of pyrolysis liquid. In this study, biochar produced by carbonization of printed circuit boards was used for catalytic reforming processes to produce energy-rich liquids and chemicals from a mixture of karanja seed oil cake and waste furniture wood. The catalytic process was performed by changing the reactor temperature from 300°C to 700°C at 50°C intervals. The results showed a maximum liquid oil recovery of 53.9 wt% at 500°C. Compared to the noncatalytic reaction, pyrolysis of biomass with biochar recovered 11.59% more liquid. This study demonstrated a viable technique to recover more liquid products and industrial chemicals by employing sustainable catalysts from e-waste. The physical analysis of the liquid showed that the liquid can be used as a fuel for boilers and furnaces. The chemical characterization through gas chromatography-mass spectroscopy (GC-MS) showed the presence of various chemical elements used for medicinal and industrial applications.

1. Introduction

Due to the reduction of fossil fuels, researchers have turned their attention to find possible alternate energy sources such

as wind, solar, and biomass, which have the ability to regenerate themselves. Every year, a huge amount of biomass is generated, which is not used properly. The improper handling of biomass is also causing environmental problems

[1]. A variety of methods can be used to transform waste biomass into more useful energy sources and chemicals. Biomass contributes 10% of the global total energy needs. The total energy potential of the biomass is estimated as 1.08×10^{11} tonnes of oil equivalent [2].

Enormous availability, renewability, CO₂ neutrality, and technical availability are the driving forces for the use of waste biomass materials for producing fuels and chemicals [3]. Heat applied to waste biomass materials under an inert atmosphere can trigger a variety of thermochemical processes. Char, condensable pyrolysis liquid, and noncondensable gases are the three types of products produced in these processes. The condensed pyrolysis liquid may be separated from an aqueous phase which contains the majority of lignin-derived compounds [4]. The feed, process, and its parameters influence the composition and yields of these products. Numerous conversion routes for biomass waste and feedstock have been investigated, and some are currently under growth. The two main categories of conversion processes are thermochemical and biological [5]. Among various conversion methods, pyrolysis is the ultimate one due to carbon neutrality and economic viability. Pyrolysis is inexpensive technology for the conversion of variety of feedstocks. It reduces the emission of greenhouse gases as well as wastes. This process also reduces the risk of waster pollutions. Compared to slow and intermediate pyrolysis, fast pyrolysis is the advanced one which gives more bio-oil yield (70 wt%) with reduced char formation [6]. The production of pyrolysis liquid is varied with respect to the method of pyrolysis and reaction parameters. The production of focused yield can be optimized experimentally by changing process variables. The liquid produced during pyrolysis may be utilized as a fuel or a chemical feedstock. [7]. Many literatures have produced pyrolysis liquid through the fast pyrolysis method and utilized it for various applications. Bridgwater et al. [8] produced bio-oil through a pyrolysis method and utilized it for heating boilers and furnaces. In addition to that, it can be used to operate engines to produce power. The use of pyrolysis liquid for engine operation has received favourable comments since it emits fewer greenhouse gases than fossil fuels [9].

India has around 250 species of plants and trees, which produce oil-bearing seeds. Every seed almost has 30 to 40% oil which is extracted by various processes. Oilseed cakes are the derivatives produced next to the extraction of oils from the seeds. Oil cakes are the potential biomass generally used as a feed for the poultry industry. Every year, a massive amount of deoiled cakes are produced. According to Mohanty et al. [10], 158.7 million tonnes of oil cakes were produced globally between 2020 and 2021, which was more than the production achieved between 2018 and 2019 [11]. The oil cakes are rich in protein and a perfect source for biochemical and thermochemical processes. A variety of oil cakes, especially edible oil cakes, have many advantages to being used as a feedstock for pyrolysis since they cannot be used as a feed material for animals [12]. Gerçel [13] conducted pyrolysis experiments using sunflower oil cake. The authors investigated the impact of sweep gas flow rate and temperature on pyrolysis yields. In this study, 48.69 wt% of

