Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk

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HIGHLIGHTS
- Pyrolysis behaviors of four agriculture residues were compared.
- Higher bio-oil yield obtained (47.3 wt%) for corn cob.
- Optimum temperature 450 °C for CC & RH and 400 °C for RS & WS.
- Organic carbon conversion high in CC and RH than WS and RS.

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ABSTRACT

Pyrolysis studies on conventional biomass were carried out in fixed bed reactor at different temperatures 300, 350, 400 and 450 °C. Agricultural residues such as corn cob, wheat straw, rice straw and rice husk showed that the optimum temperatures for these residues are 450, 400, 400 and 450 °C respectively. The maximum bio-oil yield in case of corn cob, wheat straw, rice straw and rice husk are 47.3, 36.7, 28.4 and 38.1 wt% respectively. The effects of pyrolysis temperature and biomass type on the yield and composition of pyrolysis products were investigated. All bio-oils contents were mainly composed of oxygenated hydrocarbons. The higher area percentages of phenolic compounds were observed in the corn cob bio-oil than other bio-oils. From FT-IR and 1H NMR spectra showed a high percentage of aliphatic functional groups for all bio-oils and distribution of products is different due to differences in the composition of agricultural biomass.

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1. Introduction

Biomass has been considered as a potential and renewable source of energy that can be used for the production of variety of chemicals and materials (Bridgewater and Grassi, 1991; Chum and Overend, 2001; Antal, 1983). The advantages of biomass over conventional fossil fuels are their low sulfur and nitrogen contents and no net emissions of CO2 to the atmosphere (Bridgewater and Grassi, 1991; Probstein and Hicks, 1982). Biomass resources cover a wide range of materials such as forest residues, energy crops, organic wastes, agricultural residues, etc. Agricultural waste, a readily available biomass, is produced annually worldwide and is vastly underutilized (Williams and Nugranad, 2000).

Agricultural biomass residues are composed of cellulose, hemicellulose and lignin and possess a high-energy content (Meshitsuka and Isogai, 1996; Worasuwannarak et al., 2007). Agricultural residues such as rice straw and rice husks are abundant in rice growing countries such as Brunei, China and India (Gidde and Jivani, 2007). Agriculture residue such as corn cob and wheat straw are also being a viable feed for bio-fuels production.

In developing countries, the large quantities of agricultural residues are currently utilised either as raw material for paper industry, or as animal feed sources. But generally since the collection and disposal of these residues are becoming more difficult and expensive, it is left unused as waste material or simply burned in the fields, thereby creating significant environmental problems. The conversion methods may be physical, biological, chemical or thermal to give a solid, liquid or gaseous fuel. The most promising method seems to be thermochemical one for the production of bio-oils. Pyrolysis of biomass is one of the most efficient technologies used to produce biofuels. The process is carried out at elevated
temperatures under an inert atmosphere which is maintained using either argon or nitrogen gas. The process yields bio-oil, solid residue, and gaseous products. These products can be used directly or after processing as fuel (Yin et al., 2013).

