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Article

Biorefining of Pigeon Pea: Residue Conversion by Pyrolysis

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Abstract: Pyrolysis is an important technology to convert lignocellulosic biomass to a renewable liquid energy carrier known as pyrolysis oil or bio-oil. Herein we report the pyrolysis of pigeon pea wood, a widely available biomass in the Philippines, in a semi-continuous reactor at gram scale. The effects of process conditions such as temperature (400–600 °C), nitrogen flow rate (7–15 mL min^{-1}) and particle size of the biomass feed (0.5–1.3 mm) on the product yields were determined. A Box-Behnken three-level, three-factor fractional factorial design was carried out to establish process-product yield relations. Of particular interest is the liquid product (bio-oil), of which the yield was shown to depend on all independent variables in a complex manner. The optimal conditions for highest bio-oil yield (54 wt.% on dry feed intake) were a temperature of 466 °C, a nitrogen flow rate of 14 mL min^{-1} and a particle size of 1.3 mm. Validation of the optimized conditions proved that the average (n = 3) experimental bio-oil yield (52 wt.%) is in good agreement with the predicted value from the model. The properties of product oils were determined using various analytical techniques including gas chromatography-mass spectrometry (GC–MS), gel-permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (^{13}C- and HSQC-NMR) and elemental and proximate analyses. The bio-oils were shown to have low ash content (0.2%), high heating value (29 MJ kg^{-1}) and contain high value-added phenolics compounds (41%, GC peak area) as well as low molecular weight aldehydes and carboxylic acids. GPC analysis indicated the presence of a considerable amount of higher molecular weight compounds. NMR measurements showed that a large proportion of bio-oil contains aliphatic carbons (~60%), likely formed from the decomposition of (hemi)cellulose components, which are abundantly present in the starting pigeon pea wood. Subsequent preliminary scale-up pyrolysis experiments in a fluidized bed reactor (~100 g_{feed} h^{-1}, 475 °C and N_2 flow rate of 1.5 L min^{-1}) gave a non-optimized bio-oil yield of 44 wt.%. Further fractionation and/or processing are required to upgrade these bio-oils to biofuels and biobased chemicals.

Keywords: pigeon pea; lignocellulosic biomass; pyrolysis; bio-oil; phenolics

Highlights

- Pigeon pea wood was pyrolyzed aiming at high bio-oil yields;
- Optimized yields were 54 wt.% on dry feed intake;
- The bio-oils have a higher H/C ratio and a similar O/C ratio than reported for other woods, due to the presence of low amounts of lignin in the pigeon pea wood feed;
- The bio-oil contains a vast range of functional groups of aliphatic, aromatic, aldehydes, ketones, carboxylic acids, phenolics and also oligomeric products, based GC–MS and GPC analysis, as well as the NMR measurements (^{13}C- and HSQC-NMR);
- This present work contributes to the development of efficient biorefining concepts for pigeon peas.

1. Introduction

The negative environmental impact caused by the burning and use of fossils fuel resources, coupled with increasing worldwide demands for energy and materials, have accelerated research on alternative sustainable resources such as biomass. Pyrolysis is the most commonly used thermochemical conversion for the direct transformation of these renewable (non-food) resources to bio-oil, which can be converted to fuels (i.e., middle distillates) and chemicals (i.e., butadiene, phenolics, aromatics) [1–6]. Pyrolysis technology is commercially available at a ton per hour input scale and optimized yields of about 70% of bio-oil on dry biomass feed have been reported [7–11]. Typically, bio-oil contains considerable amounts of water, is acidic, and has a relatively low heating value. As such, upgrading is required to make the bio-oils suitable to be used as a replacement for fossil fuels (e.g., by hydrotreatment or alcohol treatments) [12–15]. Another option is to fractionate the bio-oil into several fractions containing certain organic product groups, like a pyrolytic lignin fraction, a sugar fraction, an organic acid fraction and a low molecular weight phenolic fraction [16–18]. These fractions or individual components within the fractions, have potential to serve as bio-based chemicals. Examples are the use of phenolics in the resins industry, volatile organic acids as deicers and levoglucosan and hydroxyacetaldehyde in the pharmaceutical industry [19–22].

Pigeon pea [*Cajanus cajan* (L.) Millsp.] wood is a potentially interesting biomass feed for pyrolysis. Pigeon pea is a perennial shrub, which grows to a height of about 3.6 m with a lot of fruiting branches and is found in most backyards and marginal lands in South(east) Asia (e.g., in the Philippines) due to suitable conditions for growth [23–28]. An interesting option to valorize the pigeon pea is the cascading biorefinery approach, which aims to maximize the inherent value of all of its components (Figure 1) [27,28]. Most of the current research programs for pigeon pea valorization focus on the use of pods, seeds and leaves as food, animal feed, traditional medicine, fertilizer and soil erosion material, whereas the remaining parts are generally treated as waste. The stem, woody stalk and other residues (e.g., hull and shavings) can be particularly valuable as feedstock for a pyrolysis process to generate, for example, bio-oils. This work ultimately aims to make a significant contribution to this approach.

The International Crop Research Institute in Semiarid Tropics (ICRISAT) reported that about 15–20 tons ha^{-1} of fuel wood from pigeon pea plantations can be obtained, with an energy density of about 4000 kcal kg^{-1} [29]. Moreover, in view of the recent interest in the use of (local) agricultural residues for energy production, thermochemical conversion studies on pigeon pea wood have been reported. However, these studies mainly focus on the production of solid fuels (char, briquettes) or high caloric gases. For example, Katyal and Iyer studied the thermal behavior of pigeon pea stalk using a thermogravimetric analyzer (TGA) and identified temperature ranges for relevant thermal transitions [30]. In addition, gasification experiments were performed in a pilot-scale downdraft gasifier system at a scale of 2 kg h^{-1}. The gasifier was operated successfully, and a gas phase composed of 28% of CO and 5% of H_2 was reported [30]. Rajkumar and Venkatachalam investigated the properties of briquettes from pigeon pea stalk [31]. Pigeon pea briquettes showed worse properties than those of pure cotton stalk and combinations of cotton and soybean stalks (75% and 25%, respectively) in terms of density, impact resistance and compressive strength [31]. Furthermore, Khardiwar et al.

studied the physical and chemical properties of pigeon pea briquettes, soybean briquettes and mixtures thereof [32]. The authors report that pigeon pea briquettes have the lowest density, but highest ash fusion temperature and show comparable volatile matter and heating value when compared to soybean and mixed biomass briquettes [32]. Gangil reported on the kinetics of thermal conversions of pigeon pea crop residues using a thermogravimetric analysis [33] and particularly considered those transition that are beneficial for the formation of binder-less briquettes. The activation energies for the various transitions were determined using the Kissinger–Akahira–Sunose approach [33]. Tinwala et al. reported the pyrolysis of pigeon pea husk at 500 °C in a fixed bed pyrolyzer [34]. The bio-oil yield was 30% and other product were char (33%) and gas (33%) [34].

