

Pyrolysis of Coconut Cloth in a Microwave Reactor: Effect of Pyrolysis Parameters on Product Yield and Characterization of Liquid Product and Biochar

Qiqi Dai, Jin Li,* Yang Cao, Xiaocui Wei, Hongbiao Tang, and Jingjing Sun

Pyrolysis of coconut cloth was investigated with the influence of pyrolysis process parameters on the maximum products yield and their chemical compositions. With the microwave reactor, the process parameters were as follows: temperature (450 °C to 650 °C), heating rate (10 °C/min to 30 °C/min), and nitrogen flow rate (80 °C/min to 120 cm³/min). The highest liquid yield of 38.3% was observed at 550 °C for the heating rate of 20 °C/min. The characteristics of bio-oil and biochar were analyzed using chromatographic and spectroscopic techniques, such as nuclear magnetic resonance spectroscopy (HNMR), Fourier transformed infrared spectroscopy (FTIR), gas chromatography-mass spectroscopy (GC-MS), scanning electron microscopy-energy dispersive X-Ray (SEM-EDX), X-ray powder diffraction (XRD), and elemental analysis. The bio-oil contained a higher amount of phenolic compounds at 79.6%. The obtained biochar had a calorific value of 27.8 MJ/kg, which made it a promising candidate for solid fuel.

Keywords: Pyrolysis; Coconut cloth; Bio-oil; Biochar; Characterization

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INTRODUCTION

Currently, many fossil fuel energy sources have been developed and utilized, such as oil, natural gas, and coal. Although they can promote rapid economic development, they also bring ecological problems, such as resource depletion and environmental pollution. These problems create the need to find renewable fuels. In this respect, biomass is a renewable energy source that is rich, with low sulfur and nitrogen content and low ash content (Jahirul *et al.* 2012). Because biomass is composed of abundant carbon, there are many applications in energy, such as heating, power supply, and transportation fuels (Riva *et al.* 2019). In these applications, biomass requires a multi-step conversion of raw materials, and thermochemical conversion is an effective way. In thermochemical processes, pyrolysis is receiving more attention than other processes because its conditions can be optimized to produce high energy density pyrolysis oils as well as derived biochars and gases (Demiral and Şensöz 2006). Pyrolysis is generally defined as the conversion of biomass into complex liquid fuels, char, and gases through heating, usually in the absence of oxygen (Garcia-Perez *et al.* 2007). Biomass pyrolysis methods include rapid cracking, direct liquefaction (Feng *et al.* 2016), vacuum pyrolysis (Cai *et al.* 2016), and microwave pyrolysis (Yin 2012). Among them, microwave pyrolysis is a better heating method, and the heat conduction method is volume heating, which is superior to the traditional electric

heating process. Compared with the traditional heating method, microwave heating is fast and has high efficiency, uniformity, easy control, and selective heating, thus improving the yield of bio-oil (Mamaeva *et al.* 2016). The thermal conductivity of the raw material is poor, and the microwave heating method uses a large amount of heating from the inside to the outside, which can achieve the purpose of deep heating so that the heating process of the pyrolysis process is faster and more uniform (Zhang *et al.* 2017). Therefore, microwave pyrolysis can be regarded as a better heating method.

Various biomass materials that can be used for pyrolysis include wood, energy plants, forest residues, aquatic plants, and industrial waste, and these are all considered renewable energy sources (Park *et al.* 2014). Coconut cloth is a high-quality agricultural product in biomass. Coconut cloth belongs to tropical biomass, and the main production in Hainan is rich in coconut resources, with an annual global output of 62.5 million tons. According to the literature survey, only 50% of Hainan's coconut cloth is used, and most of that material is abandoned, resulting in a great waste of resources (Raj and Joy 2015). The study of coconut cloth is rare. Coconut is a tropical biomass agricultural waste in Hainan. It contains higher lignin and obtains higher phenolic liquid fuels. Phenol and phenolic derivatives have important applications in the pharmaceutical, synthetic fiber and perfume industries. This study provides a theoretical basis for the pyrolysis conditions of microwave pyrolysis coconut cloth and lays the foundation for the comprehensive utilization of tropical biomass coconut cloth wastes in Hainan. For the efficient use of biomass resources, a detailed study of other parts of the coconut, such as coconut cloth, was carried out. The coconut cloth is a thick layer of brown fiber, accounting for 33% to 35% of the quality of coconut fruit, and is mainly composed of cellulose, lignin, and hemicellulose. The cellulose composition is a renewable resource with an extremely high yield.

Therefore, coconut cloth was selected as feedstock for bio-oil and biochar production. The aims of this study are to determine the influences of pyrolysis parameters on product yields and characterize the bio-oil product using different spectroscopic and chromatographic methods to evaluate whether it can be used instead of fossil fuels.

EXPERIMENTAL

Materials and Methods

Feedstock preparation and product analysis

The biomass sample (coconut cloth) was collected from Hainan (China). Prior to its use, coconut cloth was dried and ground into smaller granules using a pulverizer. Approximate compositions of coconut cloth and biochars were determined according to ASTM D3172-07 (2007), on a dry basis. The percentage of fixed carbon content was calculated by means of the difference. Ultimate analysis was performed to determine the elemental compositions of coconut cloth, and the liquid products and biochars were analyzed using a CHONS elemental analyzer (Flash 2000; Thermo Fisher Scientific, Waltham, MA, USA).

Characterization of liquid product

Physical properties of the liquid products were tested, including density, viscosity, water content, *etc.*, according to ASTM standard test methods. The kinematic viscosity of the bio-oil at 40 °C was measured according to ASTM D4486-10 (2010), and water content of the bio-oil was determined using a Karl-Fischer titrator (KF-MA-1; Ben Ang Instrument Co., Ltd., Shanghai, China).

Fourier transform infrared spectroscopy (FTIR) (TENSOR27; Bruker Corporation, Billerica, MA, USA) was used to determine the chemical groups (bonds) present in the bio-oil. The pH of the bio-oil was analyzed using a PHS-3E pH meter (Yantai Stark Instrument Co., Ltd., Shanghai, China) and measured at room temperature. The nuclear magnetic resonance spectroscopy (¹HNMR) analysis of the bio-oil was performed using a NMR spectrometer (Bruker-400M; Bruker Corporation, Billerica, MA, USA). The bio-oil samples were analyzed by gas chromatography-mass spectrometry (GC-MS) (HP 6890/5973 MSD; Agilent Technologies, Inc., Santa Clara, CA, USA), which was equipped with a TCD detector and HP-5ms column (30 m × 250 μm × 0.25 μm).