Previous work on pyrolysis of corn cob, wheat straw, rice straw and rice husk has been carried out (Balagarurumathy et al., 2015; Park et al., 2014; Pottmaier et al., 2013; Yu et al., 2016; Cao et al., 2004; Ceramic et al., 2016; Shariff et al., 2016). Park et al. used around 100 g of rice straw and carried out slow pyrolysis at 300, 400, 500, 600 and 700 °C with a heating rate of 10 °C min⁻¹. Almost same yields of bio-oil and bio-char (39%) have been obtained at higher temperatures above 500 °C. The bio-oil yield slightly decreased, while the gas yield increased at 700 °C. Rice straw pyrolysis in hydrogen and nitrogen environments has been carried out by Balagarurumathy et al. and observed maximum bio-oil 31.0% and 12.8% under N₂ and H₂ atmosphere at 400 °C in both cases. The higher amount of bio-oil was observed under the N₂ environment than H₂ environment. Pottmaier et al. carried out slow pyrolysis of wheat straw and rice straw at 250–900 °C. They observed that slow pyrolysis, in 100 mL min⁻¹ nitrogen, for RH and WS, at a heating rate of 50 °C min⁻¹, shows an increase of volatiles release as a function of final pyrolysis temperature for 250, 350, 500, 600, 700, 900 °C as follows: 31.5 ≤ 35.7 < 64.1 ≤ 62.6 < 65.9 < 68.1 (wt%) (for wheat straw), 21.3 < 53.4 ≤ 64.6 < 60.9 < 63.9 < 63.4 (wt%) (for rice husk), Cao et al. has carried out pyrolysis of corn cob and concluded that the liquid products were approximately 34–40.96 (wt%), the gas products were 27–40.96% (wt%) and the solid products 23.6–31.6 (wt%). There were fewer changes for the yields of these products above 600 °C. Shariff et al. were investigated the characteristic of corn cob as a biomass feedstock for slow pyrolysis process and observed that the weight loss of corn cob feedstock was prominent in the temperature range of 250–350 °C. Two distinct peaks of derivative thermogravimetric (DTG) curve indicate the difficulty of corn cob feedstock to degrade due to its high fixed carbon content. The overall findings showed that corn cob is suitable to be used as the feedstock for slow pyrolysis because of its high volatile matter and low percentages of nitrogen and sulfur. The main interest in pyrolysis process is conversion of biomass to potential fuels such as bio-oil and bio-char which can be stored or transported much easier as compared to biomass. In addition, bio-oil obtained from the pyrolysis process can be considered as a source of useful chemicals and bio-chars can be converted to value added products such as activated carbons and potentially can also be used for soil amendment (Meyer et al., 2011).

To the best of our knowledge there is no report on slow pyrolysis of agriculture biomass residue and comparisons on production of bio-oil and bio-char. The focus of this research is to study the effects of different pyrolysis temperatures (300–450 °C) on the slow pyrolysis of corn cob, wheat straw, rice straw and rice husk to understand comparative studies under identical conditions. The experiments have been carried out at temperatures of 300, 350, 400 and 450 °C in nitrogen atmosphere and products such as bio-oil and bio-char have been obtained. The liquid and solid products have been characterized using various analytical techniques such as Fourier Transform-Infrared Spectroscopy (FT-IR), Nuclear Magnetic Resonance Spectroscopy (¹H NMR), Gas Chromatography–Mass Spectrometry (GC–MS), Total organic carbon (TOC) and X-ray Diffraction (XRD).

2. Materials and methodology

2.1. Materials

Agriculture biomass residues Corn cob (CC), Wheat straw (WS), Rice straw (RS) and Rice husk (RH) were used in this study collected from Uttarakhand, Dehradun district (India). They were dried in sun and then crushed and sieved to obtain particle size between 0.5 and 2 mm.

2.2. Characterisation methods

The thermo-gravimetric analysis was carried out in Shimadzu DTG-60 instrument. These tests were conducted using 2–10 mg of the agriculture biomass residue sample material at a heating rate of 10 °C/min with a temperature range of 25–900 °C in the N₂ atmosphere. The gross calorific value was found using Parr 6300 Bomb Calorimeter. The elemental composition of C, H, N, S and O was measured by using an Elementar vario micro cube unit. Moisture content has been obtained using HR-83 Mettler Toledo Halogen Moisture Analyzer. The ¹H NMR spectra have been recorded in the Bruker Avance 500 Plus instrument using CDCl₃ as a solvent. Powder X-ray diffraction patterns were collected on Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu Kα radiation source. Diffraction patterns in the 2°–8° region have been recorded with a 0.04 step size (step time = 4 s). The FT-IR spectra were recorded on Nicolet 8700 FT-IR spectrometer over a range of 400–4000 cm⁻¹ with the sample powder diluted in KBr plates. The organic fraction of the bio-oil was analyzed using gas chromatography–mass spectrometry (GC/MS, Agilent 7890 B). The carrier gas was He and column flow rate was 1 ml min⁻¹. A HP-1 column (25 m × 0.32 mm × 0.17 μm) was used for the separation. An oven isothermal program was set at 50 °C for 2 min, followed by a heating rate of 5 °C min⁻¹ till 280 °C where it was held for 5 min. The injected volume was 0.4 μl in a split less mode. Compounds were identified by way of the National Institute of Standards and Technology (NIST) library of mass spectra. TOC analysis of feed and bio-char was performed for obtaining total organic carbon conversion of the feed by using Shimadzu TOC-L unit with solid sample module SSM-5000A. Volatile matter has been calculated by measuring the weight loss in the sample after placing it in a muffle furnace at 950 °C for 2 min similar to ASTM-D3175. Volatile matter and ash analysis of the feed was carried out using oven dried feedstock.