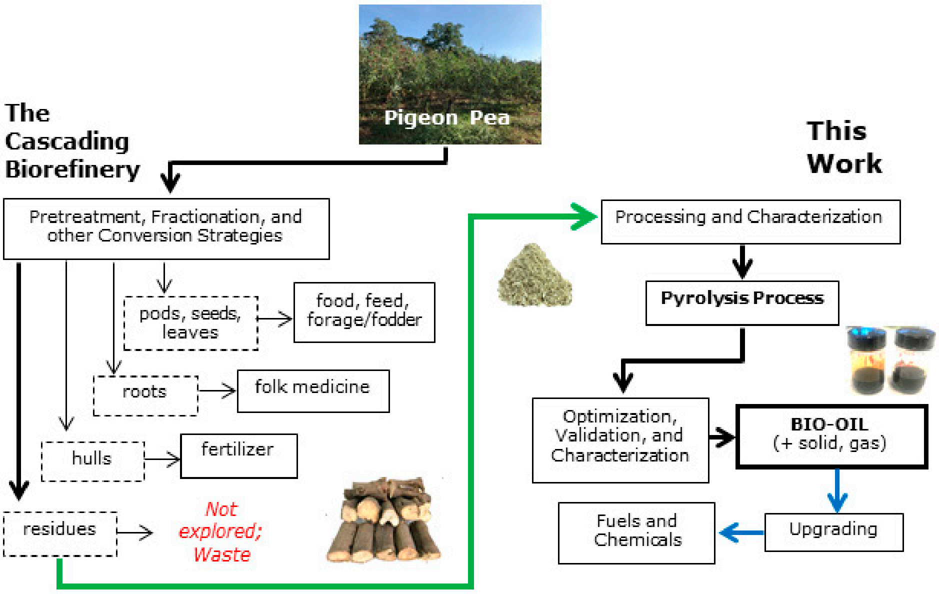

Figure 1. Integrating pyrolysis technology in a cascading biorefinery approach for pigeon pea [27,28].

Recently, some of us determined relevant properties of pigeon pea wood residues for thermochemical conversions including proximate, elemental composition and heating value [35]. The chemical composition and particularly the cellulose and hemicellulose content of pigeon pea wood generally falls within the wide range for lignocellulosic (woody) biomass (Table 1) [35]. However, pigeon pea wood has a significantly lower lignin mass fraction (about 18%) than a typical softwood (pine; 23–33% of the mass) [36]. As a consequence, pigeon pea wood has a relatively high cellulose content (e.g., compared to sugarcane bagasse, sorghum straw, rice straw and grasses) and hemicellulose content. These characteristics, particularly the relatively low lignin content, may be advantageous for pyrolysis processes.

To the best of our knowledge, studies on the use of pigeon pea wood for pyrolysis to produce bio-oils have not been reported. These oils are potentially more valuable energy carriers than the starting biomass when considering energy density, easy of transportation and ash content. Herein we report our investigations to gain insights in the potential of pigeon pea wood as feedstock for pyrolysis using a semi-continuous reactor at gram scale. Optimization of the pyrolysis process (temperature, N_2 flow rate and biomass particle size) was carried out using a Response Surface Method (RSM) to determine the operating conditions for highest bio-oil yield. The bio-oils were characterized in terms of physical, thermochemical and molecular properties using various analytical techniques. Finally, pigeon pea wood was pyrolyzed in a fluidized bed reactor (~100 g_{feed} h^{-1}) and the yield of bio-oil was determined. This investigation provides the proof of principle of pigeon pea wood pyrolysis and may be used as the basis for further design and scale-up of the technology.

Table 1. Relevant physicochemical properties of pigeon pea wood used in this study [35].

Property	Value
Proximate Analysis	
Moisture (%)	9.9
Volatile matter (%)	65.9
Ash (%)	12.3
Fixed carbon (%)	21.8
Heating Value (MJ kg^{-1})	17.1
Ultimate Analysis	
Carbon (%)	41.1
Hydrogen (%)	6.2
Nitrogen (%)	0.9
Oxygen (%)	51.9
Lignocellulosic Analysis	
Cellulose (%)	34.0–34.6
Hemicellulose (%)	34.2–35.5
Lignin (%)	17.8–18.2

2. Experimental Section

2.1. Biomass Preparation and Characterization

Pigeon pea (ICP 7035 variety) wood samples were collected from the pigeon pea plantation area located at the municipality of Magalang, province of Pampanga in the Philippines. The wood samples were size-reduced using a hammer mill and sun- and oven-dried until the moisture content was less than 10% (Kern moisture analyzer model DBS 60–3, Germany). The milled samples were sieved using standard testing sieves in combination with a Ro-Tap sieve shaker (ANSI/ASAE S319.4, R2012, Chicago, USA). Sieved samples were obtained with average sizes of 0.5 mm (range from 0.42 to 0.60 mm, ASTM No. 40 and 30); 0.9 mm (0.85 to 1.00 mm, ASTM No. 20 and 18) and 1.3 mm (1.00 to 1.70 mm, ASTM No. 18 and 12). Thermogravimetric analysis (TGA) of the pigeon wood feed was performed using a TGA 7 from Perkin–Elmer (Massachusetts, USA). The pigeon pea wood sample was heated under a nitrogen atmosphere (nitrogen flow of 30 mL min^{-1}), with heating rate of 10 °C min^{-1} and temperature ramp of 35–600 °C.

2.2. Pyrolysis Experiments and Experimental Design

Pyrolysis experiments were carried out in a semi-continuous setup (continuous with respect to N_2 gas and batch regarding biomass) using gram amounts of biomass input (Figure 2) [37]. The setup consists of a reactor (loaded with biomass at the start of the reaction), a catchpot and a condenser system, which were interconnected with tubes. Typically, pyrolysis was performed by placing 1.0 g of pigeon pea wood sample into the reactor at ambient conditions. The sample was held in place by quartz wool filters supported by a grid. The reactor was then placed in a hot sand bath to start the pyrolysis process. Temperature profiling experiments indicated that it takes about 10–15 min to attain the actual pyrolysis temperature. A total of fifteen pyrolysis runs were carried out at temperatures between 400 and 600 °C, nitrogen flow rates of 7, 11 and 15 mL min^{-1} and biomass particle sizes of 0.5, 0.9 and 1.3 mm. Nitrogen flow rates were based on previous experiments in the setup as reported in ref [37]. Each pyrolysis experiment was conducted with a constant flow of N_2 gas (Linde Gas, 99.999% purity) for 15 min The pyrolysis vapor diluted with nitrogen gas was condensed at a temperature of −40 °C (liquid nitrogen–ethanol mixture). The mass of bio-oil produced (m_{bo}) was determined from the difference of the weight of the tube linings and condensers before and after pyrolysis. The bio-oil was collected from the tube linings and condensers by thoroughly washing them with tetrahydrofuran (THF, Sigma Aldrich, anhydrous, ≥99.9%, with 250 ppm BHT as inhibitor, typically about 3 g). The bio-oil yield was calculated using Equation (1):

$$\%\ Bio\ oil\ yield = \frac{m_{bo}}{m_{pw}} \times 100 \tag{1}$$

where m_{bo} is the mass of bio-oil produced (g) and m_{pw} the mass of pigeon pea wood intake (g).