pyrolysis liquid was produced at 550°C with 53% of aliphatic and aromatic subfractions. The chemical elements appeared in the liquid are used as chemical feedstocks for fertilizers and food industries. Pütün et al. [14] carried out slow pyrolysis experiments on soybean cake. At 550°C, the study produced a maximum of 33.78 wt% pyrolysis liquid. In this study, column chromatography was used to characterize the produced pyrolysis liquid. The analysis showed that the pyrolysis liquid has similar properties to transportation fuel. The experiments were conducted at different pyrolysis temperatures and at different heating rates. The pyrolysis liquid in this study had a higher heating value of 36.79 MJ/kg. Karanja seed oil cake is the residue left after karanja seed is crushed for karanja oil. Karanja seed oil cake is widely used as an organic soil input. As part of the bioenergy mission initiative, India is working on the extensive planting of Karanja and Jatropha trees. In 2020, around 0.145 MT of karanja seed cake was produced. These seeds cannot be utilized as live feedstock directly because of their toxicity. Many authors have previously pyrolyzed karanja seeds to produce pyrolysis liquid char and gaseous products [15–17]. Nayan et al. [18] conducted pyrolysis experiment to produce higher energy pyrolysis liquid. The authors produced diesel closed pyrolysis liquid. The chemical analysis of the liquid showed the existence of alkanes, alkenes, ketones, and carboxylic acids which can be used a feed chemical for various industries. Singh et al. [19] conducted thermal cracking experiment on karanja seed oil cake to produce fuel for transportation. The study yielded 65.56 wt% of pyrolysis liquid under optimized process conditions. Due to lower heating value, the pyrolysis liquid was upgraded using a transesterification process and utilized for engine analysis.

Plywood and furniture industries have been growing fast for the last few years. The Indian market is increasing with an annual growth rate of 30%. Recycling waste furniture woods like plywood, particleboard, and medium-density fiberboard benefits the environment. It promotes environmental cleanliness and the preservation of trees. Waste furniture wood contains a variety of adhesives which are used during fabrication [20]. These additives are hazardous to human health when they are burning in the open air [21]. Moreover, furniture woods are covered with wax and paint to resist water and fire, which contains a variety of additives and binders. These woods cannot be used for direct energy recovery since the burning of these woods in an open atmosphere causes severe health issues for all living organisms [22, 23]. Thus, land filling and burning are unfavourable to the environment, a thermochemical pathway such as pyrolysis is considered as a possible way to dispose waste furniture wood [24]. Waste furniture woods are useful as feedstock in pyrolysis due to their higher lignocellulosic content [25]. Thirugnanam et al. [26] carried out a pyrolysis experiments on waste medium-density fiberboard (MDF) with the aim of finding an appropriate recycling method. The findings indicate that pyrolyzing MDF may provide fuels while avoiding the environmental difficulties. Foong et al. [27] utilized pyrolysis as a disposable and recovery method to convert waste furniture boards into valuable chemicals. According to FT-IR analysis, the pyrolysis liquid

produced at a temperature between 250–550°C has more volatile materials. The products obtained through pyrolysis had a higher concentration of phenols, which can be used as additives for various applications.