2.3. Experimental procedure

Slow pyrolysis of corn cob, wheat straw, rice straw and rice husk were performed in a glass reactor (length: 280 mm; i.d. 34 mm) under atmospheric pressure of nitrogen and it has shown in Fig. S1. Briefly, 10 g of biomass was loaded into the reactor and the residual air in the reactor was purged using carrier gas nitrogen (flow rate: 50 ml min⁻¹). The starting temperature was the ambient room temperature at 25 °C and the heating rate to reach the pyrolysis temperature was set around 20 °C min⁻¹. Once final pyrolysis temperature was attained, the reactor was maintained at the required temperature for a period of 1 h to ensure that all condensable vapours were collected. Biomass bed temperature has been taken as the pyrolysis temperature and another thermocouple indicated the skin temperature of the reactor. The vapours formed after the reaction was condensed using cooling water maintained at 4 °C (Krishna et al., 2015). Water in bio-oil was removed by the addition of anhydride sodium sulphate and diethyle ether was used to recover the organic fraction. Conversion as defined in this process is the amount of solid that has been converted into liquid or gaseous products. The remaining solid after the reaction left in the reactor is termed as bio-char. Various equations to calculate the yield of various fractions are given below (Krishna et al., 2015).

Bio – oil yield, wt.% = \[ \frac{(W_4) - (W_1)}{W_2} \times 100 \] Weight of feed
Weight of empty measuring cylinder.

Reaction, \( W_4 \) = Weight of measuring cylinder with bio oil, \( W_3 \) = Weight of empty measuring cylinder.

Conversion, \( \% = \frac{W_1 - W_2}{W_1} \times 100 \)

Where, \( W_1 = \) Weight of empty reactor, \( W_2 = \) Weight of reactor after reaction, \( W_4 = \) Weight of measuring cylinder with bio oil, \( W_3 = \) Weight of empty measuring cylinder.

The experiments have been carried out in duplicates and the average values have been reported which are within the standard deviation of ±1%. The organic fraction of the bio-oil was characterised using FT-IR, \(^1\)H NMR and GC–MS. The solid bio-char has been characterised using TGO, FT-IR and XRD.

3. Results and discussions

3.1. Characterization of agriculture biomass residues

The ultimate and proximate analysis of corn cob, wheat straw, rice straw and rice husk are shown in Table 1. The contents of carbon and hydrogen in rice husk and corn cob were higher than that in rice straw and wheat straw. From the elemental composition perspective, sulfur and nitrogen were found to be in small amounts in all samples except rice husk that has highest nitrogen and corn cob that has highest sulfur content. The estimated moisture contents of available agriculture biomass residue showed slightly different results for most of the agriculture biomass residue. The marginal differences in reported values are mainly due to agricultural biomass residue obtained from different feed. The lowest volatile content was found in the rice husk i.e. 73.41 wt% and the highest volatile content in the corn cob i.e. 91.16 wt%.

The samples of corn cob, wheat straw had low ash contents that were less than 7 wt%, whereas in the case of rice straw and rice husk had substantially higher ash content i.e. greater than 15. It is beneficial from another perspective that the inorganic compounds present in the agriculture waste resources with higher ash contents have potential to be used as catalysts in the thermal conversion technologies e.g. gasification and pyrolysis (Kenney et al., 2013).