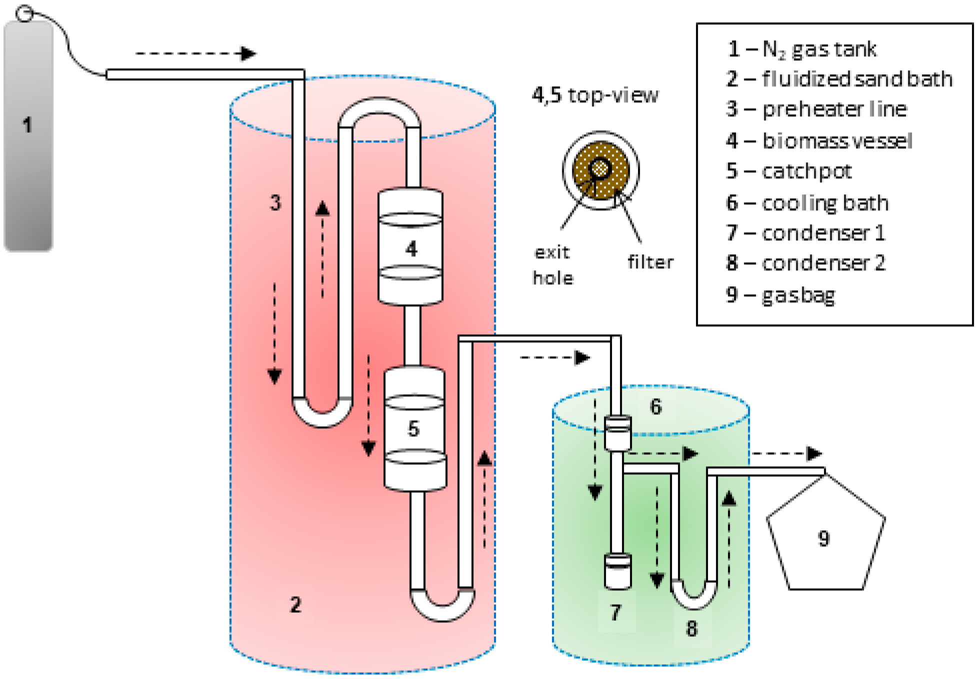

Figure 2. Schematic diagram of the reactor setup for the pyrolysis of pigeon pea wood.

The non-condensable gases were collected in a gasbag (SKC Tedlar sample bag, 3 L, equipped with a polypropylene septum), weighed by water displacement and subsequently analyzed by gas chromatography-thermal conductivity detector (GC-TCD). For this purpose, a Hewlett–Packard 5890 Series II GC was used (USA). The injector temperature was 150 °C, whereas the detector temperature was set at 90 °C. The oven temperature was kept at 40 °C for 2 min, then heated up to 90 °C at 20 °C min^{-1} and kept at this temperature for 2 min. A Poraplot Q (Al_2O_3/Na_2SO_4) and a molecular sieve (5 Å) column were used for separation. The results were quantified by using a reference gas with known composition. The solid products (i.e., ash, char) were also recovered and weighed. All pyrolysis experiments were done in duplicate and the average yields of products were calculated and are reported.

A response surface methodology (RSM) was applied to determine the influence of pyrolysis temperature, particle size and N_2 flow rate, coded as X_1, X_2 and X_3 (independent variables), on the bio-oil yield, coded as Y (dependent variable). A Box-Behnken three-level, three-factor fractional factorial design was used (Table 2). Four combinations of the factor variables and three center points were included in the design to determine reproducibility.

The data were analyzed using the Design Expert 7.1 Software package (StatEase, Minneapolis, MN, USA). A parameter was regarded statistically relevant when the *P*-value was below 0.05. Backward elimination and elimination of outliers was carried out using diagnostics tests to improve the model. The optimum condition based on the mathematical model and surface regression graphs were provided by the software. The resulting mathematical model was validated by performing a pyrolysis experiment in triplicate at the proposed optimum values by the model.

Table 2. Box-Behnken three-level three-factor fractional factorial design matrix.

Run	Coded Factors			Independent Variables			Response, Y
	X_1	X_2	X_3	Temperature (°C)	Particle Size (mm)	N_2 Flow Rate (mL min^{-1})	Bio-Oil Yield (wt.%)
1	+1	+1	0	600	1.3	11	51
2	+1	−1	0	600	0.5	11	41
3	−1	+1	0	400	1.3	11	50
4	−1	−1	0	400	0.5	11	44
5	+1	0	+1	600	0.9	15	48
6	+1	0	−1	600	0.9	7	36
7	−1	0	+1	400	0.9	15	54
8	−1	0	−1	400	0.9	7	48
9	0	+1	+1	500	1.3	15	54
10	0	+1	−1	500	1.3	7	47
11	0	−1	+1	500	0.5	15	48
12	0	−1	−1	500	0.5	7	48
13	0	0	0	500	0.9	11	47
14	0	0	0	500	0.9	11	46
15	0	0	0	500	0.9	11	45

2.3. Bio-Oil Characterization

The water content of bio-oils (THF-collected liquid products, see Section 2.2) was measured using a Karl–Fischer Titrator (Metrohm, MRD 296, with 302 SM Titrino and 703 Ti stand, Switzerland), following the ASTM E203 standard. About 0.010 g of sample was injected in a glass chamber containing the Hydranal solvent and titrations were carried out using a suitable titrant (Composit 5 K). Triplicate measurements for each sample were conducted and the average value is reported. The total acid number, heating value, ash content and elemental composition of bio-oils (after removal of THF by evaporation) were determined. The total acid number (TAN) titration was performed following ASTM D 3339–07 using about 0.25 g of bio-oil [38]. The calorific value in term of the high heating value (HHV) was calculated from the elemental composition using the Boie Equation (Equation (2)) [39].

$$\text{HHV (kJ kg}^{-1}) = (35.160 \times \text{C}) + (116225 \times \text{H}) - (11.090 \times \text{O}) + (6280 \times \text{N}) + (10.465 \times \text{S}) \quad (2)$$

The proximate composition was determined according to ASTM D5142 on a thermal gravimetric analyzer (TGA 4000) from Perkin Elmer Instruments. The analyses were carried out from 25 to 950 °C under an inert nitrogen gas as well as air at a heating rate of 20 °C min^{-1}. The moisture content was taken as the weight loss between 25 and 110 °C. The ash content was taken as the amount of residue when heating a sample in air until 950 °C. The fixed carbon content (%) was taken as 100% minus the amount of volatile matter (%) and ash content (%). The elemental composition of the bio-oils was determined using an elemental analyzer (Vario Micro Cube Elemental CHNS/O, Germany). The oxygen content was determined by difference. All experiments were carried out in duplicate, and the average value is provided.

Gas chromatography-mass spectroscopy (GC–MS) analyses were performed on a Hewlett- Packard (HP 6890 series GC system, USA) GC combined with a Quadrupole Hewlett–Packard 6890 mass selective detector. A RTX-1701 capillary column (0.25 µm film thickness, 30 m × 0.25 mm i.d.) was used for separation. Helium was used as a carrier gas (2 mL min^{-1}). The injector temperature was fixed at 280 °C. The following oven temperature profile was used: 40 °C for 5 min, from 40 °C to 250 °C at a rate of 5 °C min^{-1}, 250 °C for 10 min. Before analyses, the samples were diluted with THF (dilution factor of 10).

The average molecular weights (M_n and M_w) and polydispersity of the bio-oils were determined by gel permeation chromatography (GPC). A Hewlett Packard HP1100 (USA) combined with a GBC LC1240 RI detector was used. Three mixed-e columns (300 × 7.5 mm PL gel, 3 µm) in series were applied for separation. Prior to GPC analysis, the bio-oil sample was dissolved in THF and filtered through a 0.45 μm PTFE syringe filter. Separation was achieved using THF as the mobile phase. Calibration was performed using polystyrene standards (580 to 19,720 Da) with a narrow molecular weight distribution. Data analysis was performed with PSS WinGPC UniChrom software (Massachusetts, USA).

