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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 agricultures residue 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 ^{1}H 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.

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 CO_2 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

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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 (Balagurumurthy et al., 2015; Park et al., 2014; Pottmaier et al., 2013; Yu et al., 2016; Cao et al., 2004; Ceranic 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 Balagurumurthy et al. and observed maximum bio-oil 31.0% and 12.8% under N_2 and H_2 atmosphere at 400 °C in both cases. The higher amount of bio-oil was observed under the N_2 environment than H_2 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 < 56.7 < 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 (^{1}H 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 N_2 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 ^{1}H NMR spectra have been recorded in the Bruker Avance 500 Plus instrument using $CDCl_3$ 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 2–80° 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 anhydrate sodium sulphate and diethyl 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).

$$\text{Bio}-\text{oil yield, wt.\%} = \frac{(W_4) - (W_3)}{\text{Weight of feed}} \times 100$$