Catalytic pyrolysis is a potential option which produces more hydrocarbons with greater quality than the conventional route [28]. Dhanalakshmi et al. [29] utilized nanoHZSM-5 zeolite for maximum pyrolysis liquid yield from blended cotton shells and municipal plastic wastes. Compared to conventional pyrolysis, catalytic pyrolysis produced 4.21% more pyrolysis liquid. Use of an ecofriendly catalyst for pyrolysis has been under consideration for recent years. Valizadeh et al. [30] utilized eggshell-type Ni/Al₂O₃ for pyrolysis of food waste. This investigation indicated that the food waste can be disposed of safely using Ni/Al₂O₃ catalyst, which also serves as a clean, reliable source of energy. Kaliappan et al. [31] processed forestry wood through a waste eggshell-catalytic pyrolysis process. The authors produced 16.95% more pyrolysis liquid than a noncatalytic pyrolysis. In another study, Areeprasert and Khaobang [32] used ecofriendly biochar produced from printed circuit boards as a catalyst for liquid production from e-wastes. In the present investigation, mixed biomass wastes of karanja seed oil cake and waste furniture wood were pyrolyzed on a fluidized bed reactor at various temperatures ranging from 300°C to 700°C at 50°C intervals. From the collected literature survey, it can be known that there has been no work published on pyrolysis with the combination of karanja seed oil cake and waste furniture wood. For all the experiments, the particle size, heating rate, and sweep gas flow rate were maintained constant. The pyrolysis product yields were analyzed and characterized using various chromatographic techniques. The analysis was done with the aim of investigating its potential use for fuels and chemicals.

2. Materials and Methods

2.1. Materials. The karanja seed oil cake used for this study was supplied by M/s Srinivasa Oil Industries, Coimbatore, India. The seed oil cake has a particle size of 1 mm to 2 mm. The waste furniture wood was obtained from a local furniture manufacturing unit. The collected wood was initially in solid form with irregular shapes, which was cut into small pieces using a manual cutter. The cut wood materials were also converted into wood particles of a size between 1 mm and 2 mm. The samples were initially dried for 15 days and dried further in an oven for 2 hours before conducting pyrolysis experiments. The biochar catalyst used for this study was derived from printed circuit board. A traditional carbonization process was employed to prepare the biochar. The slow pyrolysis was conducted at 300°C with a longer residence time of 5 hours. For the production of char, a fixed bed reactor was employed. The temperature for the reactor was raised at the rate of 10°C/min.

2.2. Analysis Procedure. The analysis procedure consists of two stages, such as feedstock analysis and product analysis. Proximate and ultimate analyses (N2410650CHNS 2400 Elemental Analyzer) of the sample materials and liquid

samples were conducted by following ASTM standards. The liquid oil obtained through pyrolysis has a mixture of aqueous and organic phases. The aqueous phase from the organic phase was separated by centrifuging the pyrolysis liquid at 2000 rpm. The obtained organic phase was tested to find its physical and chemical nature. The basic physical properties of the liquid were found using a standard viscometer (Neminath Instruments, India), pH meter (Lutronmake, Sunshine Instruments, India), and Pensky-Martens closed-cup (EIE Instruments, India) apparatus. A gas chromatograph with a mass selective detector was used for the identification of different chemical compounds in the liquid sample. The NIST library of mass spectra was used for the identification of the substances in the liquid sample.

2.3. Reactor Facility. The fluidized bed reactor employed for this work has an internal diameter of 50 mm with 1 m height. The cylindrical reactor is fully surrounded by an insulating material. The reactor consists of a biomass feeding system, water cooled condenser, a char collection system, and a liquid collection system. The reactor can be connected with compressed air and nitrogen. Nitrogen is supplied during the pyrolysis experiment since it is inert. The cutoff valve is used to change air and nitrogen. Sand particles of an average size of 0.5 mm are used as a fluidization agent. Initially, air is admitted to get the material to fluidize. Then, the compressed air was cut to supply nitrogen. The nitrogen was admitted through the bottom of the reactor and fluidize along with the sand particles. The reactor is heated with the aid of an electrical heater and controlled with the help of an autotransformer. Once the temperature of the reactor reaches the desired temperature, the cut-out unit stops the current supply. Hence, the temperature of the reactor throughout the experiment was maintained constant. The temperature at five different points can be measured with the aid of thermocouples. An ammeter and voltmeter are used to give proper heat input. The whole setup is provided with an auto cut off unit which helps to keep the temperature constant for the particular run.