^{13}C-NMR spectra were acquired on a Varian Unity Plus spectrometer (400 MHz, California, USA). A 90° pulse and an inverse-gated decoupling sequence with a relaxation delay of 10 s was applied. The sweep width was 225 ppm, and a total 1024 scans were recorded. Samples were prepared by dissolving about 100 mg of bio-oil in deuterated dimethyl sulfoxide (DMSO-d$_6$, Sigma-Aldrich, 99.5 atom% D). Heteronuclear single quantum correlation (HSQC) spectra were recorded on a Bruker NMR spectrometer (600 MHz, Germany). The following settings were used: a 11 ppm sweep width in the ^{1}H domain and a 220-ppm sweep width in the ^{13}C domain. NMR samples were obtained by rinsing the condenser and piping of the reactor after reaction with DMSO-d$_6$ instead of THF.

Larger scale pyrolysis of pigeon pea wood (average 2 mm particle sizes) was carried out in a controlled, continuously operated laboratory-scale set-up equipped with a fluidized bed reactor (Figure S1 in the Supplementary Information). Briefly, approximately 100 g of pigeon pea wood was fed into the reactor during 1 h. Silica sand (200 g) with a mean diameter of 250 μm was used as the bed material. A fluidized sand bed temperature of 475 °C and an N_2 flow rate of ca. 1.5 L min^{-1} were used. Pyrolysis vapors were condensed in two sequential electrostatic precipitators/condensers and weighted for mass balance calculations.

3. Results and Discussion

3.1. Description of a Typical Experiment

Proximate and ultimate analyses, as well as relevant physicochemical properties of the pigeon pea wood used for pyrolysis were compiled from the literature and are reported in Table 1 [35]. Notably, the lignin content of pigeon pea wood is significantly lower (18%) than the lignin content of most softwoods, which typically ranges from 26% to 37%. A TGA profile of the pigeon pea wood used in this study is presented in Figure S2 in the Supplementary Information. Pigeon pea wood was pyrolyzed in a small-scale setup using 1.0 g biomass sample. Benchmark pyrolysis experiments were initially performed at a temperature of 500 °C and a nitrogen flow rate of 11 mL min^{-1} using 0.9 mm particle size (3 trials). After the reaction, 46 wt.% ± 1.1 wt.% (relative to dry biomass intake) of a condensed product (two phases in the condenser, a dark brown heavy oil phase and a separate water phase) was obtained. Workup by the addition of THF resulted in the formation of a homogeneous (single-phase), brown liquid. The water content of this liquid was 19 wt.% (Karl–Fischer titration). A non-condensable gas phase (17 wt.% ± 0.7 wt.%) as well as a solid phase (ash and char) (23 wt.% ± 0.7 wt.%) were also obtained (mass balance closure of 86 wt.%). The gas phase was analyzed by GC-TCD and show the presence of CO (6 wt.% based on feed intake), CO_2 (9 wt.%), CH_4 (2 wt.%), propylene (0.3 wt.%), ethane (0.1 wt.%) and traces of ethylene and propane, suggesting the occurrence of decarboxylation/decarbonylation reactions during pyrolysis.

3.2. Optimization Studies

The pyrolysis process was subsequently optimized and validated. Measurements were performed at least in duplicate and the average yields are provided. Good reproducibility (standard deviation $\leq$ 1 wt.%) and mass balance closures ($\geq$85%, Table S1) were achieved in all the runs. Fifteen pyrolysis experiments were performed following the RSM method to determine the effects of temperature, particle size of pigeon pea wood and N_2 flow rate on the yield of bio-oil. The product yields are summarized in Table 2 (and Table S1 in the Supplementary Information). The best model (a reduced quadratic model) is given in Equation (3), with the coded values of A (temperature), B (particle size) and C (N_2 flow rate).

$$Biooil\ yield\ (wt.\%) = 46.16 - 0.24\,A + 3.58\,B + 0.093\,C + AB - 2.95\,AC + 4.85\,C^2 \tag{3}$$

Relevant statistical data in the form of an analysis of variance (ANOVA) are given in Table 3. From this table it is evident that the *F*-value of the model is high (27.28), implying that the model is significant and adequate to represent the actual relationship between the response and the variables. Moreover, the *P*-value of the model is less than 0.05 (0.0004), implying that the model is statistically significant. Figure 3 presents a parity plot of the experimental bio-oil yields versus the model predictions. It clearly reveals that the model yields are in good agreement with the experimental ones. The R^2 value (0.9646), in combination with high values for the predicted and the adjusted R^2, suggest that the model represent the dataset well. According to the model, the bio-oil yield is affected by all independent variables in a complex manner. The highest value of *F* (80.31) and a significant and lowest *P*-value (0.0001) imply that the biomass particle size (*B*) has a major impact on bio-oil yield.

Table 3. Analysis of variance (ANOVA) for the response surface analysis of bio-oil yield from pigeon pea wood pyrolysis.

Source	*Seq. SS* [a]	*DF* [b]	*MS* [c]	*F* [d]	*P* [e]
Model	164.06	6	27.34	27.28	0.0004
A (Temperature)	0.32	1	0.32	0.32	0.5920
B (Biomass particle size)	80.51	1	80.51	80.31	0.0001
C (N_2 flow rate)	0.033	1	0.033	0.033	0.8622
AB	4.04	1	4.04	4.03	0.0915
AC	18.19	1	18.19	18.15	0.0053
C^2	58.17	1	58.17	58.03	0.0003
Residual	6.01	6	1		
Lack of Fit	2.77	4	0.69	0.43	0.788
Pure Error	3.25	2	1.62		
Corr. Total	170.07	12			

Other statistics: $CV = 2.09\%$; $R^2 = 0.9646$; adjusted $R^2 = 0.9293$; predicted $R^2 = 0.8345$; adequate precision = 18.165

[a] Sum of sequence; [b] degrees of freedom; [c] mean square; [d] *F*-value; [e] *P*-value (probability > *F*).

The effects of temperature, particle size of pigeon pea wood and N_2 flow rate on the yield of bio-oil according to model predictions are presented in three-dimensional response surface plots. Figure 4 shows the interactive effects of particle size and N_2 flow rates on bio-oil yield at two temperatures (400 °C, left and 466 °C, right). The following observations can be drawn: (1) bio-oil yields are considerably reduced at intermediate N_2 flow rates, whereas the effect of temperature is less pronounced within the temperature window explored, and (2) bio-oil yields are surprisingly highest when using larger particle sizes. The latter observation is not expected considering that small biomass particle sizes are generally preferred in pyrolysis due to their faster and uniform heating. However, the positive effect of the use of large particles on oil yields was also reported by Abnisa et al. They showed that increasing the particle size from 0.5 mm to 2.5 mm at a constant temperature of 600 °C resulted in an increase in bio-oil yield (up to 43.5 wt.%) when using palm shells as feedstock [40]. Onay et al., on the other hand, found an optimum particle size between 0.6 and 1.8 mm to obtain maximum liquid yields (67 wt.%–68 wt.%) in the fast pyrolysis of rapeseed at either 500 °C or 550 °C in a fixed-bed reactor [41]. Akhtar and Amin propose that the unexpected higher yield of liquids when larger biomass particles are used is related to the chemical composition of the biomass feed [42]. The latter is supported by the work of Guedes et al., though they proved that the optimum particle size does depend not only on the composition of the biomass feed, but also on the operating parameters [43], making it difficult to generalize the effects of particle size. As such, the design and specification of the pyrolysis reactor system (i.e., relatively low heating rates than conventional fast pyrolysis) most likely also contributed to the observed higher yields of bio-oil when using larger pigeon pea wood particles.

