

## Research Article

# Production and Characterization of Maximum Liquid Oil Products through Individual and Copyrolysis of Pressed Neem Oil Cake and Waste Thermocol Mixture

P. Madhu <sup>1</sup>, M. Sasireka <sup>2</sup>, Ravi Samikannu <sup>3</sup>, K. Vinoth,<sup>4</sup> A. Udhaya Kumar,<sup>5</sup> Pravin P. Patil,<sup>6</sup> S. Kaliappan <sup>7</sup> and Atkilt Mulu Gebrekidan <sup>8</sup>

<sup>1</sup>Department of Mechanical Engineering, Karpagam College of Engineering, Coimbatore, Tamilnadu, 641032, India

<sup>2</sup>Department of Electronics and Instrumentation Engineering, Kongu Engineering College, Perundurai, Tamilnadu, 638060, India

<sup>3</sup>Department of Electrical Computer and Telecommunications Engineering, Faculty of Engineering and Technology, Botswana International University of Science and Technology, Private Bag-16, Palapye, Botswana

<sup>4</sup>Department of Electrical and Electronics Engineering, Vel Tech Rangarajan Dr. Sagunthala R&D Institute of Science and Technology, Chennai, Tamilnadu, 600062, India

<sup>5</sup>Department of Electrical and Electronics Engineering, M.Kumarasamy College of Engineering, Karur, Tamilnadu, 639113, India

<sup>6</sup>Department of Mechanical Engineering, Graphic Era Deemed to be University, Bell Road, Clement Town Dehradun, Uttarakhand, 248002, India

<sup>7</sup>Department of Mechanical Engineering, Velammal Institute of Technology, Chennai, Tamilnadu, 601204, India

<sup>8</sup>Faculty of Mechanical Engineering, Arba Minch Institute of Technology, Arba Minch University, P.O. Box 21, Arba Minch, Ethiopia

Correspondence should be addressed to Atkilt Mulu Gebrekidan; [atkilt.mulu@amu.edu.et](mailto:atkilt.mulu@amu.edu.et)

Received 16 February 2022; Revised 9 April 2022; Accepted 18 April 2022; Published 5 May 2022

Academic Editor: Quyet Van Le

Copyright © 2022 P. Madhu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, individual and copyrolysis experiments were performed with pressed neem oil cake (NOC) and waste thermocol (WT) to produce high grade liquid oil. The effects of reactor temperature, heating rate, feed ratio, and reaction time on product yields were investigated to identify the optimum parameters for maximum oil yield. The maximum oil yield of 49.3 wt%, 73.4 wt% and 88.5 wt% was obtained from NOC pyrolysis, copyrolysis, and WT pyrolysis under optimized conditions. During copyrolysis, the maximum oil product was obtained under NOC/WT ratio of 1 : 2 and at the temperature of 550°C. The liquid oils obtained from thermal and copyrolysis were subjected to detailed physicochemical analysis. When compared to biomass pyrolysis, the copyrolysis of WT and NOC had a substantial improvement in oil properties. The copyrolysis oil shows higher heating value of 40.3 MJ/kg with reduced water content. In addition to that, the copyrolysis oil obtained under optimized conditions is analyzed with Fourier transform infrared spectroscopy (FT-IR) and Gas chromatography–mass spectrometry (GC-MS) analysis to determine the chemical characterization. The analysis showed the presence of aliphatic and aromatic hydrocarbons in the oil.

## 1. Introduction

The need for energy in developing countries due to population growth leads to a shortage of resources. The necessity of renewable energy sources and efficient technologies for converting renewable sources into alternative fuels has now been recognized by the scientific community [1]. As a result,

solar, hydro, wind, and biomass play an essential role in increasing renewable energy security with reduced pollution. The utilization of low polluting fuels like biomass has attracted more attention nowadays [2]. Furthermore, by 2035, biomass sources have the potential to contribute about 10% of global total energy consumption and biofuels will account for approximately 27% of global transportation fuels

[3]. Biomass is a potential source that is now being used in all energy sectors to replace fossil fuels. Agricultural residues are the kind of biomass from which valuable chemical elements and energy rich fuels can be extorted by various thermochemical conversion processes [4]. Biomass has many advantages, including low sulphur content and zero CO<sub>2</sub> emissions during recycling [5]. Various physical, chemical, and biological conversion processes are used to transform biomass into liquid, solid, and gaseous biofuel [6]. The main reason for biomass utilized for energy recovery is due to its low cost, year round availability, and higher conversion efficiency. Biofuels, in general, make no contribution towards CO<sub>2</sub> accumulation in the atmosphere [7].

Plastics are used for a variety of applications and are growing more popular every year as a result of their various advantages. But recycling and disposal are the two main disadvantages and are challengeable. Disposal and conversion of solid plastic waste are complicated one for most developing countries [8]. Plastics in various forms, such as low density polyethylene, polyethylene terephthalate, polyvinyl chloride, and polystyrene, are mostly produced for single use and accumulate in the world in huge volumes. They are waste commodity plastics becoming more prevalent. They dissolve slowly in the soil and contaminate it. So it should not be disposed of through the land filling method. They are not biodegradable, and it takes more than 400 years to break them down [9]. Currently, less than 9% of total plastic waste is physically recycled, 12% is burned, and the remainder ends up in landfills and the oceans [10]. It is a transparent material, but sometimes colourants can be added to it to make it colourful. It is thermally resistant, light in weight, inexpensive, and strong, making it suitable for a variety of applications. It is generally called polystyrene or thermocol which is recyclable and comes in two different types, such as expanded and solid.

The two possible sources for the production of alternative fuels are biomass and waste polymers. Pyrolysis, hydrolysis, and catalytic cracking are the common techniques used for the conversion of wastes into valuable fuels. Among other thermochemical conversion techniques, pyrolysis is a hopeful option due to its ease of operation and higher oil yield [11]. It is a thermal degradation process of feedstocks in which the biopolymers are broken down at elevated temperature in an oxygen-deficient environment to generate energy rich liquids, charcoal, and gaseous products [12]. Reactor temperature, pretreatment of the raw material, particle size, and heating rate of the reaction had an impact on the yield of the biofuel produced during pyrolysis. At lower temperature (<300°C), higher solids are formed. The breakdown of the existing glycosidic linkages in the polysaccharide structures generates mixes of levoglucosan, anhydrides, and oligosaccharides when the pyrolysis temperature is 300–450°C. Acetaldehyde, glyoxal, and acrolein chemicals are generated when the pyrolysis process is performed at temperatures more than 450°C [13]. Biofuel from biomass can be obtained through catalytic and noncatalytic processes. The components obtained from these processes are a combination of acids, alcohols, and phenols. Hydrocarbon in the oil can be obtained through synergistic effect and thermal cracking of

biomass [14]. According to this study, the oil product obtained through the pyrolysis of palm oil empty fruit bunch can be considered an energy rich alternative fuel. Biofuels produced by biomass pyrolysis have some drawbacks, including higher oxygen content, poor heating value, and corrosive in nature. Pyrolysis of biomass combined with polymer is an efficient way for the production of energy rich synthetic liquid fuel by increasing the feedstock's total H/Ceff [15]. It could adjust carbon, hydrogen, and oxygen content prominent to positive synergistic effects. *Jatropha*, *Mahua*, *Karanja*, *Sorghum*, and *Kusum* are the dedicated energy plants widely available in India for the production of biofuels. These plants are generally grown all over the world. The benefits of pyrolysis of different oil seed cakes have been reported in several studies [16–18]. A huge amount of solid waste is produced every year as pressed oil cake, which is the outcome of the oil industries.