2.4. Experimental Procedure. The fast pyrolysis experiments were conducted by varying the temperature from 300°C to 700°C. The feedstocks for the experiments were prepared by blending oil cakes and waste furniture wood dust at 1:1 ratio. The biochar catalyst was also mixed with the raw material for the catalytic pyrolysis process. 20 grams of biochar was mixed with 100 grams of blended material. The nitrogen flow rate was set at 1.25 m³/hr for all experimental runs. The flow rate of the nitrogen is maintained more than the minimum fluidization velocity of 0.11 m³/hr. Once the reactor reaches the desired temperature, the screw feeder starts to feed the blended material along with the catalyst. The gaseous products released from the reactor were condensed to recover the liquid oil products. The condenser is provided with surplus ice water at the temperature of 5°C. Upon heating, the feed materials started to volatilize, and it is admitted through the condenser. The condensed liquid was collected and stored separately. The char products were collected from the reactor and cyclone separator. For every

TABLE 1: Feedstock characteristics.

Material	Proximate analysis (wt%)		Ultimate analysis (ash free basis in wt%)		Calorific value (MJ/kg)	
	Volatiles matter	Fixed carbon	Hydrogen	Nitrogen		Sulphur
Standard	ASTM D3175	ASTM D3173	ASTM D3174	ASTM D5373	ASTM D5373	ASTM D240
Karanja seed oil cake	75.3	13.1	5.30	48.52	—	18.34
Waste furniture wood	68.4	26.3	1.4	52.4	0.08	20.84

%of O = 100% - (C% + H% + N% + S%).

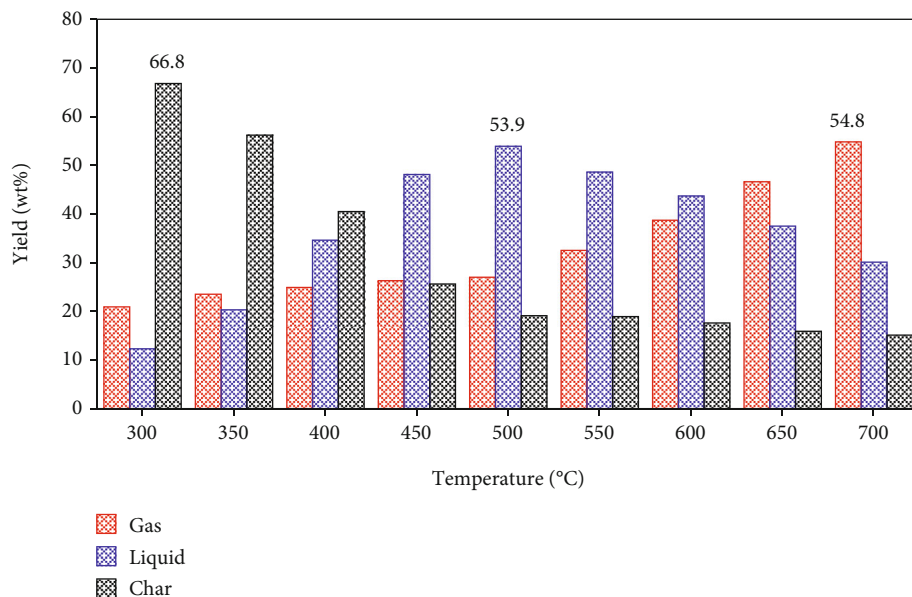


FIGURE 1: Product distribution at different pyrolysis temperature.