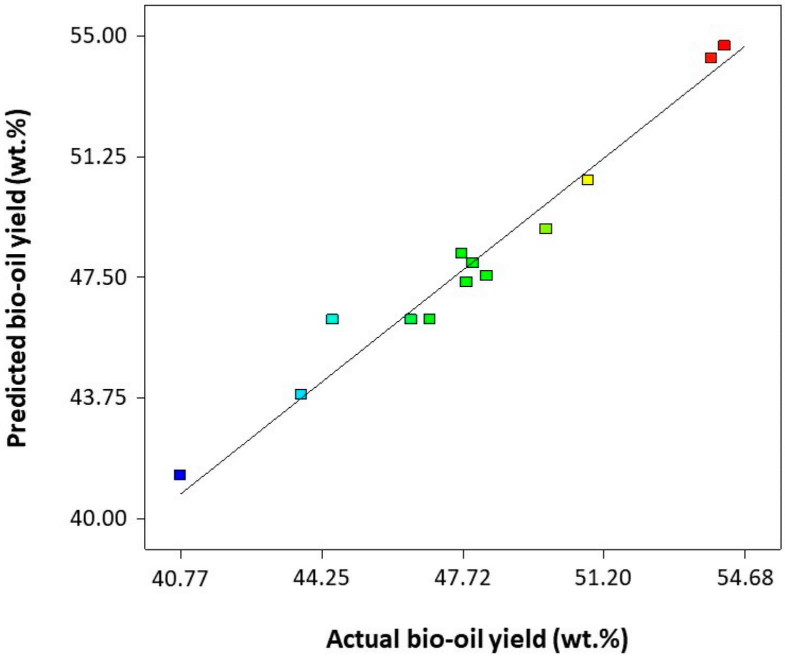

Figure 3. Parity plot showing the predicted and experimental bio-oil yields from pigeon pea wood pyrolysis.

As stated above, the data in Figure 4 also reveal that intermediate N_2 flow rates have a negative effect on yields and actually flow rates at either the high or low end are best. As such, it appears that two opposite variables are operative, one favoring high bio-oil yields at low N_2 flow rate and one at high N_2 flow rate. High gas flow rates are typically used in pyrolysis processes to decrease the residence time of vapors within the reactor, avoiding secondary cracking reactions leading to solids formation [44,45]. Hence, far, we do not have a clear explanation for the positive effects of low N_2 flow rates on bio-oil yields in the current setup.

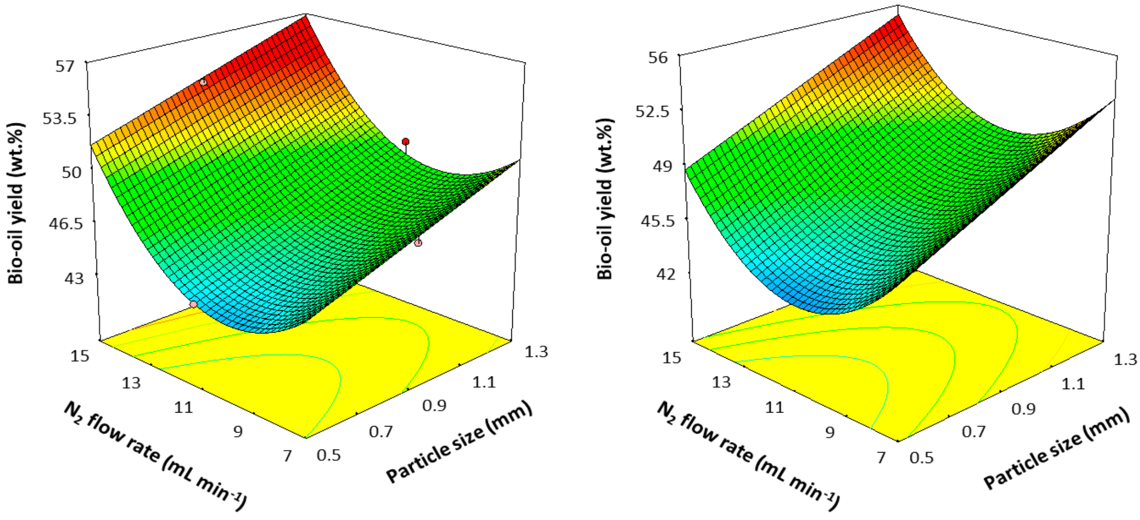

Figure 4. Response surface plots showing the effects of particle size and N_2 flow rate on the bio-oil yield from the pyrolysis of pigeon pea wood at a fixed temperature of 400 °C (**left**) and 466 °C (**right**).

3.3. Validation of Optimized Model Conditions and Comparison of Bio-Oil Yields Obtained in a Fluidized Bed Reactor

With the model available, the optimum pyrolysis temperature, biomass particle size and N_2 flow rate regarding bio-oil yield can be determined. The highest bio-oil yield predicted by the model was 54 wt.% at a temperature of 466 °C, a biomass particle size of 1.3 mm and a nitrogen flow rate of 14 mL min^{-1}. To verify the accuracy of the model, three validation experiments were performed at these optimum conditions. An average bio-oil yield of 52 wt.% was obtained, indicating that the model may be used within the experimental ranges to predict bio-oil yields with a good accuracy.

A preliminary scale-up experiment using a fluidized bed pyrolysis reactor at a scale of 100 g h^{-1} input was also performed. Pyrolysis of pigeon pea wood at 475 °C and a N_2 flow rate of 1.5 L mL^{-1} gave a non-optimized bio-oil yield of 44 wt.%. The latter is 8 wt.% lower than for the reactions in the small scale set up at close to similar conditions. As such, further experiments will be required in this setup to optimize the oil yields and these will be performed in subsequent studies.

3.4. Properties and Molecular Composition of the Bio-Oils

The physicochemical properties and composition of the bio-oil (i.e., water content, ash content, high heating value, total acid number, volatile matter, fixed carbon, etc.) from pigeon pea wood pyrolysis at optimum conditions were determined and the results are summarized in Table 4. The water content of the bio-oil (Karl–Fischer titration) was 20 wt.%. Low water contents in biomass and pyrolysis oils are preferred as water has a negative effect on the energy density [46,47].

Table 4. Relevant properties of the bio-oil [a] from pigeon pea wood pyrolysis at optimized conditions.

Properties	Values
TAN (mg KOH g^{-1})	84
Heating value (MJ kg^{-1})	29
Proximate analysis	
Ash (%)	0.2
Volatile matter (%)	51
Fixed carbon (%)	48
Elemental composition (wet basis)	
Carbon (%)	55
Hydrogen (%)	11
Oxygen (%)	34
Nitrogen (%)	0.01
Sulfur (%)	0.11
Molecular weight determination	
M_w (g mol^{-1})	440
M_n (g mol^{-1})	230
Polydispersity index (M_w/M_n)	1.9

[a] Tetrahydrofuran (THF)-collected bio-oil followed by removal of the THF by evaporation.

The ash content of the bio-oil based on TGA measurements was 0.16%, which is relatively low compared to bio-oils from other woody biomass sources such as pinewood (e.g., ash contents reported in the literature ranged from 0.03% to 3.0%) [48]. Low ash contents are preferred as ash has a negative effect on the storage stability and combustion characteristics [48]. The acidity of the bio-oil in terms of TAN value was 85 mg KOH g^{-1}, which is comparable to literature values for woody biomass such as pinewood (20–99 mg KOH g^{-1} sample) [38,49]. The acidity of bio-oils is mainly derived from the presence of small organic acids (e.g., acetic acid, propionic acid), which are primarily formed from the decomposition of hemicellulose components of biomass [38,49]. Other compounds in bio-oils known to add to the acidity include phenolics, fatty and resin acids and hydroxy acids [38,49].