*Azadirachta indica* is a versatile medicinal plant with a broad range of biological activities. It is commonly called as neem tree and is cultivated in every part of the Indian subcontinent. All parts of the tree have been utilized as traditional medicine for household remedies against a variety of human illnesses [19]. The neem seed has a maximum oil content of 40–50% by weight and is primarily used to produce almost 3.5 lakhs tonnes of oil every year [20]. Neem oil is usually used for various medicinal purposes, and part of it is used for the production of biodiesel through various chemical processes. NOC is considered an imperative agro industrial by-product of the oil industry and is available in plenty. The WT utilized in this study is expanded polystyrene, which is widely manufactured across the world and used in a variety of purposes, including packaging, disposable cups, and insulators. However, once recycled, expanded polystyrene foam waste loses its foam qualities. It is feasible to re-gas recovered polystyrene, but this increases the cost of the product compared to virgin material [21]. The majority of WT trash is disposed by land filling, which is not environmentally friendly because WT is not biodegradable [22]. The copyrolysis of biomaterial with polymer is simple, cost-effective, and produces high-quality liquid products [23]. When compared to individual pyrolysis, the copyrolysis process yields more oil due to its synergistic effect [24]. Many researchers have investigated the copyrolysis of many polymeric materials with various biomass [25]. Shadangi and Mohanty [26] used a fixed bed reactor to copyrolyze *Karanja* and *Niger* seeds with thermocol under a 2:1 blending ratio to generate maximum oil with improved heating value. Mohapatra and Singh [27] examined the effects of process parameters and blending ratio on product yield by utilizing sugarcane bagasse and waste thermocol. When compared to biomass pyrolysis oil, the copyrolysis oil has a higher heating value, carbon, and hydrogen content [28].

To the best of the authors' knowledge, no study has been published on the pyrolysis of NOC blended with WT to produce pyrolysis oil. The aim of this study is to explore the pyrolysis technique as an effective and ecologically responsible way to dispose of WT along with NOC by transferring them into value-added compounds. In this study, experiments were conducted under different temperature, heating

rate, and blending ratios to investigate the effects on end products. With the aim of utilizing polymeric materials with biomass for the production of energy rich biofuel, WT pellets were mixed with NOC under different blending ratios. The pyrolysis oil obtained from thermal and copyrolysis was subjected to a detailed physicochemical analysis. In addition to that, a detailed chemical analysis was done on copyrolysis oil to identify the various chemical compounds present in the oil. The results obtained in this study offer a fundamental understanding of WT pyrolysis and present a novel waste reduction and hazard mitigation strategy.

## 2. Materials and Methods

The pressed neem cakes were collected from local oil mills located in Coimbatore, India. In order to remove the traces of oil and moisture, the material was dried in direct sunlight for one week. The WT sheets were collected from a local vendor. Before conducting pyrolysis experiments, NOC were cleaned carefully. After cleaning, they were air dried in the sunlight for a week. The material was further milled in a ball mill to prepare it for further analysis. In order to prepare for proximate and component analyses, the material was dried in an oven maintained at  $\pm 100^\circ\text{C}$  for 45 minutes. The NOC used for pyrolysis was maintained at 0.5 to 1.0 mm. WT used for this study was heated at  $\pm 120^\circ\text{C}$  for 60 min in an oven and then powdered using a hammer mill. NOC and WT granules were stored in airtight polythene containers until they were used for a further study.

**2.1. Characterization.** The proximate analyses of the selected feedstocks were performed in accordance with ASTM standards. The concentrations of carbon, hydrogen, nitrogen, and sulphur were analyzed using an Elementar Vario EL-III analyzer. The difference between the total compositions was used to determine the oxygen concentration of the samples. The heating value of the materials was calculated by Dulong using equations (1) and (2) proposed by Madhu et al. [29].

$$\text{HHV}_{\text{dry}} (\text{MJ/kg}) = \frac{338.2 \times C + 1442.8 \times (H - (O/8))}{1000}, \quad (1)$$

$$\text{LHV}_{\text{dry}} (\text{MJ/kg}) = \text{HHV} - (0.218 \times H). \quad (2)$$

The BRUKER Optik FT-IR spectrometer was employed to identify the functional groups of the oil sample. The spectroscopy collected the spectral with the range of 500–4000 $\text{cm}^{-1}$ . A THERMO GC-TRACE ULTRA VER: 5.0, equipped with a THERMO MS DSQ-II analyzer, was used for the analysis of total chemical elements. The temperature of the column was initially set at  $70^\circ\text{C}$  and then increased to  $300^\circ\text{C}$  at a rate of  $15^\circ\text{C}/\text{min}$ . The spectra in this study were collected at 40–650 $m/z$ .

**2.2. Experimental Setup.** The pyrolysis and copyrolysis experiments were conducted in a stainless steel tubular reactor (L: 15 cm, ID: 10 cm). The reactor was heated electrically and insulated perfectly using mineral wool and Chromel-Alumel. The temperature of the reactor was controlled by

PID a controller and measured with the help of thermocouples fixed at two different points within the reactor. The condenser unit was connected with sufficient ice water maintained at  $5^\circ\text{C}$ . For each run, the reactor was packed with 50 g of feedstock. The evolved gas condensed at the condenser was collected and stored in a borosilicate bottle. In order to separate the oil from the aqueous phase, the collected liquid was centrifuged at 3000 rpm. Figure 1 shows the reactor used for the study.

**2.3. Experimental Procedure.** In this study, three different series of tests were carried out. In the first series, the pyrolysis of NOC was performed to identify the optimum pyrolysis temperature for maximum oil yield by changing the reactor temperature from 350 to  $550^\circ\text{C}$ . The temperature range selected for this analysis was based on the thermal decomposition behavior of NOC obtained through TGA analysis. A maximum weight loss of 75.5% was obtained at temperatures ranging from 350 to  $550^\circ\text{C}$ . The next set of tests deals with determining the effect of heating rate on the pyrolysis yield of the NOC sample by varying the heating rate from 10 to  $40^\circ\text{C}/\text{min}$ . In the third series, the copyrolysis experiments on NOC and WT were performed (1:1 ratio) by keeping the reactor temperature at  $500^\circ\text{C}$  with  $20^\circ\text{C}/\text{min}$  heating rate. The fourth set of readings was taken by varying the blend ratios of NOC:WT as 1:0, 2:1, 1:1, 1:2, and 0:1 at  $550^\circ\text{C}$ . These experiments are also conducted at  $20^\circ\text{C}/\text{min}$  heating rate. To collect the condensable vapours, the condenser was attached to a flask. The amount of char that remained was also found. The material balance method was utilized to determine the weight of noncondensable gas products.