The calorific values of the samples are reported in the ultimate analysis (see Table 1). The heating/calorific values of the agriculture waste samples determined by Bomb Calorimeter. Corn cob showed the highest highest heating values (HHV) i.e. about 16 MJ/kg. Whereas, in the case of rice husk showed the lowest HHV value i.e. about 12.87 MJ/kg. The considerable heating values of the agriculture waste residues showed that these locally available renewable resources can potentially be converted to substantial amount of bio-energy products from effective conversion technologies.

Thermal decomposition of four agriculture residues was determined by thermo gravimetric analysis (TGA) under \( N_2 \) atmosphere. DTG (rate of weight loss) and TGA (weight loss) curves are presented as supplementary figures Fig. S2a, S2b, S2c and S2d. Thermal decomposition of residues consist of mainly three stages: the loss of moisture bound by at low temperature around 100 °C, primary pyrolysis in the temperature range (200–500 °C) and secondary decomposition at high temperatures over 700 °C (Brebu and Vasile, 2010). Below 120 °C, the weight loss in the residues corresponded to free water evaporation. For lignocellulosic biomass, the primary classes of thermally degradable biopolymers are cellulose, hemicelluloses and lignin. Hemicellulose decomposes in the temperature range of 220–315 °C. Cellulose pyrolysis occurs at higher temperature range (315–400 °C). Among the three components, lignin is the most difficult to decompose, which covers a wider temperature range of up to 900 °C. DTG showed the maximum weight loss in four agriculture residues were between 310 and 342 °C. Major decomposition of agriculture residues happened slowly in a wide range (300–450 °C) of temperatures with a maximal mass loss rate at 312, 310, 302 and 342 °C of corn cob, wheat straw, rice straw and rice husk due to the ultimate, proximate and chemical composition were different in the different agriculture residues. The FT-IR spectra of four agriculture residues (corn cob, wheat straw, rice straw and rice husk) is shown in Fig. S3. All the agriculture residues showed sharp peaks corresponding to the 3424 cm\(^{-1}\) stretching vibrations is originated due to stretching of O–H groups for intra-molecular hydrogen bonds between cellulose chains. The bands at around 2914 cm\(^{-1}\), related to asymmetric and symmetric methylene stretching in the spectra of all the agriculture residues. The band around 1380–1430 cm\(^{-1}\) is associated with the amount of the crystalline cellulose and the intensity of this band is more pronounced in corn cob as compared to others may be due to high cellulose content. The bands at ~1246, ~1375 and ~1157 cm\(^{-1}\) are assigned to C–H stretching, CH\(_2\) wagging and C–O stretching respectively in cellulose. Absorption bands at ~1638 cm\(^{-1}\) are originated from lignin, which includes the aromatic skeleton vibrations involving both C–C stretching. Stretching vibrations at 1246 and 1732 cm\(^{-1}\) is due to C=O and C–O bonds of the acetyl ester units present in hemicelluloses (Yuan et al., 2015). The bands at 1740–1730 and 1560–1480 cm\(^{-1}\) for the entire four agriculture residue can be considered due to hemicellulose content and its showed crystallinity, which is supported by XRD also (Meshitsuka and Isogai, 1996).

3.2. Product yields

Slow pyrolysis of corn cob, wheat straw, rice straw and rice husk under nitrogen atmosphere has been carried out at 300, 350, 400 and 450 °C. The pyrolysis products yield obtained from corn cob, wheat straw, rice straw and rice husk consisting of gas, bio-oil and bio-char is presented in Table 2.