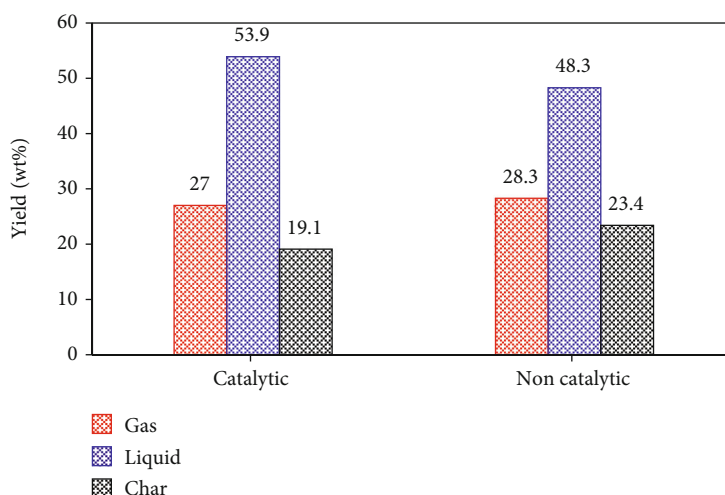


FIGURE 2: Catalytic and noncatalytic process yield.

run, the yield products were measured, and the effect of temperature on product yields was assessed. The mass of char and liquid products was found using a digital weighing machine and the weight of gaseous products was found by material balance. The liquid products obtained at the maximum yield point were collected and analyzed to determine their physical and chemical nature.

3. Results and Discussion

3.1. Feedstock Characterization. Table 1 shows the properties of the feedstock materials. From the table, it can be understood that both materials have a higher percentage of volatile materials, which gives a higher confidence to produce maximum liquid products during pyrolysis. Compared to waste furniture wood, karanja seed oil cake has a higher volatile

TABLE 2: Properties of the fuel.

Items	Pyrolysis liquid	Diesel [39]
Density (kg/m ³)	975	850
Viscosity (cSt)	4.0	3.9
Flash point (°C)	67	57
pH	1.4	0.1
Calorific value in MJ/kg	22.41	43.60

content (75.3 wt%). Higher volatile materials in the materials can be devolatilized easily [33]. The table also gives information about the heating value of the substance. The lower moisture content of both the substances is lower than 10 wt%, which is most suitable for the pyrolysis process [34]. Ash content is the other property that indicates the

TABLE 3: GC-MS analysis of the liquid.

RT/min	Compound	Molecular formula	% Area
2.34	2,3-Dihydro-benzofuran	C ₈ H ₈ O	0.41
2.95	2-Pyridone	C ₅ H ₅	1.92
4.02	3-Pyridinol, 2-Nitro-	C ₅ H ₄ N ₂ O ₃	2.11
5.22	3-Methoxy-1,2-benzenediol	C ₇ H ₈ O ₃	1.09
6.57	n-Methyloctadecanamide	C ₁₉ H ₃₉ NO	2.70
7.55	2-Isopropyl-2,5-dihydrofuran	C ₇ H ₁₂ O	2.04
7.94	Indole	C ₈ H ₇ N	2.11
8.30	Phenol, 2,6-dimethoxy	C ₈ H ₁₀ O ₃	6.94
8.58	Furfural	C ₅ H ₄ O ₂	0.79
9.01	Cyclohexanone	C ₆ H ₁₀ O	1.87
10.22	Ethanone, 1-(2-furanyl)-	C ₈ H ₁₀ O	0.74
11.05	Hydroquinone	C ₆ H ₆ O ₂	1.36
11.67	6,7-Benzo-phenothiazine-5,5-dioxide	C ₁₆ H ₁₁ NO ₂ S	9.03
11.93	Palmitamide	C ₁₆ H ₃₃ NO	4.10
14.37	Acetic acid, mercapto-, methyl ester	C ₃ H ₆ O ₂ S	3.60
14.55	Hexadecanenitrile	C ₁₆ H ₃₁ N	3.83
14.70	Acetone	C ₃ H ₆ O	2.18
14.98	2-Methyl-1-buten-3-yne	C ₅ H ₆	6.44
16.02	3-Furanmethanol	C ₅ H ₆ O ₂	3.13
17.55	Benzene, (1-methylethyl)-	C ₉ H ₁₂	0.91
18.32	Vanillin	C ₈ H ₈ O ₃	3.71
19.78	β -Alanine, N-(2-bromobenzoyl)-, pentyl ester	C ₁₅ H ₂₀ BrNO ₃	2.76
20.03	Phenol, 2-methyl-	CH ₃ C ₆ H ₄	1.45
20.37	2,4-Hexadiyne	C ₆ H ₆	3.70
20.97	Vinylsyringol	C ₁₀ H ₁₂ O	2.52
21.60	Pyridine	C ₅ H ₅ N	1.77
22.83	Oleic acid amide	C ₁₈ H ₃₅ NO	6.43
24.01	Erucylamide	C ₂₂ H ₄₃ NO	1.20
25.39	2,2'-Dioxospirilloxanthin	C ₄₂ H ₅₆ O ₄	0.84
26.08	Phenol, 2-methoxy	C ₇ H ₈ O ₂	1.48
27.91	2,6-Dimethylphenol	C ₈ H ₁₀ O	2.15
28.33	2,3,5-Trimethoxytoluene	C ₁₀ H ₁₄ O ₃	0.85
29.94	Methyl palmitate	C ₁₇ H ₃₄ O ₂	2.70
30.12	Dodecamethylcyclohexasiloxane	C ₁₂ H ₃₆ O ₆ Si ₆	4.55
30.57	<i>trans</i> -Propenylsyringol	C ₁₁ H ₁₄ O ₃	4.14