$$\text{Oil yield (wt\%)} = \frac{\text{Amount of oil}}{\text{Total feed}}, \quad (3)$$

$$\text{Char yield (wt\%)} = \frac{\text{Amount of char}}{\text{Total feed}}, \quad (4)$$

$$\text{Gas yield (wt\%)} = 100 - (\text{oil yield} + \text{char yield}). \quad (5)$$

## 3. Results and Discussion

**3.1. Feedstock Characterization.** The results of proximate and component analysis of NOC and WT samples are presented in Table 1. From the analysis, it is evident that the selected material contains a large amount of volatiles, which gives anticipation for the production of higher liquid oil. The total hydrocarbon content for NOC is found to be 56.89 wt% with H/C and O/C ratio of 1.21 and 0.577, respectively. The heating value of the NOC is found to be 17.92 MJ/kg which is nearer to pressed rubber seed oil cake (19.58 MJ/kg) [30], rapeseed oil cake (19.49 MJ/kg) [31], and sesame oil cake (19.78 MJ/kg) [32]. The presence of ash in NOC is found to be lower (5.32 wt%) than *Madhuca Indica* oil cake (14.63 wt%), *Jatropha* oil cake (8.07 wt%), *Pongamia pinnata* oil cake (10.17 wt%) [33] and rubber seed oil cake [30].

**3.2. Thermogravimetric Analysis of NOC and WT.** The results of TGA analysis are shown in Figure 2 which shows the weight loss curves of NOC and WT. The curve shows



FIGURE 1: Reactor setup.

TABLE 1: Feedstock characteristics.

Parameters	NOC	WT
Proximate analysis in wt%		
Volatile matter	78.25	98.18
Fixed carbon	8.91	0.49
Moisture content	7.52	0.24
Ash	5.32	1.09
Ultimate analysis in wt%		
Carbon	51.62	89.2
Hydrogen	5.27	8.82
Nitrogen	3.1	0.01
Oxygen <sup>a</sup>	39.7	1.97
Sulphur	0.31	—
H/C ratio	1.21	1.10
O/C ratio	0.577	0.37
Empirical formula	CH <sub>1.21</sub> N <sub>0.05</sub> O <sub>0.57</sub>	CH <sub>1.10</sub> N <sub>9.79</sub> O <sub>0.03</sub>
Heating value in MJ/kg	17.92	40.49

<sup>a</sup>By difference.

the thermal degradation curves of the feedstock materials heated at 10°C/min. The results reveal that the total breakdown of the biomass takes place primarily in three stages: moisture removal, devolatilization, and char formation. 10% of mass loss occurred at temperatures up to 250°C, which reflects the evaporation of moisture content and low molecular weight components. A considerable portion of NOC (65 wt%) disintegrated in three stages between 250°C and 450°C, owing to predominantly cellulose and hemicellulose decompositions. The conversion of NOC into carbon residue occurs in the last stage at 500°C to 700°C. The decomposition of lignin causes around 15% of the mass loss at this stage. After 500°C, the material exhibits steady straight line degradation, indicating lignin breakdown, and this is referred to as passive pyrolysis. For WT, the structure is not as complicated as biomass. The curve revealed that considerable mass loss was found in a single phase [34]. The figure shows the deterioration of WT begins at 370°C and ends around at 500°C, with considerable weight loss of 96%, which is referred to as active pyrolysis zone. At 700°C, the residual

mass was found to be 2 wt% and the result was verified with other reports [35, 36].

**3.3. Pyrolysis Behavior of NOC.** According to the TGA profile, the active pyrolysis of NOC takes place between 200°C and 550°C. As a result, NOC pyrolysis was conducted at the active pyrolysis temperature of 350°C to 550°C with 50°C temperature interval. Process temperatures and heating rates were investigated for their impact on product yield and quality.

**3.3.1. Influence of Pyrolysis Temperature.** The results for the first series of experiments are given in Figure 3. The tests were conducted on a fixed temperature of 350 to 550°C. By increasing the reactor temperature, the char products decreased but the gas yield increased, indicating that pyrolysis continued faster at a higher temperature. However, the gas yield did not change much until the temperature reached 500°C. At 500°C, the higher oil production of 46.6 wt% was recorded. The TGA curve shown in Figure 2 can be used to explain the declining trend of oil yield with respect to temperature. Around 375°C, the breakdown of hemicelluloses and cellulose is completed, as shown in the TGA curve. The breakdown of lignin is promoted at higher temperature, yielding the majority of char [37]. It is due to the fact that the rate of generation of condensable products by lignin breakdown is slower than the rate of breaking of condensable products into noncondensable gases above 500°C. Hence, the yield of noncondensable gas products reached maximum after 500°C. According to the findings, the oil yield increased from 31.4 wt% to 46.6 wt% when the temperature is increased from 350°C to 500°C. Beyond 500°C, the yield decreased to 42.5 wt%. It is also confirmed with the previous studies [38, 39]. With increasing pyrolysis temperature, a continuous decrement of char yield was recorded. The yield was 46.1 wt% at 350°C and reduced to 25.0 wt% at 550°C. The total time for complete reaction was dropped from 66 minutes at 350°C to 34 minutes at 550°C, showing that higher temperature releases more volatiles in short duration [40].

**3.3.2. Influence of Heating Rate.** The pyrolysis yield of NOC with respect to heating rate is revealed in Figure 4. The results showed a reduction in char from 31.9 wt% to 28.4 wt% when the heating rate was increased from 10 to 40°C/min. However, increasing the heating rate from 10 to 20°C/min increases the oil production from 48.1 to 49.3 wt%. The yield of oil is further reduced with the increase of heating rate from 49.3 wt% (20°C/min) to 45.7 wt% (40°C/min). At higher heating, the yield of gas was high (25.9 wt%) and low at 10°C/min (20.0 wt%). The increased gas yield with a reduction in char at a higher heating rate is the effect of rapid depolymerization of solid components and the production of noncondensable gases during rapid heating [41]. With an increased heating rate, the total time required for a complete reaction was decreased from 51 minutes to 30 minutes. From Figure 4, it is clearly understood that the maximum oil product of 49.3 wt% was obtained from NOC at an optimum process temperature of 500°C and at 20°C/

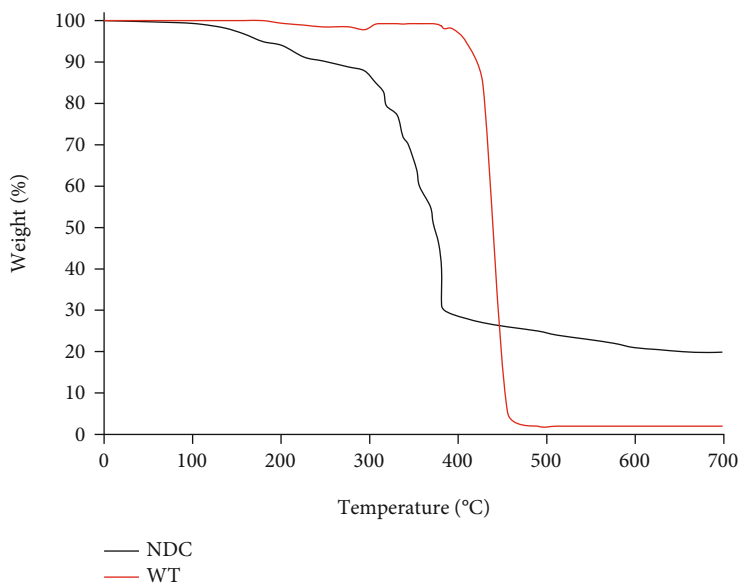


FIGURE 2: TGA thermogram of NOC and WT.