The maximum bio-oil yield of 47.3, 36.7, 28.4 and 38.1 wt\% were obtained at 450, 400, 400 and 450 °C for corn cob, wheat straw, rice straw and rice husk respectively. As the temperature increased from 300 to 400 °C, the bio-oil yield increased in the case of wheat straw and rice straw. With further increase in the temperature, bio-oil yield decreased. But for corn cob and rice husk, with the temperature elevated from 300 to 450 °C, the bio-oil yield increases. The yield of solid bio-char of corn cob, wheat straw, rice straw and rice husk were decreased as the temperature increases from 300 to 450 °C and the gas yield increased steadily from 350 to 450 °C. The bio-oil yield increases and conversion was seen to increase with increase in temperature due to the primary decomposition of holocellulose and lignin. Previous studies showed that
bio-oil yields from the pyrolysis of biomass increased incrementally as the temperature was raised to a certain temperature (Balagurunmurthy et al., 2015; Krishna et al., 2016). After this specific temperature that has been changed depending on the conditions (i.e., type of biomass, type of reactor, and type of pyrolysis), further increases in pyrolysis temperatures generated lower yields of bio-oils and increasing the yields of non-condensable gas products due to secondary cracking. It is believed that each biomass has the potential to provide a maximum bio-oil yield at a certain pyrolysis temperature. It is clearly seen from Table 2, that each biomass has the potential to provide a maximum bio-oil yield at a certain pyrolysis temperature. For both wheat straw and rice straw maximum bio-oil yield was observed at 400 °C, whereas in the case of corn cob and rice husk maximum bio-oil yield was observed at 450 °C. Product distribution obtained at different temperatures from different types of agriculture biomass residues suggested that it had a significant effect on product distribution due to the structural differences in the different biomass as evident from TGA/DTG and FTIR.

### 3.3. Total organic carbon (TOC) analysis of corn cob, wheat straw, rice straw and rice husk and bio-chars

To understand the conversion on the basis of total organic carbon (TOC), TOC analysis of corn cob, wheat straw, rice straw and rice husk and bio-chars obtained after pyrolysis at different temperatures was investigated and results are presented in Table S1. TOC results indicated that rice husk showed better organic conversion than corn cob, wheat straw and rice straw. Carbon, the main element in all of the produced bio-chars was present in significantly greater amounts in the bio-chars than in the agriculture residue. Relatively the total organic conversion is higher in the case of rice husk bio-chars than the other residues. The highest conversion of raw biomass has been occurred (56.62%) in the case of rice husk. The higher amount of organic carbon (54.98, 53.24, 54.41 and 51.78%) at 300, 350, 400 and 450 °C were present in the case of wheat straw bio-chars than other three agriculture residues. An increase in the carbon content of bio-chars produced by pyrolysis to makes them suitable precursors for the production of activated carbons.

### 3.4. Bio-oil characterization

**3.4.1. Gas chromatography–mass spectrometry (GC–MS) of bio-oil**

GC–MS analysis has been carried out to identify the compounds in bio-oils from the pyrolysis of biomass. The effect of temperature on components of bio-oil from corn cob, wheat straw, rice straw and rice husk pyrolysis and their relative mass contents detected by GC–MS. Here we have shown only optimum temperatures bio-oils in Table 3. Small peaks on the chromatograms or peaks belonging to unidentified compounds are not presented in the table. As expected, the pyrolysis bio-oils were a complex mixture of organic compounds containing a mass of highly oxygenated compounds, such as phenols, ketones carboxylic acids, etc. It has been reported that bio-oils produced from different types of biomass samples under similar conditions have similar composition. Table 3 shows that the corn cob, wheat straw, rice straw and rice husk bio-oils (450 °C, 400 °C, 400°C and 450 °C) had a large amount of compounds including Phenol, 2-methoxy (relative area were 12.4%, 8.5%, 4.4%, 2.0% respectively), Phenol, 2,6-dimethoxy (relative area were 7.2%, 6.6%, 2.5%, 1.3% respectively), 2–methoxy-4-vinylphenol, (relative area were 7.9%, 6.2%, 2.8%, 1.9% respectively), Phenol, 4-ethyl-2-methoxy (relative area were 4.9%, 4.1%, 3.1%, 1.4% respectively), Furamethanol (relative area were 4.1%, 3.4%, 3.1%, 1.1% respectively), Cathecol (relative area were 5.2%, 4.1%, 3.1%, 3.5% respectively), Phenol, 2-methyl (relative area were 3.1%, 2.3%, 3.7%, 1.8% respectively), Phenol, 4-ethyl (relative area were 6.0%, 2.1%, 4%, 4.3% respectively), Benzofuran, 2,3-dihydro-(relative area were 9.1%, 3.7%, 3.4%, 3.2% respectively) and 2-cyclo penten-1-one,3-methyl-(relative area were 2.6%, 1.7%, 1.7%, 1.2% respectively). Furfural was another significant compound found in corn cob (450 °C) and wheat straw (400 °C) bio-oils with relative area of 4.9%, 1.9% respectively. Phenol, 1,2-Benzenediol, 4-methyl was found in corn cob (450 °C) and wheat straw (400 °C) bio-oils with relative area of 1.4%, 2.3% respectively. n-Hexadecanoic acid was the compound with the highest area % in the rice husk bio-oil (450 °C), GC–MS profile with a relative area of 16.8%. It was also found in the wheat straw bio-oil (400 °C) with a relative area of 16.4%. Thus, bio-oil is a complex mixture with a lot of chemical compounds. Furfural, cyclopenten and phenolic compounds are the main chemical compounds in the bio-oil for the four kinds of biomass (Tsai et al., 2007; Chen et al., 2011).