The high heating value (HHV) of the bio-oil was calculated from the elemental composition using Boie Equation (Equation (2)) and found to be 28.8 MJ kg^{-1}, which is higher than the HHVs of bio-oils produced from pyrolysis of typical woods (17 MJ kg^{-1}) [50–52] and by far lower than the HHVs for crude oil based fuels (42 MJ kg^{-1}) [53]. This value is also much higher than the starting pigeon pea wood (15.6 MJ kg^{-1}). As such, considerable energy intensification has occurred during pyrolysis, combined with a reduction of ash contents.

The bio-oil contains 55% of carbon, 11% of hydrogen and 34% of oxygen and low levels of sulfur and nitrogen (<0.11%) (Table 4). To compare the elemental composition of the bio-oil from pigeon pea wood pyrolysis with that the starting biomass, a van Krevelen plot was constructed (Figure 5). In this figure, the values for wood and bio-oils from wood are given, as well as the value for crude oil for comparison [54,55]. When considering the biomass feeds, it is evident that the O/C and H/C values for pigeon pea wood are higher than those for "average" wood. This is due to the relatively low content of lignin in the feed (*vide supra*). After pyrolysis, the H/C value increases and the O/C value is reduced. A similar trend is observed for the pyrolysis of wood. Of interest is the higher H/C ratio of the bio-oil derived from pigeon pea wood than for other wood sources. It is even at the high end when compared to the H/C ratio of crude oils. Though further processing to a crude oil type of feed will be required (e.g., by catalytic hydrotreatment), this is an interesting observation as it implies that the hydrogen consumption for hydroprocessing, a key variable cost contributor for the process, will be lower compared to other woody bio-oils.

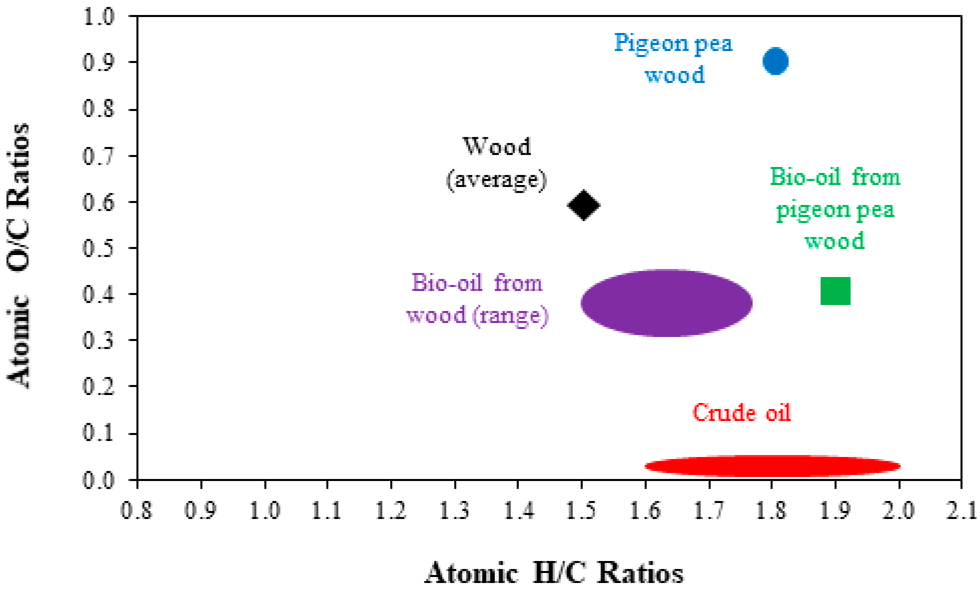

Figure 5. van Krevelen diagram (dry basis) for pigeon pea wood (blue circle) and its product bio-oil (green square) obtained after pyrolysis reaction at optimized conditions, in comparison with woody biomass feeds and products [35].

The chemical composition of the product oil was investigated by GC–MS. Table 5 summarizes the compounds identified, together with their amounts based on peak area. Phenolic compounds and their derivatives are abundant in the bio-oil (total 40.7% GC–MS peak area), namely, 2-methoxyphenol (guaiacol), 2,3-dimethylphenol (xylenol), 2,6-dimethoxyphenol (syringol), etc. The presence of phenolics in bio-oil is thought to be due to thermal decomposition of the lignin fraction in the feed [56–59]. The presence of high amounts of phenolics is surprising, as the feed contains relatively small amounts of lignin (*vide supra*). Speculatively, it is possible that the lignin in the pigeon wood has a relatively low molecular weight and is less condensed than in typical lignocellulosic biomass sources. As a consequence, thermal pyrolysis may lead to higher than anticipated amounts of phenolics. Renewable phenolic compounds are of interest considering their industrial applications such as the use as precursors for bio-based aromatics and products thereof (e.g., resins) [20–22]. In addition, low-molecular weight carboxylic acids, ketones, aldehydes and esters (e.g., C10–C12) were present, which are formed from the thermal depolymerization of the cellulose and hemicellulose fraction in the pigeon pea wood sample [56–59].

Table 5. GC detectables in the bio-oil obtained from pigeon pea wood pyrolysis at optimized conditions (semi-quantitative analysis by GC–MS).

Functional Group/Compound Name	Peak Area (%)
Acids	
acetic acid	8.9
propanoic acid	1.3
4-hydroxy-3-methoxybenzoic acid	3.3
Ketones	
1-hydroxy-2-propanone	5.6
1-hydroxy-2-butanone	1.4
1-(acetyloxy)-2-propanone	1.2
Butyrolactone	3.0
3-methyl-1,2-cyclopentanedione	3.9
3-ethyl-2-hydroxy-2-cyclopenten-1-one	1.1
1-(2,4,6-trihydroxy-3-methylphenyl)-1-butanone	2.6
Aldehydes	
propanal	1.3
furfural	1.2
pentanal	1.8
4,6-dimethoxysalicylaldehyde	0.8
4-methyl-2,5-dimethoxybenzaldehyde	1.6
Esters	
2-methyl-2-propenoic acid ethyl ester	0.8
Phenolics	
phenol	1.5
2-methylphenol	0.8
2-methoxyphenol	8.2
2,3-dimethylphenol	0.6
2-methoxy-4-methylphenol	2.6
3-methoxy-1,2-benzenediol	1.5
4-ethyl-2-methoxyphenol	3.4
2-methoxy-4-vinylphenol	2.3
2,6-dimethoxyphenol	11
eugenol	1.4
2-methoxy-4-(1-propenyl)phenol	3.4
2,6-dimethoxy-4-(2-propenyl)phenol	1.7
5-tert-butylpyrogallol	2.3
N- and S-containing compounds	
3-amino-2,6-dimethoxypyridine	9.4
1-methyl-N-vanillyl-(+-)-2-phenethanamine	1.5
4-methoxy-2-methyl-1-(methylthio)benzene	2.4
1-[4-(methylthio)phenyl] ethanone	0.3
Others	
3-furanmethanol	1.7
1,2,3-trimethoxy-5-methylbenzene	4.2
	100

The GPC chromatogram for the bio-oil obtained from pigeon pea wood pyrolysis at optimized conditions is presented in Figure 6. It shows a number of sharp strong peaks in the low molecular weight region (i.e., between ~100 and 200 g mol^{-1}), an indication for the presence of considerable quantities of low molecular weight products, in line with the GC-data. Higher molecular weight compounds (i.e., dimers, trimers and oligomeric products from depolymerization of the individual biopolymers in the feed) between ~300 to 500 g mol^{-1} are also present. Notably, some tailing is observed, suggesting the presence of higher molecular weight fragments in the bio-oil. The molecular weight (M_w) of bio-oil was 440 and the number averaged molecular weights (M_n) was 230 g mol^{-1}. Hassan et al. and Ingram et al. determined the molecular weights of pyrolysis oils derived from pinewood and oak wood at 450 °C and found a similar weight average molecular range from 390 to 460 g mol^{-1} [60,61].