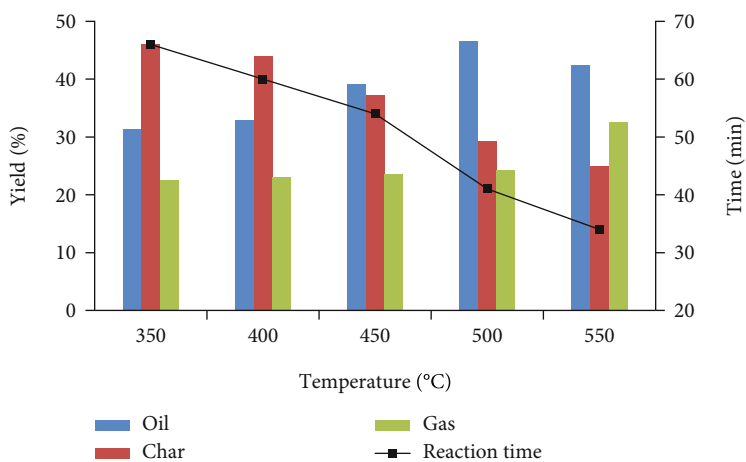


FIGURE 3: Effect of temperature on yields of NOC thermal pyrolysis.

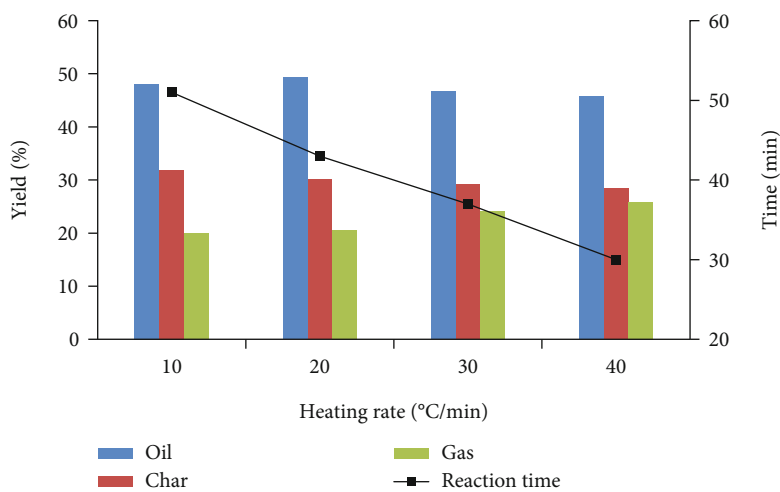


FIGURE 4: Effect of heating rate on yields of NOC thermal pyrolysis.

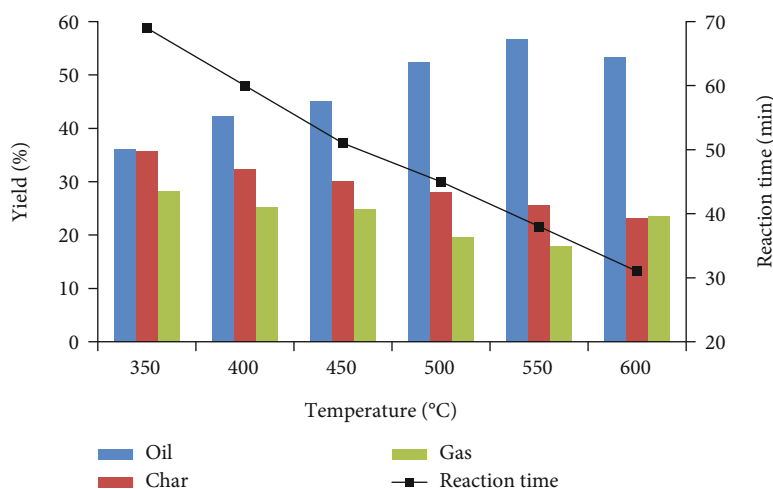


FIGURE 5: Effect of temperature on yields of WT thermal pyrolysis.

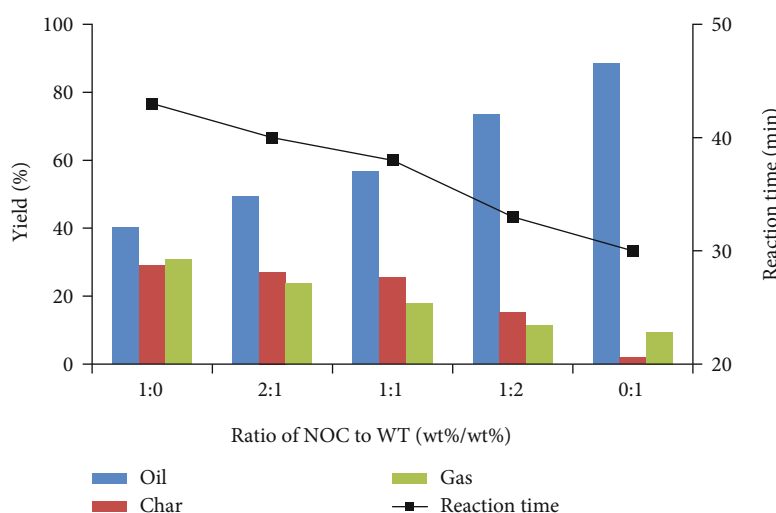


FIGURE 6: Effect of blending ratio on copyrolysis.

min heating rate. Based on the results, the copyrolysis characteristics were conducted by keeping the reactor at fixed temperature under 20°C/min heating rate.

**3.4. Copyrolysis with Waste Thermocol.** In order to find the possible improvements in pyrolysis product yields and properties, copyrolysis of NOC and WT was performed at 1:1 ratio. Figure 5 depicts the influence of reactor temperature on WT pyrolysis. Up to 550°C, there was possible increment in oil yield and decrement in char and gas yield. The char and gas products reduced from 35.7 wt% and 28.2 wt% to 25.6 wt% and 17.8 wt% with increased temperature from 350 to 550°C. The maximum oil production is recorded at a temperature of 550°C. Further increments in temperature reduce oil yield with increased gas fractions. The decrement in oil yield is endorsed by the increment in gas products. The increased oil yield is mostly attributable to the synergistic effect of NOC and WT owing to radical interaction [42]. Several studies have also reported that the highest tempera-

ture for copyrolysis is 550°C [43, 44]. Based on this result, the copyrolysis of NOC and WT was conducted at 550°C by varying the blending ratios of 1:0, 2:1, 1:1, 1:2, and 0:1 at 20°C/min.