Characterization of biochar

The physical form of biochar was studied by scanning electron microscopy (SEM) (Quanta FEG250; Jeol Corporation, Jeol, Japan). The surface area of the biochar was estimated by nitrogen adsorption at 77 K using an automatic adsorption instrument (ASAP2460; Micromeritics Instrument Corporation, Norcross, GA, USA). To understand the characteristics of the biochar powder, X-ray diffraction (XRD) was performed using AXIS SUPRA X-ray powder diffraction (Kratos Analytical, Ltd., Manchester, England). Functional groups were analyzed in the infrared region of 370 cm⁻¹ to 7500 cm⁻¹. Morphology and elemental characteristics were determined by using an energy dispersive X-ray (EDX) spectrometer (Bruker d8 Advance; Bruker Corporation, Bremen, Germany).

Calorific value

Ultimate analysis was used to calculate the high heating value (HHV). Equation 1 was used to calculate the HHV because the oxygen content in the precursors and the products was greater than 15% (Rout *et al.* 2016):

$$\text{HHV (MJ/kg)} = 0.336C + 1.418H - (0.153 - 0.000720 O)O + 0.0941S \quad (1)$$

Experimental apparatus

The pyrolysis test was conducted in a laboratory-scale microwave pyrolysis reactor, and pyrolysis of the biomass material (coconut cloth) was performed in a laboratory-scale microwave oven tube (CY-PY1100C-M; Hunan Changyi Microwave Technology Co., Ltd., Changsha, Hunan). The oven had a heating area of 80 cm × 220 cm (diameter × width) and a maximum output of 2.8 kW. A thermocouple was used to measure temperature in the microwave oven. Figure 1 shows the microwave pyrolysis apparatus. The first was connected to the condenser tube, and the second bottle was placed in a dichloromethane solution.

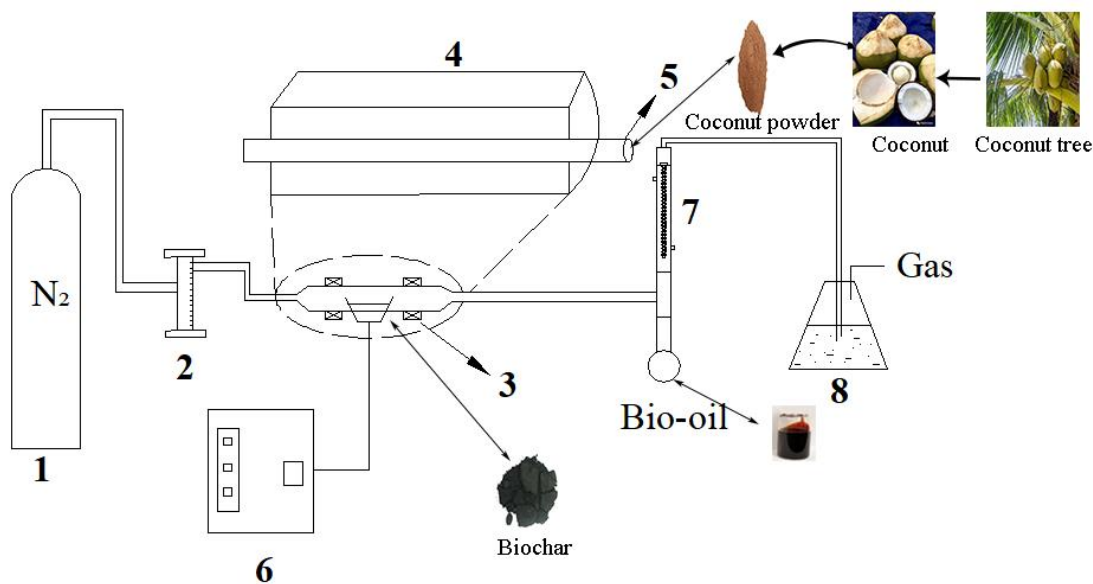


Fig. 1. Systematic illustration of experimental set-up. 1) Nitrogen cylinder; 2) Flowmeter 3) Microwave transmitter 4) Reaction device 5) Quartz tube 6) PID controller 7) Condenser 8) collector

Experimental procedure

To explore the optimum operating conditions to achieve the most extreme bio-oil yield, pyrolysis experiments of coconut cloth were divided into three sets to examine the influence of operating parameters. The pyrolysis experiments were conducted by placing 20 g of dry biomass sample in a microwave pyrolysis reactor. Table 1 shows the conditions of experiments conducted for pyrolysis of coconut cloth. The yields of bio-oil and biochar were determined by weighing. The yields of biochar, bio-oil, and pyrolysis gases are given as in Eq. 1, Eq. 2, and Eq. 3, respectively. Each experiment was repeated three times and the average value was determined.

$$\text{Liquid yield (\%)} = (\text{Total liquid product weight} / \text{Feed weight}) \times 100 \quad (1)$$

$$\text{Biochar yield (\%)} = (\text{Biochar weight} / \text{Feed weight}) \times 100 \quad (2)$$

$$\text{Gas yield (\%)} = 100 - (\text{Liquid yield} + \text{Biochar yield}) \quad (3)$$

Table 1. Conditions of Experiments Conducted for Pyrolysis of Coconut Cloth

Experiment	Values of Variable Parameter	Values of Microwave Parameters for Verifying Optimum Conditions
Effect of Temperature (°C)	450, 500, 550, 600, 650	Heating rates: 20 °C/min N ₂ flow rate: 80 cm ³ /min
Effect of Heating Rates (°C/min)	10, 15, 20, 25, 30	Temperature: 550 °C N ₂ flow rate: 80 cm ³ /min
Effect of N ₂ Flow Rate (cm ³ /min)	60, 80, 100, 120	Temperature: 550 °C Heating rates: 20 °C/min

Note: The heating rate is controllable. The heating rate is the programmed temperature rise heating. A certain heating rate is set to heat from room temperature to a specified temperature and then react at this temperature for a certain time.