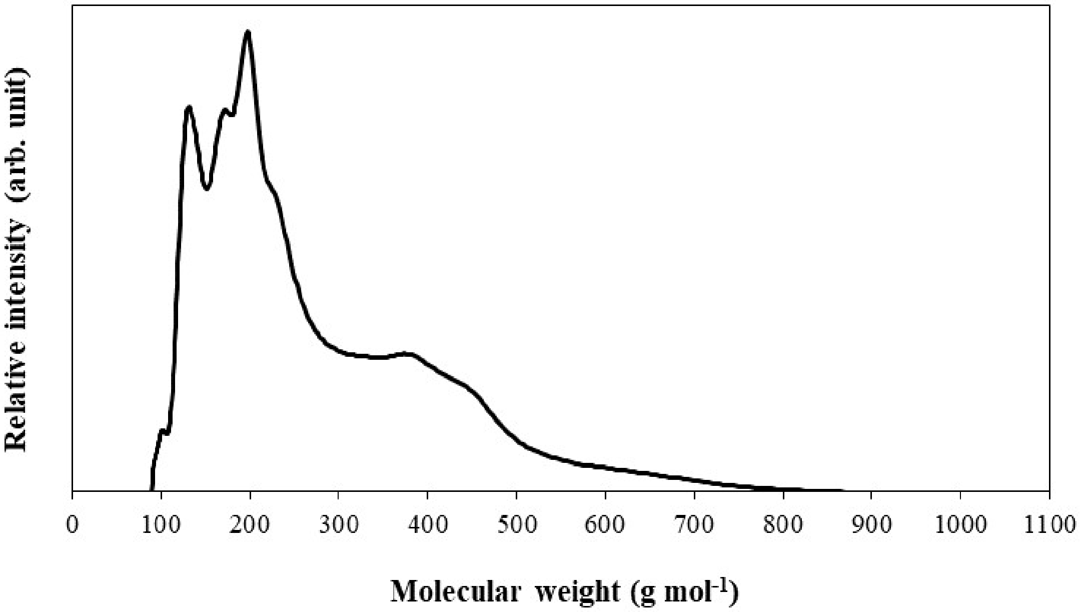

Figure 6. GPC chromatogram of bio-oil obtained from pigeon pea wood pyrolysis at optimized conditions.

Further insights into the chemical composition of the pigeon pea wood bio-oil were obtained by NMR measurements (^{13}C- and 2D HSQC-NMR). The advantage of NMR over GC is that information on the chemical composition of the complete sample is obtained and not only of the GC detectable fraction. Figure 7 shows the ^{13}C-NMR spectrum of the pigeon pea wood bio-oil, showing numerous peaks of different functional groups. Table 6 summarizes the ^{13}C-NMR chemical shift ranges and their assignments for various types of carbon present in the bio-oil [58,62–64]. By integration of the spectrum, a rough estimate of the contents of various functional groups in the bio-oil sample can be obtained (Table 6). Carbonyl groups are clearly present and arise from the presence of aldehydes, ketones and carboxylic acids, as confirmed by GC–MS. The aromatic carbons are associated with the presence of phenolic compounds like guaiacol and syringol (Table 5, supported by the presence of—OMe groups in the spectrum). The clear peaks in the range δ 60–80 ppm are associated with the presence of C–O groups, e.g., from sugar monomers and products thereof, as well as oligomeric sugars from the (hemi)cellulose fraction.

Finally, further insights in the chemical composition of pigeon pea wood bio-oil were obtained by 2D HSQC-NMR measurements. 2D-NMR analysis of bio-oil has two main advantages over the traditional 1-D ^{1}H- and ^{13}C-NMR: (1) the overlapping peaks, occurring to a large extent when several components are present in the sample, are reduced due to spreading of the signals into two dimensions, and (2) a higher sensitivity and shorter relaxation times are achieved. ^{1}H-^{13}C-HSQC NMR provides a 2-D plot, with on one axis the ^{1}H-NMR shift and the ^{13}C-NMR shift on the other axis. Every peak is associated with a particular C-H unit in a certain chemical environment. Ben and Ragauskas used this NMR method to characterize pyrolysis oils derived from the slow pyrolysis of lignin, cellulose and pinewood [63]. Figure 8 shows the 2D HSQC-NMR spectrum recorded for the pigeon pea wood bio-oil. A number of relevant regions were assigned belonging to different C-H bonds: (1) aromatic C-H bonds belonging to, among others, substituted phenolics (δ 105–140 ppm in the ^{13}C-NMR dimension and δ 5.5–7.5 in the ^{1}H-NMR dimension), (2) ether groups (δ 58–104 ppm in the ^{13}C-NMR dimension and δ

4.0–5.4 in the ^{1}H-NMR dimension, (3) methoxy groups (δ 54–57 ppm in the ^{13}C-NMR dimension and δ 3.7–3.9 ppm in the ^{1}H-NMR dimension) and (4) aliphatic C-H bonds (δ 5–40 ppm in the ^{13}C-NMR dimension and δ 0.7–2.8 ppm in the ^{1}H-NMR domain). The spectrum confirms the 1D ^{13}C-NMR data and reveals the presence of a large proportion of compounds with aliphatic C-H bonds and C–O bonds.

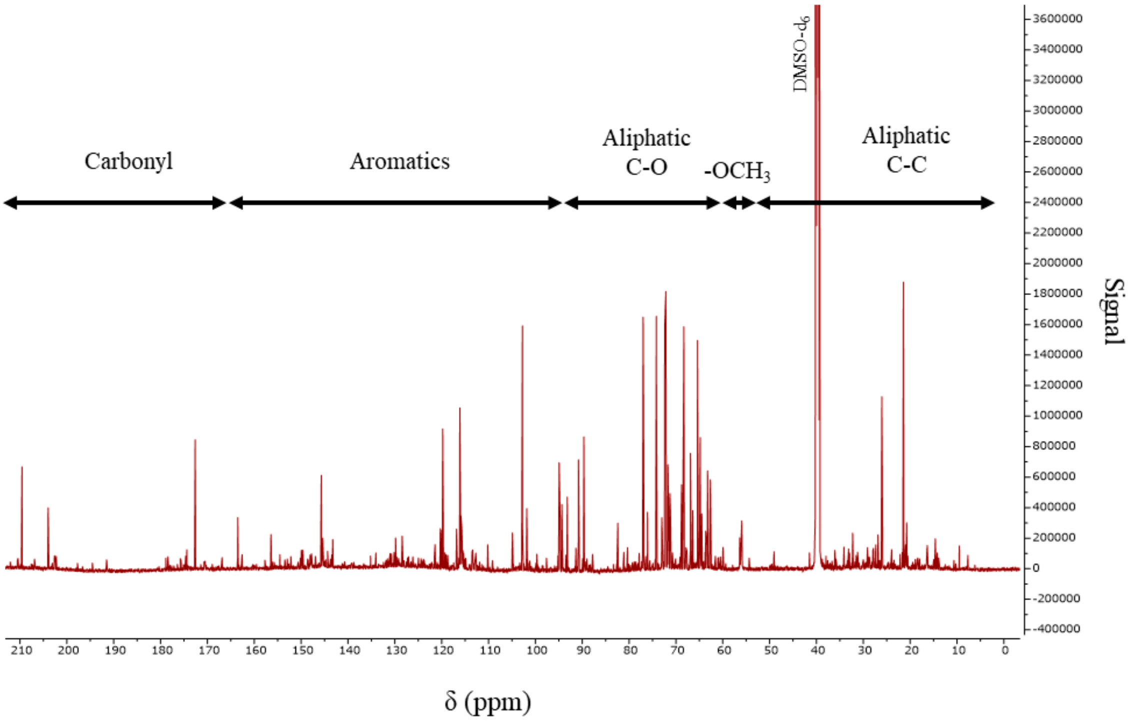

Figure 7. ^{13}C-NMR spectrum of bio-oil obtained from pigeon pea wood pyrolysis at optimized conditions, showing several peaks belonging to different functional groups as indicated.