**3.4.2. 1H Nuclear magnetic resonance (NMR) of bio-oil**

NMR analysis of the bio-oil samples has been done to understand the ratios of chemical environments of the proton. NMR spectra provided complementary functional group information to FT-IR spectra and the ability to quantify and compare integration areas between spectra (Mullen et al., 2009). Similar to FT-IR, 1H NMR spectra showed a high percentage of aliphatic functional groups for all bio-oils and a summary of integrated peak area regions assigned to different functional group classes are provided.
Fig. 1a, b, c and d below. All bio-oils displayed a low percentage of methoxy/carbohydrate functionality (4.5–6.0 ppm). The value of proton percentage of bio-oil was maximum for wheat straw and minimum for rice straw in this region (4.5–6.0 ppm). The region of the spectrum between 6.0 and 8.5 ppm corresponds to the aromatic region (Mullen et al., 2010; Biswas et al., 2016). The maximum proton content of bio-oil was obtained for rice straw at around 21% in this region. The proton percentage corresponding to rice husk was lowest in this region. The downfield spectrum regions (9.5–10 ppm) of the bio-oils arise from the aldehydes. Aromatic/hetero-aromatic functionality was also observed in all bio-oils (6.0–8.5 ppm) in agreement with findings from FT-IR.

### Table 3

<table>
<thead>
<tr>
<th>Compounds identified in bio-oil obtained under N₂ atmosphere</th>
<th>Area, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC-450 °C</td>
</tr>
<tr>
<td>Furfural</td>
<td>4.9</td>
</tr>
<tr>
<td>2-Furannethanol</td>
<td>4.1</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one, 3-methyl-</td>
<td>2.6</td>
</tr>
<tr>
<td>3-Hexen-2-one, 3-methyl-</td>
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</tr>
<tr>
<td>Phenol</td>
<td>6</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one, 2-hydroxy-3-methyl-</td>
<td>3.9</td>
</tr>
<tr>
<td>Phenol, 2-methyl-</td>
<td>3.1</td>
</tr>
<tr>
<td>Phenol, 3-methyl-</td>
<td>–</td>
</tr>
<tr>
<td>Phenol, 2-methoxy-</td>
<td>12.4</td>
</tr>
<tr>
<td>Phenol, 2,4-dimethyl-</td>
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</tr>
<tr>
<td>2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-</td>
<td>1.8</td>
</tr>
<tr>
<td>Phenol, 2,5-dimethyl-</td>
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</tr>
<tr>
<td>Phenol, 4-ethyl-</td>
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</tr>
<tr>
<td>Cresol</td>
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</tr>
<tr>
<td>Catechol</td>
<td>5.2</td>
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<tr>
<td>Benzofuran, 2,3-dihydro-</td>
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<td>2.7</td>
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<tr>
<td>Phenol, 4-ethyl-2-methoxy-</td>
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<tr>
<td>1,2-Benzenediol, 4-methyl-</td>
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<td>2-Methoxy-4-vinylphenol</td>
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<tr>
<td>Phenol, 2,6-dimethoxy-</td>
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<td>Benzaldehyde, 3-hydroxy-4-methoxy-</td>