RESULTS AND DISCUSSION

Characterization of Coconut Cloth

Table 2 shows the proximate and ultimate analyses of coconut cloth. Moisture content in coconut cloth was low (4.36 wt%). Coconut cloth biomass powder had higher volatile matter content (72.9 wt%) and lower ash content (3.98 wt%), which could result in less loss of fixed carbon for bio-oil during pyrolysis (Buckley 1991; Nayan *et al.* 2013). Fixed carbon content in coconut cloth was 18.8 wt%. Ultimate analysis showed that coconut cloth had higher amounts of C and O than H, N, and S. Low nitrogen and sulfur content in coconut cloth implied that it released smaller amounts of SO_x and NO_x during pyrolysis. With the help of elemental compositions data, the empirical formula of coconut cloth was CH_{1.30}O_{0.59}N_{0.01}. These results were similar to those of other biomass samples (Varma *et al.* 2019). The O content plays an important role in determining calorific value (Capunitan and Capareda 2014). In coconut cloth, a higher amount of carbon content than oxygen and ash contents results in a higher HHV of the feedstock (Friedl *et al.* 2005). The HHV of the feedstock was 18.6 MJ/kg. The hemicellulose, cellulose, and lignin contents of coconut cloth were 34.1 wt%, 18.7 wt%, and 35.1 wt%, respectively.

Table 2. Proximate and Ultimate Analyses of Coconut Cloth

Properties	Coconut Cloth
Moisture (wt%)	4.36
Volatile Matter (wt%)	72.91
Ash Content (wt%)	3.98
Fixed Carbon (wt%)	18.75
Ultimate Analysis (wt%)	
C	47.43
H	5.12
N	0.48
O	37.20
S	0.84
H/C Molar Ratio	1.30
O/C Molar Ratio	0.59
Empirical Formula	CH _{1.30} O _{0.59} N _{0.01}
HHV (MJ/kg)	18.58
Hemicellulose (wt%)	34.10
Cellulose (wt%)	18.73
Lignin (wt%)	35.09
Other (wt%)	12.08

Thermogravimetric analysis of coconut cloth

The thermal behavior of coconut cloth is shown in Fig. 2. The figure shows that each component of coconut cloth had a different thermal degradation temperature range. The first stage of degradation occurred as temperature increased from 25 °C to 150 °C. The DTG curve revealed that the first peak appeared at 65.5 °C, in which a small weight loss of 5.26% occurred due to removal of moisture and light-molecular weight compounds from the coconut cloth sample. The second stage of weight loss was primarily volatilization of an active pyrolysis zone temperature range of 150 °C to 400 °C that corresponded with a differential thermal gravimetry (DTG) peak at 329.87 °C, and this stage of weight loss was

primarily the breakdown of hemicellulose and cellulose molecules present in the biomass due to high decomposition rates. After this, a third stage occurred between 400 °C and 800 °C, but the weight loss rate was minimal. As the temperature increased, the DTG curve tended to be stable when it reached 800 °C, which indicated that the coconut cloth had been completely pyrolyzed. According to literature, hemicellulose and cellulose decomposition occurs at temperature ranges of 150 °C to 450 °C and 275 °C to 450 °C (Basu 2010), respectively. Higher temperatures favored biochar formation. The purpose of this experiment was to obtain higher yields of bio-oil. Therefore, according to thermogravimetric analyzer (TGA) and DTG curves shown, the pyrolysis temperature range that was optimal for the coconut cloth was 400 °C to 650 °C.

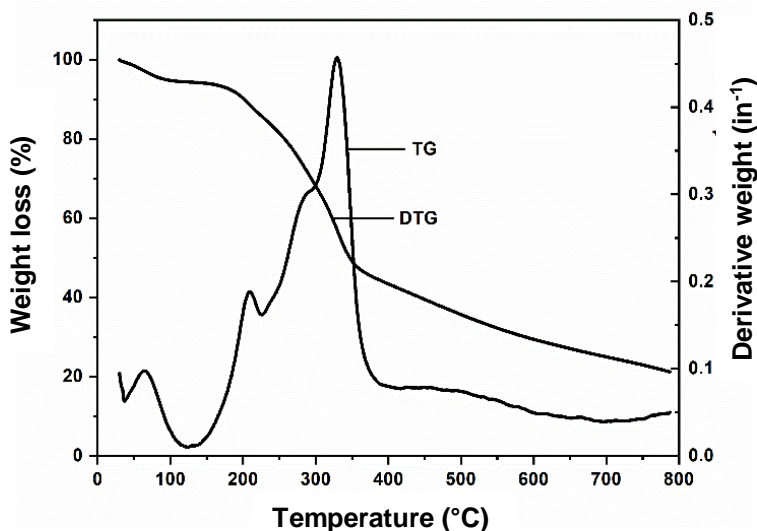


Fig. 2. TG and DTG curves at 10 °C/min heating rate

Influence of Pyrolysis Parameters' Effects on Product Yields

Effect of temperature on the products yield

Figure 3 shows the yield distribution of product during pyrolysis obtained at a different carrier gas (N₂) flow rate of 80 mL/min. Figure 3 shows that at a heating rate of 20 °C/min with the temperature increased from 450 °C to 550 °C, the yield of bio-oil increased from 35.8% to 38.3%. At 650 °C, the liquid yield decreased to 36.2%. As the temperature increased, the yield first increased and then decreased. The liquid yield decrease might be due to decomposition of the intermediate compound that non-condensable small molecule gas produced at 550 °C (Zhang *et al.* 2007). As the temperature increased, the volatile matter also gradually increased. Due to large cracking of volatile matter of carbon at higher temperatures, the yield of biochar continued to decrease with increasing temperature, and the yield of carbon decreased from 39.3% to 34.1%. As the temperature gradually increased, some non-condensable gases gradually increased, while the gas and total conversion rate increased (Chutia *et al.* 2014). The gas yield increased from 24.9% to 29.7%. According to the above analysis, cracking of coconut cloth at 550 °C was found to be a suitable temperature.