**3.5. Effect of Blending Ratio.** Figure 6 shows the effect of addition of WT blend with NOC on the pyrolysis reaction. The copyrolysis experiments were conducted at the optimum conditions mentioned previously. In order to access the production distributions at different blendings, the blending ratio of NOC to WT was changed as: 1:0, 2:1, 1:1, 1:2, and 0:1. The addition of WT with biomass enhanced the yield of oil from 40.2 wt% (1:0 ratio) to 73.4 wt% (1:2 ratio). The gas and char yield from the smaller ratio were found to be 30.8 wt% and 29.0 wt%, respectively. Similar results were reported for sugarcane bagasse, rubber cake, palm shell, and Karanja blending with waste thermocol [26, 27, 29]. The aromatic content in WT attributed to a synergistic effect leads to maximum oil production. Furthermore, it is endorsed for the

TABLE 2: Comparison of oil properties.

Properties	NOC pyrolysis oil	Copyrolysis oil	WT pyrolysis oil	Diesel
Density	1105	1005	995	780 at 15°C
Viscosity at 40°C	13.1	4.28	4.14	13–3.3 at 50°C
Flash point	112	72	69	75
pH	4.2	4.4	4.4	—
Water content (wt%)	21.5	2.0	—	—

TABLE 3: Copyrolysis oil properties obtained at different blending ratios.

Items	Ratio of NOC to WT					Diesel
	1:0	2:1	1:1	1:2	0:1	
C	70.04	74.3	77.3	80	83.5	84-87
H	7.3	7.9	8.2	9.5	10.3	11-15
N	0.62	0.59	0.41	0.34	0.28	0.01-0.03
S	0.03	0.03	0.02	0.01	0	—
O	22.01	17.18	14.07	10.15	5.92	—
H/C	1.241	1.266	1.264	1.414	1.469	—
O/C	0.235	0.173	0.136	0.095	0.053	—
Empirical formula	$\text{CH}_{1.24}\text{N}_{0.007}\text{O}_{0.23}$	$\text{CH}_{1.26}\text{N}_{0.006}\text{O}_{0.17}$	$\text{CH}_{1.26}\text{N}_{0.004}\text{O}_{0.013}$	$\text{CH}_{1.41}\text{N}_{0.003}\text{O}_{0.09}$	$\text{CH}_{1.46}\text{N}_{0.002}\text{O}_{0.053}$	—
Heating value in MJ/kg	30.4	37.6	38.3	40.3	42.0	45-46

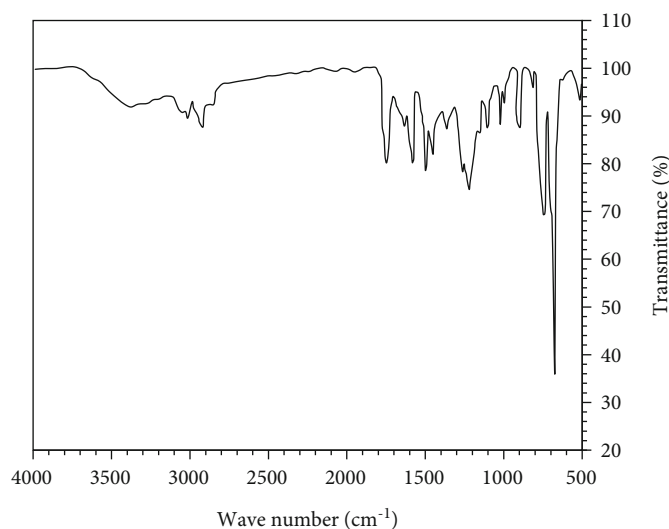


FIGURE 7: FT-IR analysis of copyrolysis oil.

transfer of hydrogen molecules from WT to biomass to produce maximum oil products [45]. From Figure 6, it is clearly visible that the maximum oil product of 73.4 wt% was obtained at 1:2 blend ratio and 88.5 wt% of oil was obtained from the thermal pyrolysis of WT.

### 3.6. Characterization Study

**3.6.1. Physical Properties.** The properties of individual and copyrolysis liquid oil acquired from NOC and WT (1:2 ratio) are displayed in Table 2. The results showed had better characteristics on copyrolysis oil than NOC thermal oil. Bio-

mass derived liquid oil contains water contents, but the copyrolysis oil was water-free. This indicates that the copyrolysis process showed improved water and soluble chemical separation from the oil/organic phase. The viscosity was decreased to 4.28 cSt, and the value is proportional to the addition of WT. There is no major difference on pH value recorded for both oil. The density of the copyrolysis oil related to the spray pattern was found to be reduced to 1005 kg/m<sup>3</sup>.

The heating values of raw NOC oil, WT oil, and copyrolysis oil were compared with diesel and reported in Table 3. The copyrolysis oils obtained under all blending ratios have

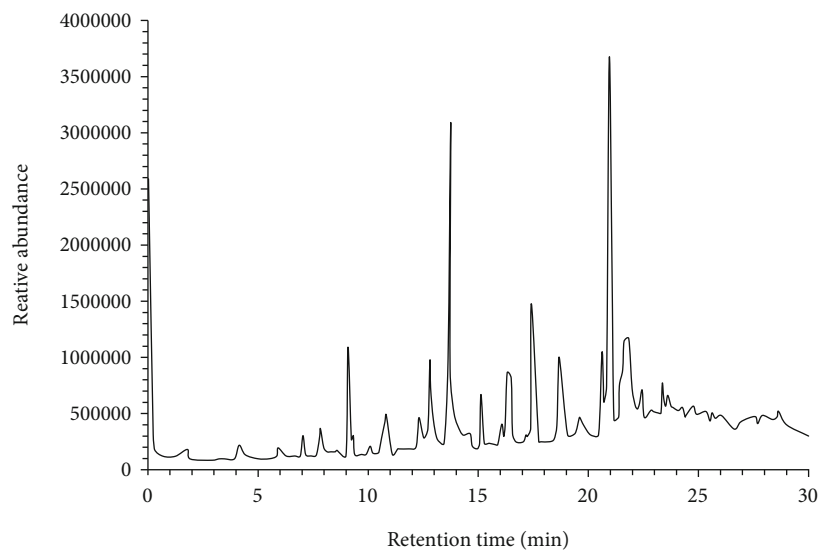


FIGURE 8: GC-MS spectrometry chromatograms of the copyrolysis oil.

TABLE 4: GC-MS analysis of the copyrolysis oil.