amount of inorganic waste that remains after combustion. According to the results of the previous studies, the value of ash in the feedstocks should be a minimum [35]. The ash content in waste furniture wood is very low (1.4 wt%) compared to karanja seed oil cake (5.3 wt%). The ash in the feedstock always restricts the production of pyrolysis biofuel and its quality. So, the ash in the feedstock is advised to be minimum. Both the materials have higher carbon content with reduced nitrogen and sulphur content. The lower nitrogen and sulphur are always recommended since they produce lower SO_x and NO_x during pyrolysis. The lower oxygen content compared to other biomass materials produces liquid products with a higher heating value.

3.2. Pyrolysis Product Yield. Figure 1 illustrates the yield of products at different reaction temperatures. For this analysis, the reactor was set at nine different temperatures. Until the reactor reaches 200°C, no liquid oil can be received. Around 250°C, a small amount of liquid oil was obtained. By increasing the temperature of the reactor, the yield of liquid collection is increased. At 200°C, the yield of liquid is very low compared to char and gas products. At this point, a maximum amount of char of 66.8 wt% was obtained. Generally, lower pyrolysis temperatures are favoured for the production of char products [36]. It was discovered that the largest amount of liquid yield (53.9 wt%) came from pyrolysis at 500°C and that increasing the pyrolysis temperature had an

unfavorable effect on the liquid yield. Beyond 500°C, the yield of liquid is decreased gradually with increasing gas fractions. At 500°C, the yield of gas was 27.0 wt% which was increased to 54.8 wt% at 700°C. At 700°C, the production of liquid was only 30.1 wt%. The char yield is continuously decreasing. At 300°C, the maximum of 66.8 wt% char was produced, and it reached 15.1 wt% at 700°C. Despite the fact that a single karanja seed oil cake and waste furniture wood component had a different spectrum of thermal breakdown, the oil cake and furniture wood mixture disintegrated in a significant overlapping step [36]. At lower temperatures, the heat transfer to the center core of the feedstock is very low, leading to incomplete decomposition. The low heat transfer to material increases the formation of char [37]. At higher temperatures, the resistance to heat transfer is very low, which helps to decompose the feedstocks. At higher temperatures, the gas yield was increased due to secondary cracking reactions [38]. Figure 2 displays the comparison between the products obtained through catalytic and noncatalytic process at optimized condition (500°C). Pyrolysis of karanja seed oil cake and waste furniture wood combination without biochar catalyst produced lower liquid yield. At optimized temperature, catalytic pyrolysis yielded 11.59% more liquid. The difference in liquid yield can be explained by the presence of high volatile biochar as a catalyst within the reactor which enhances the production of condensable volatiles [32]. The higher pyrolysis liquid during catalytic process represents the effects of synergistic effect. It is considered a beneficial effect during the reaction process.