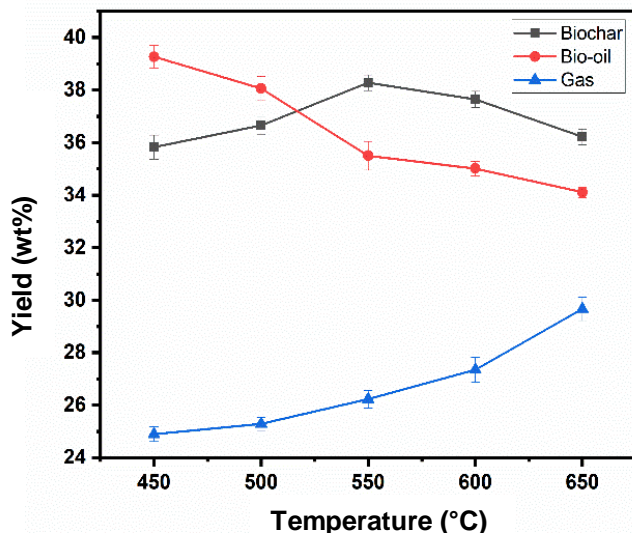


Fig. 3. Yields of pyrolysis products at different pyrolysis temperatures

Effect of heating rates on product yield

Figure 4 shows the pyrolysis product yields of coconut cloth at different heating rates (10 °C/min, 15 °C/min, 20 °C/min, 25 °C/min, and 30 °C/min) at a temperature of 550 °C. The heating rate was increased from 10 °C/min to 20 °C/min, and bio-oil yield increased from 34.7% to 37.1%. When the heating rate increased from 20 °C/min to 30 °C/min, liquid yield was reduced to 34.7%. The increase in bio-oil production was due to the higher heating rate, which reduced the quality and heat transfer limitations and avoided secondary decomposition reactions (Uzun *et al.* 2010). When the heating rate increased from 10 °C/min to 30 °C/min, carbon yield decreased from 39.6% to 32.1% and gas yield increased from 25.7% to 33.3%. Carbon yields decreased due to faster depolymerization of biomass to predominantly volatiles (Chen *et al.* 1997). Therefore, at the temperature of 550 °C, the heating rate of 20 °C/min was the best choice for liquid yield.

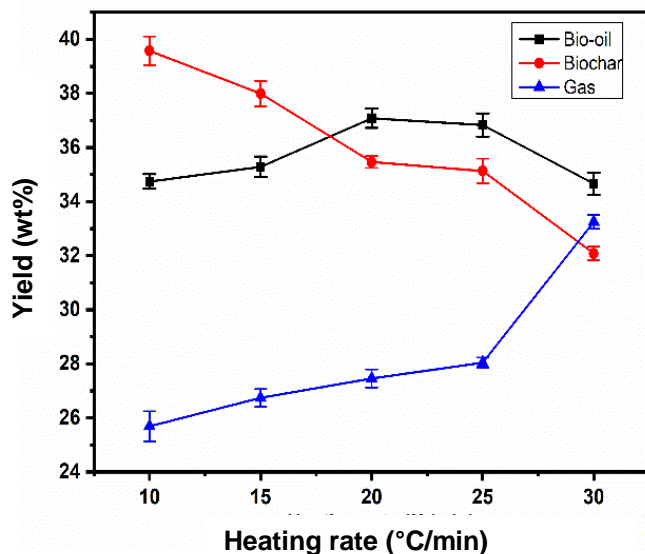


Fig. 4. Effect of heating rate on the yield of pyrolysis products

Effect of nitrogen flow rate on product yield

Pyrolysis experiments were performed to investigate the effect of N₂ flow rate on product yield, and results are shown in Fig. 5. The effects of four gas flow rates of 60 cm³/min, 80 cm³/min, 100 cm³/min, and 120 cm³/min on pyrolysis yield were studied under the pyrolysis temperature of 550 °C and the heating rate of 20 °C/min. With the increase of N₂ flow rate, liquid yield reached a maximum of 38.1% at 80 cm³/min. When the N₂ flow rate was 120 cm³/min, liquid yield dropped to 35.1%. The biochar yield decreased from 38% to 34.4%, and gas yield increased from 25.1% to 30.5%. At lower N₂ flow rates, volatiles residence times were longer, which resulted in the formation of more biochar. As flow rate of N₂ increased, more steam formation occurred, with the result that biochar yield decreased as gas yield increased.

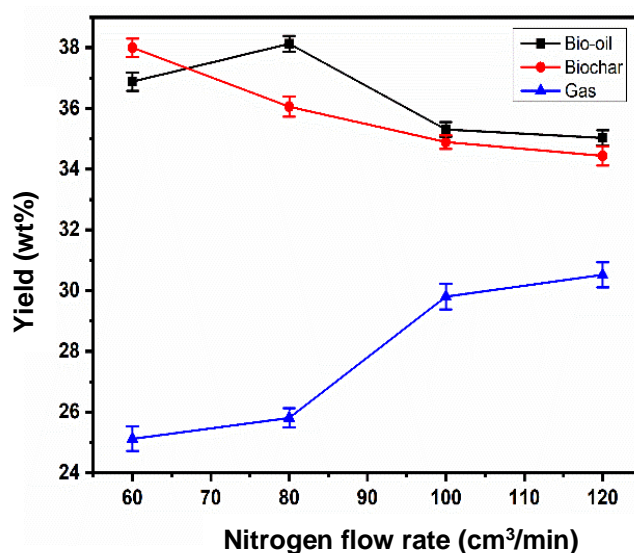


Fig. 5. Effect of nitrogen flow rate on yield of pyrolysis products

Characteristics of Bio-oil

Table 3. Elemental Composition and Physical Properties of Bio-oil

Physical Properties	Value
Colour	Dark Brown
Water Content (wt%)	13.47
Kinematic Viscosity, 40 °C, cSt	20.51
pH	3.69
Elemental Composition (wt%)	
Carbon	59.89
Hydrogen	7.2
Nitrogen	1.14
Oxygen	29.55
Sulfur	0
H/C Molar Ratio	1.44
O/C Molar Ratio	0.37
Empirical Formula	CH _{1.44} O _{0.37} N _{0.02}
HHV (MJ/kg)	26.45

Table 3 lists the elemental composition, physical properties, calorific value, and empirical formula of bio-oil. The water content was 13.5 wt%. The viscosity was 20.5 cSt. Bio-oils contain substantial amounts of organic acids, mostly acetic and formic acid, which resulted in a pH of 3.69. Calorific value of liquid fuel is an important property, as it signifies the energy value. The higher heating value of bio-oil was 26.4 MJ/kg. Nitrogen content of the bio-oil was more than the precursors of all biomass and biochar, which indicated that nitrogen remained in the liquid product during pyrolysis. The sulfur content was not found in bio-oil. The sulfur-free organic phase is one of the advantages of bio-oil for fuel applications. Therefore, bio-oil could be further processed and upgraded to directly replace fossil fuels (Venderbosch and Prins 2010). The H/C and O/C molar ratios of bio-oil were 1.44 and 0.37, respectively. The empirical formula for bio-oil was $\text{CH}_{1.44}\text{O}_{0.37}\text{N}_{0.02}$.