RT/min	Name of the compound	Molecular formula	Molecular weight	Area %
3.79	Pyridine	C <sub>5</sub> H <sub>5</sub> N	79	1.43
7.04	Phenol, 2,4-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	122	1.92
9.08	Hentriacontane	C <sub>31</sub> H <sub>64</sub>	436	1.33
10.76	Benzene,1,4,9-decatrienyl-	C <sub>16</sub> H <sub>20</sub>	212	0.76
12.80	Toluene	C <sub>7</sub> H <sub>8</sub>	92	1.41
12.83	Benzene, (1-methylethyl)-	C <sub>9</sub> H <sub>12</sub>	120	5.28
13.75	2,4-Hexadiyne	C <sub>6</sub> H <sub>6</sub>	78	13.44
13.79	Acetonitrile, (m-phenoxyphenyl)-	C <sub>14</sub> H <sub>11</sub> NO	209	6.22
16.31	Cis-1-chloro-9-octadecene	C <sub>18</sub> H <sub>35</sub> Cl	286	0.53
17.41	1-Propene, 2-(2-methylphenyl)-1- phenyl-, (z)	C <sub>10</sub> H <sub>12</sub>	208	14.51
17.93	1,2-Diphenylcyclopropane	C <sub>15</sub> H <sub>14</sub>	194	2.02
18.63	Benzene, (2-methoxy-2-propenyl)-	C <sub>10</sub> H <sub>12</sub> O	148	0.33
18.91	4-Methyl-1,2-benzenediol	C <sub>7</sub> H <sub>8</sub> O	196	2.2
19.06	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	C <sub>6</sub> H <sub>8</sub> O	248	0.18
20.61	Furfural	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	96	10.82
20.70	cis-3-Methyl-3-hexene	C <sub>7</sub> H <sub>14</sub>	210	1.02
20.99	Carbonic acid, ethyl heptadecyl ester	C <sub>27</sub> H <sub>54</sub> O <sub>3</sub>	328	0.11
21.34	Carbamic acid, ethylidenebis-, diethyl ester	C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O	204	4.45
21.40	N-Propyl 9,12-octadecadienoate	C <sub>21</sub> H <sub>38</sub> O <sub>2</sub>	322	4.92
21.55	Benzamide, N,N-dinonyl-4-butyl-	C <sub>16</sub> H <sub>25</sub> NO	428	3.52
21.67	Acetic acid, mercapto-, methyl ester	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> S	106	9.23
21.83	1,4:3,6-Dianhydro- $\alpha$ -d-glucopyranose	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	144	5.54
22.9	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	C <sub>9</sub> H <sub>10</sub> O	194	1.85
23.15	1,2-benzenedicarboxylic acid	C <sub>8</sub> H <sub>6</sub> O	429	1.41
23.92	2-Cyclopenten-1-one, 2-methyl-	C <sub>6</sub> H <sub>8</sub> O	96	2.07
24.20	Phenol, 2-methyl-	C <sub>7</sub> H <sub>8</sub> O	108	1.35
24.72	2-ethylbutanal	C <sub>6</sub> H <sub>12</sub> O	375	1.04
25.06	N-(2-bromobenzoyl)-, pentyl ester	C <sub>15</sub> H <sub>20</sub> BrNO <sub>3</sub>	340	0.54
25.91	4-Undecene, (z)-	C <sub>11</sub> H <sub>22</sub>	154	0.43
28.36	2,2-dimethyl-4-hexen-3-one	C <sub>8</sub> H <sub>14</sub> O	196	0.11



higher heating values than the biomass pyrolysis oil. The value is increased with respect to the increased polymer ratio. The result indicates that the oil produced at a 1:2 blend ratio has a higher heating value than other blends. The heating value of the WT pyrolysis oil (42.0 MJ/kg) is very near to diesel fuel. The increased heating value of the heavy pyrolysis oil was determined by the higher carbon content than the lighter oil [46]. The carbon content of the NOC pyrolysis oil was 70.04% offering a lower heating value of 30.4 MJ/kg whereas the value of carbon content was increased to 83.5% for WT pyrolysis oil, leading to a higher heating value of 42.0 MJ/kg.

**3.6.2. FT-IR Analysis.** The spectrum of copyrolysis oil found in FT-IR analysis is shown in Figure 7. The liquid oil made from the mixture of NOC and WT at 1:2 ratio was found to have the majority of aliphatic hydrocarbons. The presence of alkenes and alkanes in the oil sample was found by the absorption peaks identified between 3100 and 2850  $\text{cm}^{-1}$ . The C=O stretch vibration between 1670 and 1820  $\text{cm}^{-1}$  revealed the occurrence of oxygen, indicating a carbonyl group. The O-H stretch vibration concerning 3600 and 3200  $\text{cm}^{-1}$  and C-O stretching vibration between 1300 and 1000  $\text{cm}^{-1}$  recognized the occurrence of alcohols and esters. C=C stretching, which represents aromatic compounds, was detected between 1600 and 1400  $\text{cm}^{-1}$ . C-H bending vibrations in the range of 900–690  $\text{cm}^{-1}$  indicate the presence of aromatic hydrocarbons or arenes.

**3.6.3. GC-MS Analysis.** The GC-MS analysis of the copyrolysis oil is revealed in Figure 8. The aqueous phase in the tested sample was separated before the analysis, and the solid particles were separated by centrifuging at 3000 rpm for 15 minutes. The organic compounds were identified with respect to increased retention time. The total compounds identified in this study are reported in Table 4. The decreased oxygen content in pyrolysis oil might be related to deoxygenation reactions [47]. The oil contains the majority of aromatic groups of compounds, acids, and esters. Benzene, toluene, styrene, and some low molecular weight hydrocarbons and aromatic compounds were generated through the pyrolysis of oil cake with thermocol wastes [48]. The presence of these compounds is the cause of the increased heating value. At lower temperature (200–280°C) the lignocellulosic content in NOC degrades first to form acidic chemicals such as acetic acid [47]. According to the literature [49–51], phenols and its derivatives appeared in the pyrolysis oil are evidently due to the degradation of lignin in the NOC. According to Foong et al. [52], the lignin in the biomass material is converted into phenolic compounds through dehydration, depolymerization, and decarboxylation. Analysis of copyrolysis oil obtained at 1:2 blend ratio showed lower phenolic compounds than biomass pyrolysis oil [30, 52]. This is due to the addition of polymeric material to the biomass. The low amount of ketone, furan, styrene, and nitrogenated compounds leads to the oil becoming lighter. The copyrolysis process has altered the total composition of oil with increased hydrocarbon and abridged the formation of unfavourable chemical compounds with a higher heating

value [26]. Similar observations are also made from the previously published literature [48, 53]. The findings of this study revealed that when WT was pyrolyzed with NOC the composition of the oil was totally altered.

## 4. Conclusion

Waste thermocol pellets were combined with pressed neem cake at various blending ratios with the aim of utilizing polymeric materials with biomass for the production of energy-dense liquid oil. This study investigated some selected process parameters for producing maximum oil through individual and copyrolysis processes. According to thermogravimetric study, the decomposition of biomass material can be roughly classified into moisture evaporation and active pyrolysis zones. By optimizing the various process parameters, a maximum oil yield of 49.3 wt%, 73.4 wt%, and 88.5 wt% was obtained from individual NOC pyrolysis, copyrolysis, and individual WT pyrolysis. During individual and copyrolysis, the reactor temperature and feed ratio were the leading parameters to determine the oil yield and quality. The heating rate was the least significant factor in this study when determining the product yield. During the copyrolysis process, the maximum oil was acquired with 1:2 (NOC/WT) blending ratio at 550°C under 20°C/min heating rate. The physical characteristics of the oil obtained through the copyrolysis process at optimized conditions showed a higher heating value of 40.3 MJ/kg. The addition of WT to NOC increased the yield of pyrolysis oil from 40.2 to 88.5 wt% and the energy content from 30.4 to 42.0 MJ/kg. The heating values of the copyrolysis oils obtained at all blending ratios are higher than those of the biomass pyrolysis oil. The FT-IR and GC-MS reports of the copyrolysis oil show the presence of majority of aliphatic and aromatic hydrocarbons. Furthermore, this research suggests that copyrolysis might be a significant approach for proper waste management, particularly for the utilization of waste thermocol. Among the different compounds obtained through the copyrolysis process, the presence of maximum hydrocarbons is a valuable component which can be used as industrial chemical feedstock and fuel additives. This technology upgraded the waste-to-energy technologies for utilizing locally available low value biomass materials. To fulfill the need for fuel, further work may be extended to improve the oil yield by utilizing low-cost catalysts.