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<tr>
<td>3-Hydroxy-4-methoxybenzoic acid</td>
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<tr>
<td>1,2,3-Trimethoxybenzene</td>
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</tr>
<tr>
<td>trans-Isouegenol</td>
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</tr>
<tr>
<td>Apocynin</td>
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<tr>
<td>Homovanillyl alcohol</td>
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<td>Phenol, 2-methoxy-4-{1-propenyl}-, (Z)-</td>
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</tr>
<tr>
<td>5-tert-Butylpyrogallol</td>
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<tr>
<td>n-Hexadecanoic acid</td>
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</tr>
<tr>
<td>1,2-Cyclopentanediione, 3-methyl-</td>
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</tr>
<tr>
<td>p-Cresol</td>
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<td>Vanillin</td>
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<tr>
<td>4-Ethylcatechol</td>
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<td>1-Penten-3-ol, 2-methyl-</td>
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<tr>
<td>Hydrazine, 1-(4-ethyl phenyl)-</td>
<td>–</td>
</tr>
<tr>
<td>Octadecanoic acid</td>
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</table>
protons attached to carbon atoms at least two bonds away from a field region of the spectra, from 0.5 to 1.5 ppm represents aliphatic due to other carbonyl-bearing groups like protonated carboxylic
@ ples despite the observed C
Aldehydes functionality (9.5–10.0 ppm) was absent from all samples despite the observed C=O functional groups (1730–1700 cm\(^{-1}\)) by FT-IR. The appearance of such FT-IR bands may be due to other carbonyl-bearing groups like protonated carboxylic acids, carboxylic acid esters, amides, and ketones. The most up field region of the spectra, from 0.5 to 1.5 ppm represents aliphatic protons attached to carbon atoms at least two bonds away from a C=C or heteroatom (O or N). The next integral region from 1.5 to 3.0 ppm represents protons on aliphatic carbon atoms that may be bonded to a C=C double bond. All the bio-oils have higher percentage of protons in the spectral region from 0.5 to 3.0 ppm. The bio-oils from rice husk showed higher proton percentage than all the three samples in the region from 0.5 to 3.0 ppm. The region is further divided into two regions namely, 0.5 to 1.5 and 1.5 to 3.0 ppm. The bio-oil from corn cob, rice straw and wheat straw samples have higher percentage of protons in the region from 1.5 to 3.0 than the region from 0.5 to 1.5 which suggests the presence of unsaturation (C=C) in the bio-oil. The region of the \(^1\)H NMR spectrum at 3.0–4.5 ppm represents methoxyl protons (Kosa et al., 2011) or methylene group that joins two aromatic rings. All the bio-oils from corn cob, wheat straw and rice straw showed high proton percentage than rice husk. The \(^1\)H NMR of the bio-oils obtained from pyrolysis of four agriculture residue indicated the presence of substitute phenol and aromatic compounds.