FTIR analysis of bio-oil

The biomass pyrolysis oil component is complex, and the extracted liquid product contains a mixture of various unknown compounds. Various functional groups present in the bio-oil were detected in the FTIR spectrum. From Fig. 6 and Table 4, the strong absorption peak between 3500 cm^{-1} and 3200 cm^{-1} was the result of the presence of the O-H group. The absorption peak at 3446 cm^{-1} indicates the presence of carboxylic acids, phenols, and alcohols (Chen *et al.* 2016). The C-H stretching vibrations between 3000 cm^{-1} and 2800 cm^{-1} indicated the presence of aliphatic CH_3 and CH_2 . The N-H stretching vibration peak at 2361 cm^{-1} indicated the presence of tertiary ammonium salt. The peak at 1645 cm^{-1} representing the C=O stretching vibration was indicative of ketone, quinone, aldehyde groups, *etc.* The peaks at 1511 cm^{-1} and 1454 cm^{-1} indicated the presence of C=C bonds of alkene and aromatics in pyrolysis bio-oil, respectively. The absorption peaks at 1270 cm^{-1} and 1112 cm^{-1} indicated the presence of a high amount of oxygenated compounds in the forms of alcohol and ether.

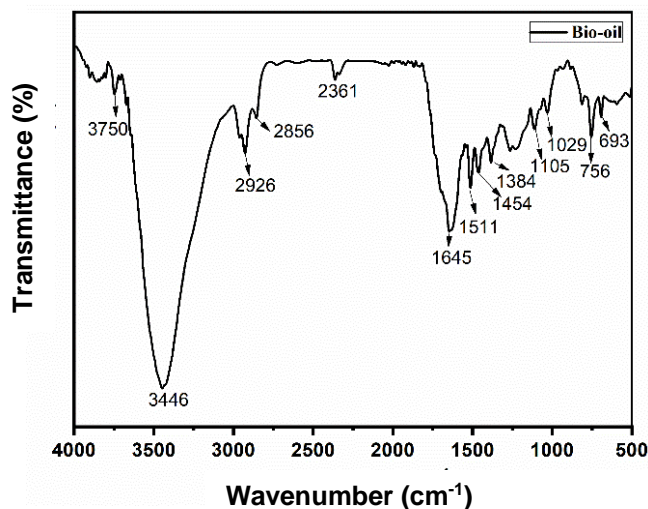


Fig. 6. FTIR spectrum of coconut cloth bio-oil

The bio-oil contained aromatic compounds, as confirmed by a C-H plane bending vibration between 700 cm^{-1} and 900 cm^{-1} . Therefore, it could be concluded that the bio-oil form contained ethers, alcohols, phenols, *etc.* A mixture of valuable organic compounds

could be upgraded into valuable liquid fuels. Further understanding of specific substances contained in the bio-oil was determined by ^1H NMR and GC-MS.

Table 4. FTIR Peak Details of Obtained Bio-oil

Wavenumber (cm^{-1})	Functional Groups	Probable Compound
3500 to 3200	O-H stretching	Phenols, alcohols
3000 to 2800	C-H stretching	Alkanes
1645	C=O stretching	Ketones, aldehyde
1511, 1454	C=C stretching	Olefins, aromatic hydrocarbons
1384	C-H stretching	Alkenes
1270	C-O stretching	Phenols, esters
1105 to 1029	C-O stretch	Ethers, esters
700 to 900	C-H in plane bending	Aromatics

GC-MS analysis of bio-oil

The GC-MS analysis of the bio-oil showed that the organic substances found in liquid products were ketones, acids, aldehydes, esters, and phenols.

Table 5. GC-MS Analysis of Pyrolysis Liquid

No.	Relative Time (min)	Peak Name	Molecular Formula	Area (%)
1	2.201	Methyl acetate	$\text{C}_3\text{H}_6\text{O}$	0.34
2	3.804	1H-Pyrazole, 1,3-dimethyl-	$\text{C}_5\text{H}_8\text{N}_2$	1.21
3	6.355	2-Cyclopenten-1-one	$\text{C}_5\text{H}_6\text{O}$	0.57
4	6.5	2-Cyclopenten-1-one, 2-methyl-	$\text{C}_6\text{H}_8\text{O}$	0.58
5	7.632	Acetic acid	$\text{C}_2\text{H}_4\text{O}$	3.96
6	7.777	3-Furaldehyde	$\text{C}_5\text{H}_{10}\text{O}_2$	1.96
7	8.657	2-Cyclopenten-1-one, 3-methyl-	$\text{C}_6\text{H}_8\text{O}$	0.82
8	8.931	2-Cyclopenten-1-one, 2,3-dimethyl-	$\text{C}_7\text{H}_{10}\text{O}$	0.80
9	9.374	2-Furancarboxaldehyde, 5-methyl-	$\text{C}_6\text{H}_{10}\text{O}_2$	1.60
10	12.92	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$\text{C}_5\text{H}_8\text{O}_2$	0.75
11	13.347	Phenol, 2-methoxy-	$\text{C}_7\text{H}_8\text{O}_2$	8.31
12	13.775	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$\text{C}_7\text{H}_{10}\text{O}_2$	0.72
13	14.588	Creosol	$\text{C}_8\text{H}_{10}\text{O}_2$	2.85
14	14.732	Maltol	$\text{C}_6\text{H}_6\text{O}_3$	0.92
15	15.169	Phenol, 2-methyl-	$\text{C}_7\text{H}_8\text{O}$	4.34
16	15.237	Phenol	$\text{C}_6\text{H}_6\text{O}$	42.99
17	15.505	Phenol, 4-ethyl-2-methoxy-	$\text{C}_9\text{H}_{10}\text{O}_2$	4.11
18	16.071	Phenol, 2,3-dimethyl-	$\text{C}_8\text{H}_{10}\text{O}$	0.83
19	16.114	Phenol, 2,4-dimethyl-	$\text{C}_8\text{H}_{10}\text{O}$	0.70
20	16.157	p-Cresol	$\text{C}_7\text{H}_8\text{O}$	7.23
21	16.259	Phenol, 3-methyl-	$\text{C}_7\text{H}_8\text{O}$	2.73
22	17.253	Phenol, 4-ethyl-	$\text{C}_8\text{H}_8\text{O}$	3.62
23	18.259	Phenol, 2,6-dimethoxy-	$\text{C}_8\text{H}_{10}\text{O}_3$	3.76
24	19.198	3-Allyl-6-methoxyphenol	$\text{C}_{10}\text{H}_{10}\text{O}_2$	2.86
25	28.13	n-Hexadecanoic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	2.58

The phenols in the bio-oil included phenol, 3-methylphenol, 4-ethylphenol, and 2,6-dimethoxyphenol. The content of phenols was attributed to the degradation of 35.1% lignin in the coconut cloth. Phenols are also an important organic chemical raw material and have important applications in the pharmaceutical, synthetic fiber, perfume, pesticide, and other industries. Phenolic derivatives play a key role in the chemical industry and are also important synthetic materials in organic chemistry. In this study of coconut cloth as a raw material, bio-oil obtained with high concentrations of phenol and phenolic compounds was feasible, which showed that bio-oil has great potential in the chemical industry.