## 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

- [1] R. A. Felseghi, E. Carcadea, M. S. Raboaca, C. N. Trufin, and C. Filote, "Hydrogen fuel cell technology for the sustainable future of stationary applications," *Energies*, vol. 12, no. 23, p. 4593, 2019.
- [2] Z. Zou, L. Ju, B. Zhou et al., "Progress in microwave pyrolysis conversion of agricultural waste to value-added biofuels: a batch to continuous approach," *Renewable and Sustainable Energy Reviews*, vol. 135, article 110148, 2021.
- [3] C. S. Dhanalakshmi, M. Mathew, and P. Madhu, "Biomass material selection for sustainable environment by the application of multi-objective optimization on the basis of ratio analysis (MOORA)," in *Materials, Design, and Manufacturing for Sustainable Environment*, pp. 345–354, Springer, Singapore, 2021.
- [4] N. H. Nam, V. N. Linh, L. D. Dung, and V. T. T. Ha, "Physico-chemical characterization of forest and agricultural residues for energy conversion processes," *Vietnam Journal of Chemistry*, vol. 58, no. 6, pp. 735–741, 2020.
- [5] Ş. Alayont, D. B. Kayan, H. Durak, E. K. Alayont, and S. Genel, "The role of acidic, alkaline and hydrothermal pretreatment on pyrolysis of wild mustard (*Sinapis arvensis*) on the properties of bio-oil and bio-char," *Bioresource Technology Reports*, vol. 17, article 100980, 2022.
- [6] H. Durak, "Characterization of products obtained from hydrothermal liquefaction of biomass (*Anchusa azurea*) compared to other thermochemical conversion methods," *Biomass Conversion and Biorefinery*, vol. 9, no. 2, pp. 459–470, 2019.
- [7] M. I. Khan, J. H. Shin, and J. D. Kim, "The promising future of microalgae: current status, challenges, and optimization of a sustainable and renewable industry for biofuels, feed, and other products," *Microbial Cell Factories*, vol. 17, no. 1, pp. 1–21, 2018.
- [8] K. R. Vanapalli, B. Samal, B. K. Dubey, and J. Bhattacharya, "Emissions and environmental burdens associated with plastic solid waste management," in *Plastics to Energy*, pp. 313–342, William Andrew Publishing, 2019.
- [9] A. Chamas, H. Moon, J. Zheng et al., "Degradation rates of plastics in the environment," *ACS Sustainable Chemical Engineering*, vol. 8, no. 9, pp. 3494–3511, 2020.
- [10] T. M. Letcher, "Introduction to plastic waste and recycling," in *Plastic Waste and Recycling*, pp. 3–12, Academic Press, 2020.
- [11] 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, Article ID 7852046, 2022.
- [12] H. Durak, "Pyrolysis of *Xanthium strumarium* in a fixed bed reactor: effects of boron catalysts and pyrolysis parameters on product yields and character," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 38, no. 10, pp. 1400–1409, 2016.
- [13] E. Yücedağ and H. Durak, "Bio-oil and bio-char from *Lactuca scariola*: significance of catalyst and temperature for assessing yield and quality of pyrolysis," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 44, no. 1, pp. 1774–1787, 2022.
- [14] S. Sunarno, R. P. Sari, T. Frimacia, S. R. Yenti, P. S. Utama, and E. Saputra, "Catalytic co-pyrolysis of palm oil empty fruit bunch and coal into liquid oil," *International Journal of Renewable Energy Development*, vol. 11, no. 2, pp. 463–469, 2022.
- [15] K. G. Burra and A. K. Gupta, "Kinetics of synergistic effects in co-pyrolysis of biomass with plastic wastes," *Applied Energy*, vol. 220, pp. 408–418, 2018.
- [16] M. Siva Sankari, S. Vivekanandhan, M. Misra, and A. K. Mohanty, "Oil cakes as sustainable agro-industrial feedstock for biocarbon materials," *ChemBioEng Reviews*, vol. 9, no. 1, pp. 21–41, 2022.
- [17] P. Schroeder, B. P. do Nascimento, G. A. Romeiro, M. K. Figueiredo, and M. C. da Cunha Veloso, "Chemical and physical analysis of the liquid fractions from soursop seed cake obtained using slow pyrolysis conditions," *Journal of Analytical and Applied Pyrolysis*, vol. 124, pp. 161–174, 2017.
- [18] A. Mohanty, P. R. Rout, B. Dubey, S. S. Meena, P. Pal, and M. Goel, "A critical review on biogas production from edible and non-edible oil cakes," *Biomass Conversion and Biorefinery*, pp. 1–18, 2021.
- [19] S. C. Kiran, C. Nagarajaiah, K. T. Prasanna, and K. Rajeshkumar, "Studies on bioavailability of nutrients in decomposed crushed seeds, oil cakes and deoiled cakes of neem (*Azadirachta indica* L.)," *Journal of Pharmacognosy and Phytochemistry*, vol. 8, no. 2, pp. 163–165, 2019.
- [20] L. A. M. Syndia, P. N. Prasad, G. Annadurai, R. R. Nair, S. Thilaga, and D. Ganesh, "Characterization of neem seed oil and de-oiled cake for its potentiality as a biofuel and bio-manure," *Int. Res. J. Pharm. Biosci.*, vol. 2, pp. 10–19, 2015.
- [21] I. M. Maafa, "Pyrolysis of polystyrene waste: a review," *Polymers*, vol. 13, no. 2, p. 225, 2021.
- [22] S. S. Bag, A. Bora, and A. K. Golder, "Turning wastes into value-added materials: polystyrene nanocomposites (PS-AgNPs) from waste thermocol and green synthesized silver nanoparticles for water disinfection application," *Polymer Composites*, vol. 42, no. 11, pp. 6094–6105, 2021.
- [23] H. Shafaghat, H. W. Lee, Y. F. Tsang et al., "In-situ\_ and \_ex-situ\_ catalytic pyrolysis/co-pyrolysis of empty fruit bunches using mesostructured aluminosilicate catalysts," *Chemical Engineering Journal*, vol. 366, pp. 330–338, 2019.
- [24] H. Hassan, B. H. Hameed, and J. K. Lim, "Co-pyrolysis of sugarcane bagasse and waste high-density polyethylene: synergistic effect and product distributions," *Energy*, vol. 191, article 116545, 2020.
- [25] Z. Wang, K. G. Burra, T. Lei, and A. K. Gupta, "Co-pyrolysis of waste plastic and solid biomass for synergistic production of biofuels and chemicals-a review," *Progress in Energy and Combustion Science*, vol. 84, article 100899, 2021.
- [26] K. P. Shadangi and K. Mohanty, "Co-pyrolysis of *Karanja* and *Niger* seeds with waste polystyrene to produce liquid fuel," *Fuel*, vol. 153, pp. 492–498, 2015.
- [27] S. S. Mohapatra and R. K. Singh, "Production and characterization of the maximum liquid product obtained from co-pyrolysis of sugarcane bagasse and thermocol waste," *Cellulose*, vol. 28, no. 7, pp. 4223–4239, 2021.
- [28] G. Hu, J. Li, X. Zhang, and Y. Li, "Investigation of waste biomass co-pyrolysis with petroleum sludge using a response surface methodology," *Journal of Environmental Management*, vol. 192, pp. 234–242, 2017.
- [29] P. Madhu, H. Kanagasabapathy, and I. N. Manickam, "Cotton shell utilization as a source of biomass energy for bio-oil by flash pyrolysis on electrically heated fluidized bed reactor,"