3.3. Physical Characterization of the Liquid. Table 2 shows various physical properties of the liquid products collected from the catalytic process. The produced liquid oil is more dense and viscous compared to diesel fuel, which may impair the injection within in the engine. By blending the liquid products with commercial diesel, the density and viscosity can be reduced. The flash point is within a reasonable range. The liquid produced from pyrolysis has a heating value that is roughly 50% lower than that of diesel, which means it would not operate engines well. The reduced calorific value of the bio-oil represents the presence of higher oxygen molecules. The presence of oxygen in the pyrolysis liquid not only affects the calorific value but also corrodes the engine or furnace parts while it is used as a fuel.

3.4. Chemical Characterization of the Liquid. A GC-MS analysis was conducted to analyze the existence of various elements in the pyrolysis liquid. Table 3 shows the result of GC analysis. There are several different compounds, but they all have relatively low peak areas. The liquid products contain more than 40 elements, which gives the liquid oil a complex nature. The majority of the elements are used as a feedstock for various chemical and pharmaceutical industries. In the pyrolysis liquid, 6,7-benzo-phenothiazine-5,5-dioxide ($C_{16}H_{11}NO_2S$), oleic acid amide ($C_{18}H_{35}NO$), 2-methyl-1-buten-3-yne (C_5H_6), phenol and 2,6-dimethoxy ($C_8H_{10}O_3$), palmitamide ($C_{16}H_{33}NO$), dodecamethylcyclohexasiloxane ($C_{12}H_{36}O_6Si_6$), and *trans*-propenylysyringol ($C_{11}H_{14}O_3$) were identified as major elements with more

area percentage. From the identified chemical compounds, 2-pyridone is identified with an area percentage of 1.92. It is used as a solvent. Pyridone's tautomerization and use as a ditopic receptor are responsible for its significant impact on the reaction between activated esters and amines in non-polar solvents. *n*-Methyloctadecanamide is another element available with the liquid sample having a molecular weight of 297.5. Indole is an aromatic heterocyclic organic compound available in pyrolysis liquid which is used for many medicinal applications. Against tuberculosis, malaria, and diabetes, indoles and their derivatives can function effectively [40]. Phenol and 2,6-dimethoxy are major elements occupying a significant portion of the pyrolysis liquid. It is a member of phenol with a molecular weight of 134.1. It is a light brown solidified substance with a boiling point of 261°C. It is used as a flavouring agent for food. Another element, palmitamide, present in the pyrolysis liquid, is used as a lubricant and lubricant additive. Hexadecanenitrile showed an area percentage of 3.83, having a molecular weight of 237.4, which is used as an industrial intermediate. Oleic acid amide, which appeared in the liquid sample, is a colourless waxy solid. It is medicinally used for treating sleep disorders. It is used for a variety of industrial applications as a slip agent for lubricants and as a corrosion inhibitor.

4. Conclusion

This study conducted preliminary research on biomass catalytic pyrolysis in order to evaluate the effectiveness of green catalysts for hydrocarbons and chemicals production. A fast pyrolysis experiment on a fluidized bed reactor was carried out on the mixture of karanja seed oil cake and waste furniture wood at a reaction temperature ranging from 300°C to 700°C to determine the effect of temperature on pyrolysis product yield. In this study, the liquid collection was increased and char yield decreased with increased temperature. At higher pyrolysis temperatures, the production of gas was increased due to secondary cracking reactions. A maximum of 53.9 wt% of liquid was collected at 500°C. The catalytic process produced more liquid than the noncatalytic process due to the presence of high volatile biochar as a catalyst inside the reactor. The higher heating value of the pyrolysis liquid showed that the liquid can be used as a medium grade fuel for heating applications. The chemical characterization of the liquid showed the presence of various chemicals used for treating various ailments, additives for lubricants, and flavouring agents for food.

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.

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