Table 6. ^{13}C-NMR integrations for specific chemical shift regions for bio-oil from pigeon pea wood pyrolysis at optimized conditions.

Type of Carbon	Chemical Shift Region, δ (ppm) [57,61]	Carbon Content (% of All Carbon in Each Spectrum)
Carbonyl	215–166.5	7.4
Aromatic	166.5–95.8	20.9
Aliphatic C–O	95.8–60.8	36.5
Methoxyl	60.8–55.2	3.6
Aliphatic C–C	55.2–0.0	26.5
Methyl Aromatic	21.6–19.1	4.3
Methyl-Aromatic at ortho position of a -OH or -OCH$_3$ group	16.1–15.4	0.8

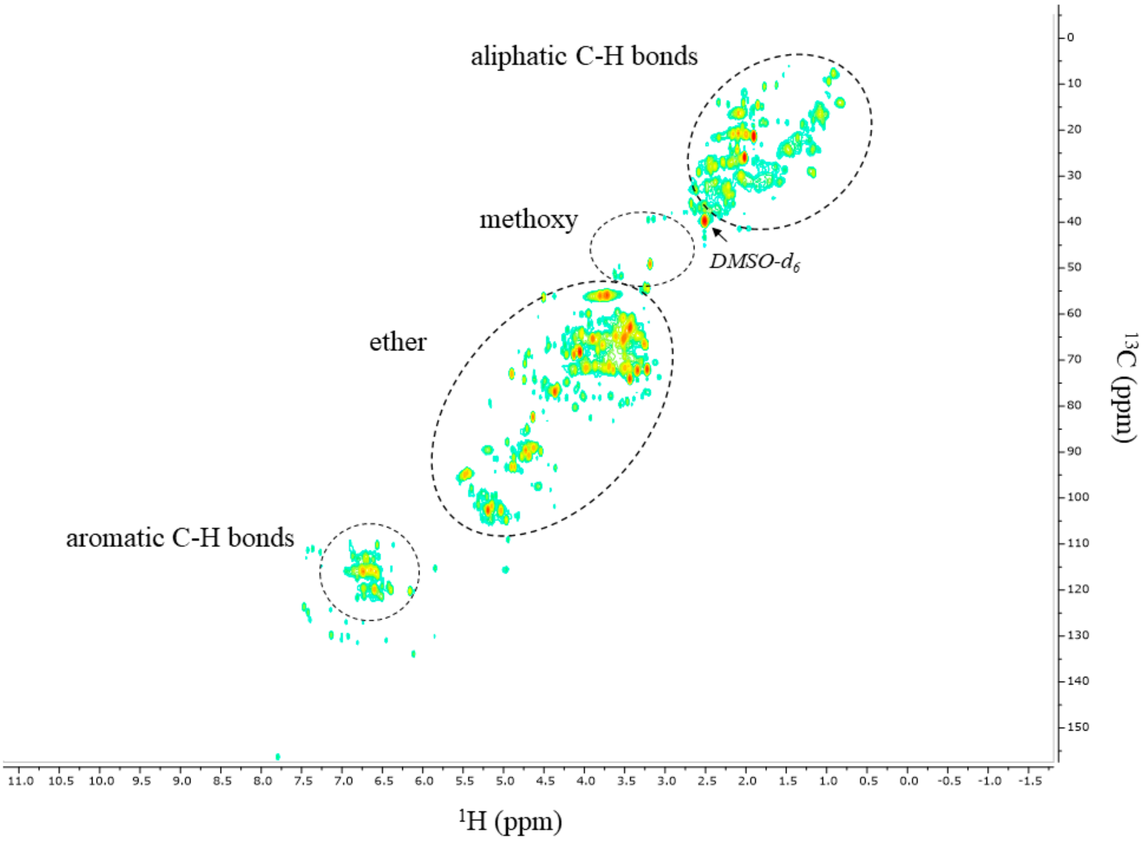

Figure 8. 2-D HSQC-NMR spectrum of bio-oil obtained from pigeon pea wood pyrolysis at optimized conditions, showing the aliphatic C–C, methoxy, ether and aromatic C-H groups.

4. Conclusions

An experimental study was performed on the pyrolysis of pigeon pea wood, a local and widely available biomass resource in among others the Philippines. After an optimization study, the highest bio oil yield attained was 54 wt.% on dry feed intake. The effects of important process variables were modeled and showed that particularly the biomass particle size and N_2 flow rate affect the bio-oil yield in a complex manner. Validation experiments (three replicate runs) indicated good agreement between the average experimental (52 wt.%) and predicted bio-oil yields. Preliminary pyrolysis experiments for pigeon pea wood on a somewhat larger scale (100 g h^{-1}) using a fluidized bed reactor resulted in a non-optimized bio-oil yield of 44 wt.%.

Characterization of the bio-oil obtained at optimum pyrolysis conditions revealed that the oil has a low ash content and a heating value considerably higher than the feed. In addition, the bio-oil has a higher H/C ratio and a similar O/C ratio than reported for other woods, which is likely due to the presence of low amounts of lignin in the pigeon pea wood feed. This is an attractive feature when considering subsequent hydrotreatment processes to obtain hydrocarbon fuels. GC–MS analysis showed that the bio-oil contains a vast range of functional groups of aliphatic, aromatic, aldehydes, ketones, carboxylic acids, phenolics. GPC analysis of bio-oil confirmed not only the presence of these low MW compounds, but also the presence of oligomeric products. NMR measurements (^{13}C- and HSQC-NMR), which give full information on the chemical composition of the bio-oil, confirms the GC–MS data for the low molecular weight, volatile fraction.

This present work is expected to contribute to the development of efficient biorefining concepts for pigeon pea. It shows that residues in the form of wood may be valorized by pyrolysis to a liquid energy carrier, which has a higher energy density, is easier to transport and contains less ash than the original feed. These findings may be used, among others, in the Philippines, to valorize local waste streams for energy generation, with a positive impact on local development and economies. In addition, this work may have a positive effect on the ambitions of many countries to develop sustainable energy solutions based on alternatives for fossil resources.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/11/2778/s1, Figure S1: Schematic diagram of the fluidized bed reactor set-up used for the pyrolysis of pigeon pea wood, Figure S2: TGA profile of the pigeon pea wood sample used for pyrolysis (N_2 atmosphere), Table S1: Solid, liquid (bio-oil) and gas yields from pigeon pea wood pyrolysis performed at various conditions in a semi-continuous reactor set-up.

Author Contributions: M.R.C.T. performed all the pyrolysis runs in the semi-continuous reactor. M.R.C.T. and H.C.G. analyzed the products and prepared the manuscript draft. E.W. performed the pyrolysis experiments in the fluidized bed reactor. H.C.G. and H.J.H. supervised the research, manuscript preparation and revision. All authors contributed to the conceptualization, writing, data analysis and review/editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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