3.4.3. Fourier transform-infra red spectroscopy (FT-IR) of bio-oil

The Fourier transform infrared (FT-IR) spectra of the oils are given in Fig. S4a and S4b. The O−H stretching vibrations between 3200 and 3400 cm\(^{-1}\) of the bio-oil indicate the presence of phenols and alcohols. The presence of alkanes is indicated by the absorbance peak of C−H vibrations between 2800 and 3000 cm\(^{-1}\) and by 1350 and 1470 cm\(^{-1}\) bands due to the C−H bending. Carbohydrate content of four biomass produced bio-oil with strong C=O stretching absorbance between 1650 and 1730 cm\(^{-1}\) indicate the presence of ketones, aldehydes and carboxylic acids (Serrano et al., 1996). The absorbance peaks between 1600 and 1630 cm\(^{-1}\) indicate the presence of alkenes and aromatics. The peaks between 900 and 1300 cm\(^{-1}\) are due to the presence of primary, secondary and tertiary alcohols and also phenols and they are showing the C−O stretching and O−H bending. Furthermore, the absorption peaks between 650−800 and 1420–1610 cm\(^{-1}\) indicate mono and polycyclic and substituted aromatic groups. Obtained bio-oil has a typical FT-IR spectrum compared with the previous studies (Balagurumurthy et al., 2015; Krishna et al., 2016). The FT-IR spectra of various bio-oil samples from four biomass show the same peaks indicating the presence of same functional groups in the bio-oil samples. The spectra differ only in the relative intensity of some peaks. The FT-IR spectra were in conflict with the various peaks obtained in the \(^1\)H NMR spectra of the bio-oils.

3.5. Bio-char characterization by powder X-ray diffraction and FT-IR

The stacked powder XRD patterns of corn cob, wheat straw, rice straw and rice husk feed and bio-chars at optimal final temperatures have been shown as Fig. S5a and S5b. From the figure, it can also be observed that the corn cob, wheat straw, rice straw and rice husk feed has a peak at 2θ around 21° attributed to the hkl 101 crystallographic planes of crystalline regions of cellulose. This peak is hardly evident in the bio-char patterns which indicate the conversion of cellulose in the feed. The peak at 2θ around 21° assigned to the crystallographic planes of cellulose are also seen to reduce with increase in pyrolysis temperature thus forming amorphous bio-char rich in carbon content. These are in confirmation with the results of FT-IR which indicates the conversion of feed cellulose into products. On the contrary, it was found that the X-ray diffraction peaks, for all the four bio-char were characterized by a broad band instead of cellulose signals (with the pyrolysis temperatures) indicating a destruction of biomass structure and a highly disordered structure (Meshitsuka and Isogai, 1996).

The functional groups in bio-chars from the pyrolysis of corn cob, wheat straw, rice straw and rice husk shown in Fig. S6, revealed that the functional groups in bio-chars were similar. Some of the functional groups observed in four bio-chars are as follows: the broad band at 3455 cm\(^{-1}\) was attributed to the hydroxyl groups (O−H) due to the water content in all the bio-chars. The presence of water in the bio-chars could be from absorption of moisture by the bio-chars or KBr during pellets preparation. The peaks at 2918–2853 cm\(^{-1}\) are assigned to the C−H stretching vibrations, saturated C−C, and C−H; the peaks at 1405 and 1585 cm\(^{-1}\) confirmed the aromatic ring C=C stretching vibration. The peak at 1095 cm\(^{-1}\) represents C−H out-of-plane bending vibrations of the alkene groups. For the four biochars, all of them shows the same functional groups. That is because the biomass material consists of cellulose, hemicellulose and lignin which have a large amount of C, H and O (Chen et al., 2014). The intensities FT-IR spectra of the pyrolytic bio-chars of all four corn cob, wheat straw, rice straw and
rice husk are weakened, indicating that many cellulose, hemicellulose and lignin structural units were broken down in pyrolysis.

4. Conclusions

Pyrolysis of four different agriculture biomass residues has seen that the product distributions under identical conditions were strongly affected by the types of biomass samples. The highest bio-oil yield was obtained from corn cob 47.30 wt%. Maximum organic carbon conversion (56.62%) calculated from TOC measurement was observed for rice husk. The contents of the bio-oils in four samples were similar and mainly composed of oxygenated hydrocarbons, that has agreed with further analysis from FT-IR and 1H NMR. The analysis of four bio-char derived from pyrolysis by XRD and FT-IR, which indicating that biomass components units were broken down in pyrolysis and converted into products.

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Appendix A. Supplementary data

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References