¹H NMR analysis of bio-oil

It was necessary to obtain evidence about the type of protons present in the bio-oil via the ¹H NMR spectrum. Figure 7 shows the ¹H NMR range of bio-oil.

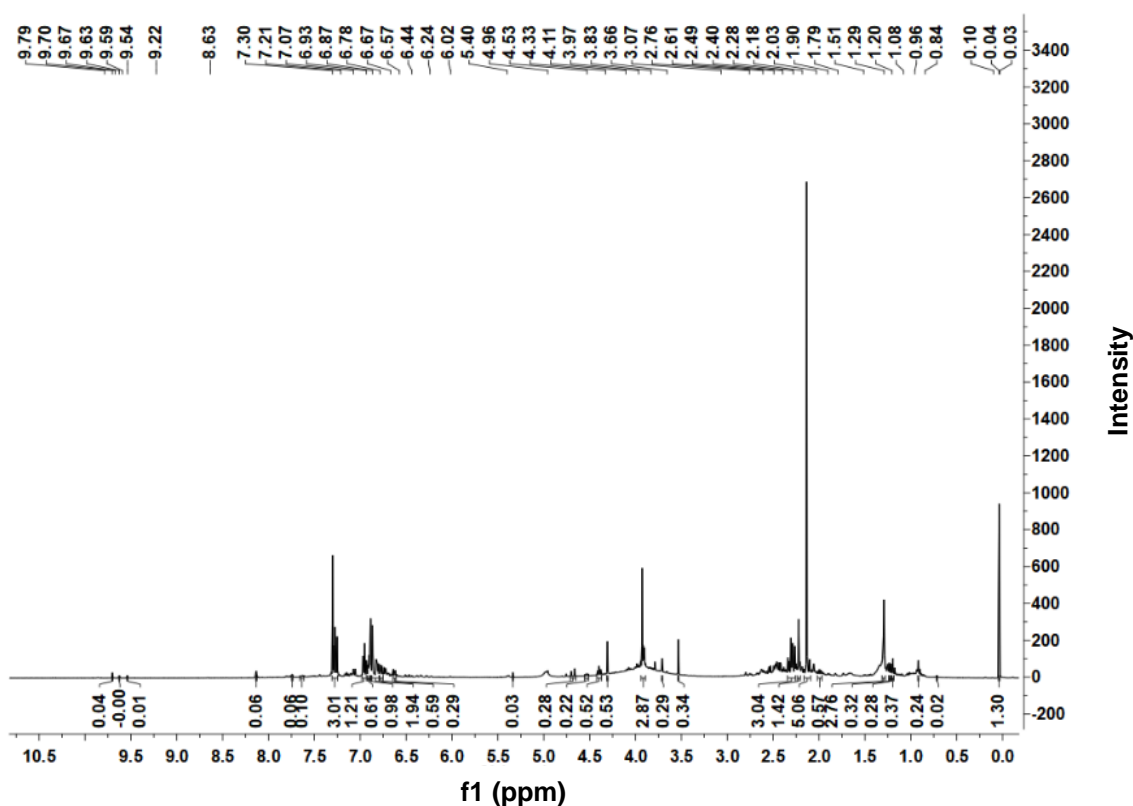


Fig. 7. ¹H NMR spectrum of bio-oil

The ¹H NMR spectra of the bio-oil are presented in Table 6 with the respective integral values of selected regions of spectra on a percentage basis. In the spectrum, 28.26% of protons in the region between 0.5 ppm to 1.5 ppm were attributed to aliphatic protons (Bordoloi *et al.* 2015). In the range of 1.5 ppm to 3.0 ppm (26.67%), CH₃, CH₂, and CH protons present in alpha or further from an aromatic ring resonate was due to the aromatic ring resonate. The resonance of the proton in the 3.0 ppm to 4.5 ppm interval was due to the proton of the methylene group attached to the aromatic ring, or due to the presence of amine and alcohol protons, where the area occupied by protons was 26.7% (Saikia *et al.* 2015). The integral region between 4.5 ppm and 6.0 ppm was due to protons of phenolic (OH) and olefinic protons (0.68%). Finally, in the 6.0 ppm to 9.0 ppm region, the protons

of the aromatic ring area was 31.9%. From the above analysis, bio-oil contained phenols, alcohols, and acids, which was consistent with FTIR and GC-MS studies.

Table 6. ^1H NMR Results of Bio-oil

Chemical Shift (ppm)	Hydrogen Type	Bio-oil (mol% of Total Hydrogen)
0.5 to 1.5	Aliphatic ($\text{CH}_3\gamma$, $\beta\text{-CH}_3$, CH_2 , and $\text{CH}\gamma$ or further from an aromatic ring)	28.22
1.5 to 3.0	CH_3 , CH_2 , and $\text{CH}\beta$ to an aromatic ring (naphthenic)	26.67
3.0 to 4.5	Ring-join methylene ($\text{Ar-CH}_2\text{-Ar}$)	12.55
4.5 to 6.0	Phenolic (OH) or olefinic proton	0.687
6.0 to 9.0	Aromatic	31.87

Characterization of Biochar

Proximate and ultimate analysis of biochar

The proximate and ultimate analysis compositions of biochar are presented in Table 7. The biochar contained higher carbon content and less oxygen content than the feedstock. Due to the high carbon content and low ash and volatile contents of biomass char, high-quality biochar with a high calorific value and a large amount of fixed carbon was obtained (Chaiwong *et al.* 2013). There was a remarkable increase of calorific value from the original biomass (18.6 MJ/kg) to the biochar (27.8 MJ/kg). When the pyrolysis temperature was 550 °C, pH of the biomass biochar was in a highly alkaline region, which could be used to repair soil by neutralizing soil acidity and increasing soil pH. Biochar had lower O/C and H/C ratios and less energy loss, smoke, and water vapor in the combustion process, which can result in high-quality biochar fuels (Zhang *et al.* 2017). In general, an O/C ratio lower than 0.2 signified a biochar half-life of 1000 years at minimum, which showed that thermal stability of biochar was very good.