- Journal of Material Cycles and Waste Management*, vol. 18, no. 1, pp. 146–155, 2016.
- [30] A. S. Reshad, P. Tiwari, and V. V. Goud, “Thermal and co-pyrolysis of rubber seed cake with waste polystyrene for bio-oil production,” *Journal of Analytical and Applied Pyrolysis*, vol. 139, pp. 333–343, 2019.
- [31] S. Ucar and A. R. Ozkan, “Characterization of products from the pyrolysis of rapeseed oil cake,” *Bioresource Technology*, vol. 99, no. 18, pp. 8771–8776, 2008.
- [32] V. Volli and R. K. Singh, “Production of bio-oil from de-oiled cakes by thermal pyrolysis,” *Fuel*, vol. 96, pp. 579–585, 2012.
- [33] R. Gottipati and S. Mishra, “A kinetic study on pyrolysis and combustion characteristics of oil cakes: effect of cellulose and lignin content,” *Journal of Fuel Chemistry and Technology*, vol. 39, no. 4, pp. 265–270, 2011.
- [34] I. Dubdub and M. Al-Yaari, “Pyrolysis of low density polyethylene: kinetic study using TGA data and ANN prediction,” *Polymers*, vol. 12, no. 4, p. 891, 2020.
- [35] J. Nisar, G. Ali, A. Shah et al., “Fuel production from waste polystyrene via pyrolysis: kinetics and products distribution,” *Waste Management*, vol. 88, pp. 236–247, 2019.
- [36] G. Özsin, A. E. Pütün, and E. Pütün, “Investigating the interactions between lignocellulosic biomass and synthetic polymers during co-pyrolysis by simultaneous thermal and spectroscopic methods,” *Biomass Conversion and Biorefinery*, vol. 9, no. 3, pp. 593–608, 2019.
- [37] C. Sowmya Dhanalakshmi and P. Madhu, “Utilization possibilities of *Albizia amara* as a source of biomass energy for bio-oil in pyrolysis process,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 41, no. 15, pp. 1908–1919, 2019.
- [38] S. Thirugnanam, R. Srinivasan, K. Anand et al., “Utilisation possibilities of waste medium-density fiberboard: a material recycling process,” *Materials Today: Proceedings*, 2021.
- [39] Y. Fan, Y. Xiong, W. Zhao, L. Jin, and Y. Chen, “Process optimization and stability characterization of the bio-oil produced from vacuum pyrolysis of grape straw,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 43, no. 13, pp. 1649–1659, 2021.
- [40] R. Serefontse, W. Ruwona, G. Danha, and E. Muzenda, “A review of the desulphurization methods used for pyrolysis oil,” *Procedia Manufacturing*, vol. 35, pp. 762–768, 2019.
- [41] R. S. Chutia, R. Katak, and T. Bhaskar, “Characterization of liquid and solid product from pyrolysis of *Pongamia glabra* deoiled cake,” *Bioresource Technology*, vol. 165, pp. 336–342, 2014.
- [42] N. I. Izzatie, M. H. Basha, Y. Uemura et al., “Co-Pyrolysis of Rice Straw and Polypropylene Using Fixed-Bed Pyrolyzer,” in *IOP Conference Series: Materials Science and Engineering*, vol. 160, no. 1p. 012033, IOP Publishing, 2016.
- [43] O. Sanahuja-Parejo, A. Veses, M. V. Navarro et al., “Drop-in biofuels from the co-pyrolysis of grape seeds and polystyrene,” *Chemical Engineering Journal*, vol. 377, article 120246, 2019.
- [44] S. Sharma, V. Dutta, and M. Eswaramoorthy, “An experimental investigation on multi-V and protrusion element on absorber plate of solar air heater,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 42, no. 22, pp. 2742–2750, 2020.
- [45] Q. Van Nguyen, Y. S. Choi, S. K. Choi, Y. W. Jeong, and Y. S. Kwon, “Improvement of bio-crude oil properties via co-pyrolysis of pine sawdust and waste polystyrene foam,” *Journal of Environmental Management*, vol. 237, pp. 24–29, 2019.
- [46] H. Durak and S. Genel, “Characterization of bio-oil and bio-char obtained from black cumin seed by hydrothermal liquefaction: investigation of potential as an energy source,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 1-11, pp. 1–11, 2020.
- [47] T. Aysu and H. Durak, “Catalytic pyrolysis of liquorice (*Glycyrrhiza glabra* L.) in a fixed-bed reactor: effects of pyrolysis parameters on product yields and character,” *Journal of Analytical and Applied Pyrolysis*, vol. 111, pp. 156–172, 2015.
- [48] A. Veses, O. Sanahuja-Parejo, M. V. Navarro et al., “From laboratory scale to pilot plant: evaluation of the catalytic co-pyrolysis of grape seeds and polystyrene wastes with CaO,” *Catalysis Today*, vol. 379, pp. 87–95, 2021.
- [49] H. Durak, “Hydrothermal liquefaction of *Glycyrrhiza glabra* L. (Liquorice): effects of catalyst on variety compounds and chromatographic characterization,” *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 42, no. 20, pp. 2471–2484, 2020.
- [50] 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.
- [51] 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, Article ID 8175552, 2022.
- [52] S. Y. Foong, R. K. Liew, C. L. Lee et al., “Strategic hazard mitigation of waste furniture boards via pyrolysis: pyrolysis behavior, mechanisms, and value-added products,” *Journal of Hazardous Materials*, vol. 421, article 126774, 2022.
- [53] M. Sarker and M. M. Rashid, “Waste plastics mixture of polystyrene and polypropylene into light grade fuel using  $\text{Fe}_2\text{O}_3$  catalyst,” *Int. J. Renew. Energy Technol. Res.*, vol. 2, no. 1, pp. 17–28, 2013.