Table 7. Proximate and Ultimate Analysis of Biochar

Properties	Biochar
Moisture (wt%)	1.86
Volatile Matter (wt%)	11.44
Ash Content (wt%)	8.48
Fixed Carbon (wt%)	78.22
Ultimate Analysis (wt%)	
C	76.88
H	2.07
N	0.51
O	7.21
S	0.78
H/C Molar Ratio	0.32
O/C Molar Ratio	0.07
Empirical Formula	$\text{CH}_{0.32}\text{O}_{0.07}\text{N}_{0.01}$
pH	10.20
HHV (MJ/kg)	27.77

FTIR analysis of biochar

Biochar was characterized by FTIR, which is shown in Fig. 8. The stretching vibration peak of O-H in the range of 3600 cm^{-1} and 3200 cm^{-1} might have been due to the release of a large amount of moisture. The 2919 cm^{-1} weak peak was due to the stretching vibration of aliphatic CH_3 . A moderate-intensity absorption peak at 1587 cm^{-1} revealed the presence of an aromatic skeleton vibration, which demonstrated the presence of lignin at this position. A strong peak at 1422 cm^{-1} indicates a representative aromatic $\text{C}=\text{O}$ and $\text{C}=\text{C}$ functional group (Aboulkas *et al.* 2017). The peak between 1200 cm^{-1} and 900 cm^{-1} indicated aromatic C-O stretching vibration and the presence of oxygen-containing functionality in the biochar. In the range of 600 cm^{-1} to 900 cm^{-1} , there was a stretching vibration peak of aromatic C-H, which indicates the presence of an adjacent aromatic hydrogen component in the biochar (Yakkala *et al.* 2013).

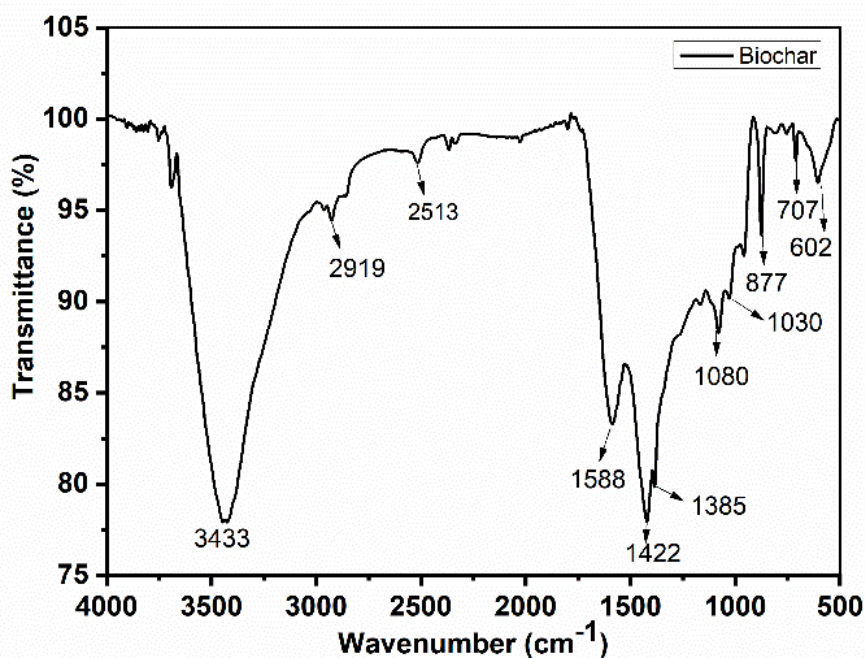


Fig. 8. FTIR spectra of biochar

SEM-EDX analysis of biochar

The SEM-EDX characterization method was used to study the morphological characteristics of coconut cloth and biochar. From Fig. 9(a) and Fig. 9(c), the SEM images of coconut cloth and biochar showed a great difference between their sample images. The interior of the coconut cloth was made of lignocellulose, which was almost filled and had a smooth surface. The morphology of biochar and its appearance on the surface left a rough appearance, which could be a honeycomb structure that showed more void space and porosity and helped improve adsorption capacity. From the EDX analysis in Fig. 9(b), the raw coconut cloth was mainly composed of high concentrations of C (59.03%) and O (40.97%). Figure 9(d) showed that the biomass carbon contained Cl (0.83%), K (1.04%), Na (0.70%), and other elements, which are important inorganic nutrients for soil fertility and crop production.

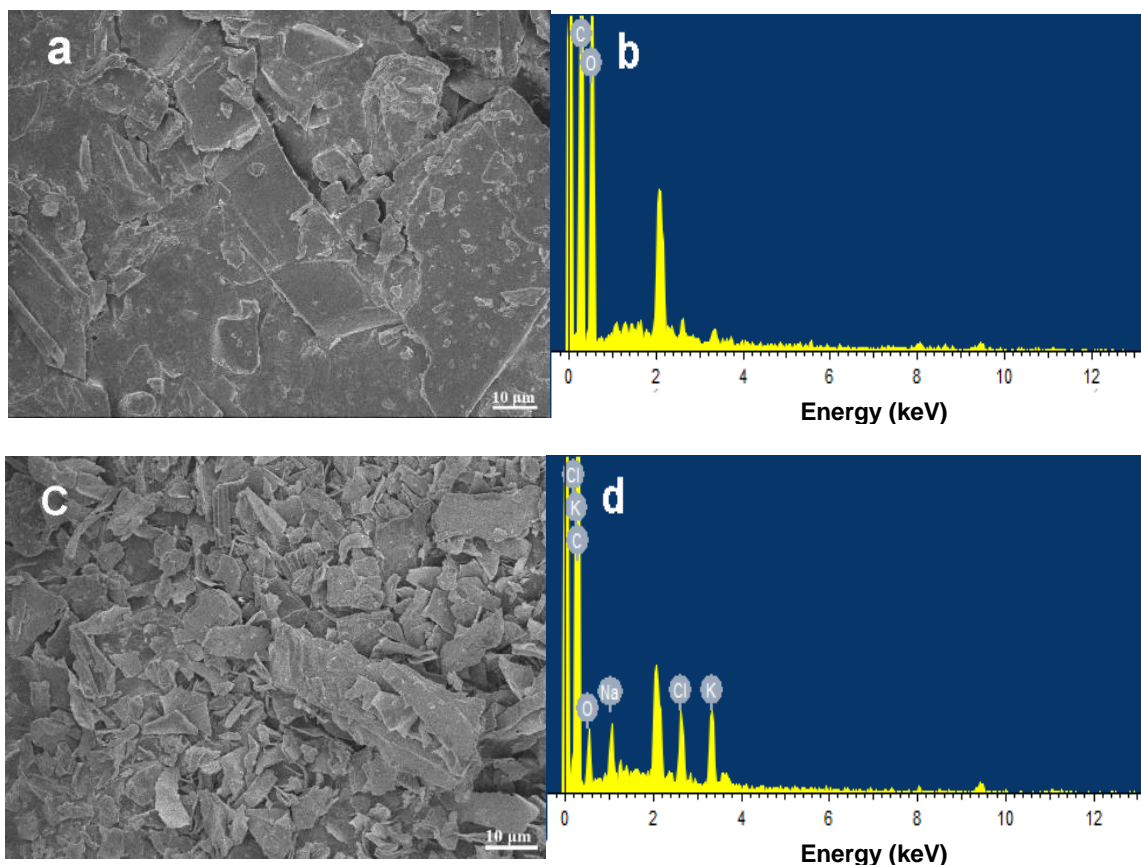


Fig. 9. SEM-EDX analysis of coconut cloth (a, b) and biochar (c, d) at 550 °C

X-ray analysis of biochar

X-ray diffraction was analyzed, and biomass crystallinity and biochar structure are given in Fig. 10. The coconut cloth showed a sharp peak at 2θ ca. 22° , which indicated the presence of crystals and amorphous matter. Pyrolysis of biochar weakened the 22° peak, and the appearance of some new peaks (28.1° , 40.7° , 50.1° , and 66.3°) indicated the degradation of cellulose and the appearance of an amorphous organic phase (Wang *et al.* 2009). The crystal phase present in the biochar was converted into an amorphous phase by pyrolysis, so the crystallization peak disappeared in the biochar (Varma *et al.* 2019).

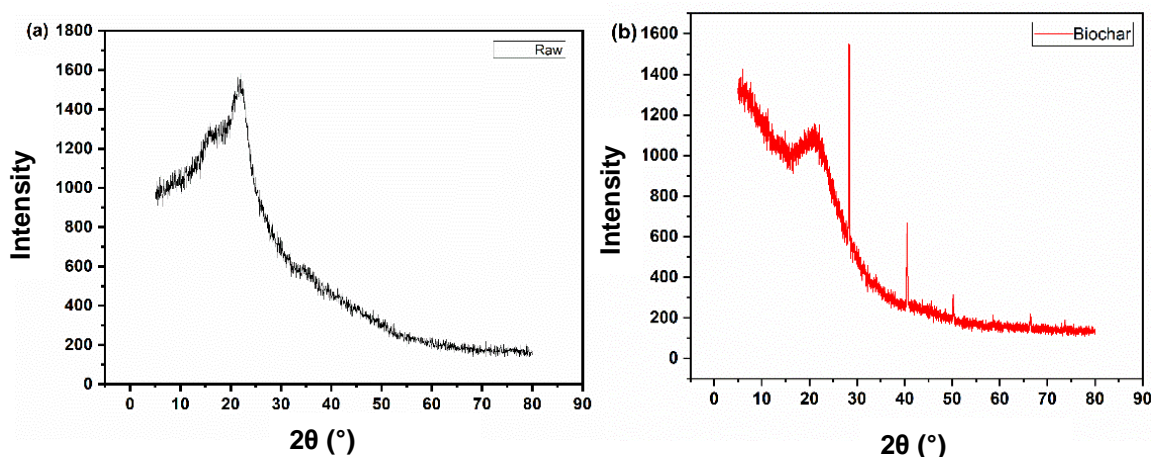


Fig. 10. X-ray diffraction analysis of coconut cloth and biochar

Typical composition of products obtained from different feedstock

Table 8 summarizes the optimum pyrolysis condition of the pyrolysis products properties. It can be observed from Table 8 that the best pyrolysis temperature, heating rate, and N₂ flow rate were 550 °C, 20 °C /min, and 80 cm³/min, respectively. It is also evident that for different biomass raw material and pyrolysis processes, and the calorific value of the products (bio-oil and biochar) and the content of phenolic derivatives of bio-oil are different.

Table 8. Characterization of Coconut Cloth Pyrolysis Oil and Literature Comparison

Feed-stock	Reactor type	Pyrolysis conditions	Bio-oil HHV MJ/kg	Biochar HHV MJ/kg	Phenolic derivatives content%	Ref
Coconut cloth	Microwave	Temperature:550 °C Heating rate:20°C /min N ₂ flow rate:80 cm ³ /min	26.45	27.77	79.57%	Present study
Corn stalk	Microwave	Temperature: 200°C Heating rate: - N ₂ flow rate: -	2.47	32	60%	(Salema <i>et al.</i> 2017)
Coconut shell	Semi batch	Temperature: 575°C Heating rate: 20°C /min N ₂ flow rate: -	19.75	23.68	66.87%	(Rout <i>et al.</i> 2016)
Wood sawdust	Semi batch	Temperature: 500°C Heating rate: 50°C /min N ₂ flow rate: 100cm ³ /min	27.82	22.03	46.62%	(Anil <i>et al.</i> 2019)
Alligator weed	Fixed bed	Temperature: 450°C Heating rate: 25°C /min N ₂ flow rate: 20cm ³ /min	8.88	20.41	16.55%	(Bhattacharjee and Biswas 2017)
Teak sawdust	tubular packed bed	Temperature: 600°C Heating rate: - N ₂ flow rate: 150cm ³ /min	25.83	28.19	22.75%	(Goutam <i>et al.</i> 2019)
Napier Grass	Fix bed	Temperature:600°C Heating rate: - N ₂ flow rate: 30cm ³ /min	28.50	27.60	27.1%	(Isah <i>et al.</i> 2015)
Orange bagasse	Semi batch	Temperature:525°C Heating rate: 75°C /min N ₂ flow rate: 20cm ³ /min	21.72	27.67	27.41%	(Bhattacharjee and Biswas 2017)

Table 8 shows that different raw materials and different pyrolysis instruments of the products have different properties. The phenolic derivatives content of the bio-oil obtained under the optimal conditions of the raw materials in this study is significantly higher than other biomass raw materials. It seems that the present process is competitive with others (Table 8).

CONCLUSIONS

1. In this study, the pyrolysis experiments of coconut cloth were performed in an inert atmosphere (N₂) in a microwave reactor. The experimental results showed that at a temperature of 550 °C, a heating rate of 20 °C/min, and an N₂ flow rate of 80 mL/min, the maximum yield of bio-oil was 38.3%.
2. The obtained bio-oil phenol content was 39.0%, and the total phenolic content was 79.6% *via* the GC-MS area normalization method.
3. The bio-oil and biochar had high calorific values due to their higher carbon content and lower oxygen content compared to biomass, so they could be used as renewable fuel.
4. From the above studies, it was concluded that coconut cloth was potential renewable fuel for pyrolysis.

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