



Hydrothermal liquefaction of rice straw: Effect of reaction environment



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ABSTRACT

Hydrothermal liquefaction of rice straw was performed at temperatures from 280 to 320 °C under different reaction environments viz., N₂, O₂ and CO₂. N₂ and CO₂ did not show any significant change in the product distribution, however, in case of liquefaction using O₂, the bio-oil yield was very low. Maximum bio-oil yield (17 wt%) as well as conversion (78%) was observed in case of liquefaction using N₂. TOC analysis indicated that the maximum organic carbon conversion (77%) was under N₂ environment. Ether soluble bio-oil obtained under O₂ environment showed higher aliphatic proton content than N₂ and CO₂, whereas, aromatic proton content was higher in case of N₂ and CO₂ than O₂. ¹H and ¹³C NMR showed that bio-oil obtained at all the conditions was highly aliphatic and aromatic in nature. GC/MS showed that bio-oil (ether and acetone soluble) obtained under different reaction conditions was composed of phenol, guaiacol, catechol, syringol and their derivatives.

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1. Introduction

To reduce the fossil imports and green house gas emissions into the atmosphere, it is necessary to shift toward renewable resources of energy. Biomass is the only sustainable source of organic carbon and is the only environment friendly equivalent to fossil fuels for the production of fuels and chemicals. Lignocellulosic biomass (forest and crop residues, energy crops etc.) is the most abundant non-edible biomass that can be used for the production of hydrocarbons without any food versus fuel issue [1]. The biorefinery concept integrates several processes and technologies for biomass conversion and this demands efficient utilization of all components of biomass to make it economically feasible [2].

Agricultural residues like straws and husks are major source of lignocellulosic biomass and in most countries including India, rice straw is a major component of agro-residues. Annually, around 731 million tons of rice straw is produced by Asia alone [3]. Arunachal Pradesh, Assam, Manipur, Meghalaya, Mizoram, Nagaland and Tripura (North eastern India) are predominantly rice producing regions and rice crop is grown in 89.46% of total area under food grain contributing to 92.32% of the total food grain production [4].

Rice straw has high energy content and medium-low lignin content. Biochemical conversion requires the elimination and sep-

aration of lignin component of biomass as it cannot be degraded by microorganisms to produce ethanol [5]. Hydrothermal liquefaction (HTL) can be used for the production of liquid hydrocarbons from rice straw in a single step. Lignocellulosic and high moisture containing aquatic biomass like algae, water hyacinth etc., can be effectively converted into value added hydrocarbons using hydrothermal liquefaction as it does not require any energy intensive pretreatment and drying step [6]. During this process, water at high temperatures and pressures (sub/supercritical water) is used for hydrolysis, extraction, structural modification and depolymerisation of biomass [7]. Hydrothermal liquefaction has been used widely for the valorisation of agricultural residues.

Catalytic hydrothermal liquefaction of wheat husk using KOH and K₂CO₃ was carried out at 280 °C and it was observed that alkaline catalysts increased the bio-oil yield. Maximum bio-oil yield of 31% was obtained using K₂CO₃ solution [8]. Supercritical ethanol and methanol has been used for the hydrothermal liquefaction of rice straw, carried out at different temperatures of 250, 280 and 300 °C and different residence times of 15, 30 and 60 min. Maximum liquid product yield calculated on dry and ash free basis (47.52 wt%) was observed using ethanol at 300 °C and 15 min reaction time. Liquid products obtained from rice straw were mainly composed of monomeric phenols [9]. Effect of different reaction environments (N₂, H₂, and CO) on hydrothermal liquefaction of corn stalk was studied at 380 °C for 30 min. The order of conversion of biomass, yield, and H/C ratio of liquid product followed the trend:

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$\text{CO} > \text{H}_2 > \text{N}_2$. Liquid products had oxygen content in the range of 10–13% and oxygen removal was in the form of CO_2 and H_2O [10].

The effect of various reaction parameters like temperature, residence time, and biomass: H_2O ratio etc., has been studied in detail during hydrothermal liquefaction by various authors [11]. But the effect of reaction environment during HTL of biomass has not been studied in detail. Various gases like CO_2 , N_2 , CO and H_2 have been used during HTL of biomass but O_2 has not been used for the process. Chandra et al. studied the effect of hydrothermal and NaOH pretreatment for production of methane from rice straw [12]. Murakami et al. carried out the hydrothermal treatment followed by steam gasification of rice straw for the production of monosaccharide and hydrogen [13]. However, no reports exist on the effect of reaction environment on HTL of rice straw. In this direction, we report herein the effect of various reaction environments [N_2 , O_2 and CO_2] on product distribution and nature of products obtained after HTL of rice straw at various temperatures of 280, 300 and 320 °C.

2. Materials and experimental procedures

2.1. Materials

Rice straw was collected from Dehradun (Uttarakhand). The calorific value of rice straw was 13.41 MJ kg^{-1} . The elemental composition of rice straw was as follows C (34.11 wt%), H (6.53 wt%), N (0.17 wt%), S (0). Moisture content of rice straw was found to be 11.95%.

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments of rice straw were conducted in a 500 ml high pressure autoclave (Autoclave Engineers) at different reaction conditions like temperature (280, 300 and 320 °C) and different reaction environment viz., N_2 , O_2 and CO_2 according to our previous published procedure [14]. All the gases in this study were applied for purging and the partial pressure of the gases used in the present study was 0.3 MPa. The pressure during the reaction is autogenous which is in the range of 6–9 MPa. Ether soluble bio-oil was termed as “bio-oil1” whereas, acetone soluble bio-oil was termed as “bio-oil2”. Acetone insoluble fraction was termed as bio-residue [14,15]. The experiments were repeated several times and the deviation of the liquid yields are within $\pm 1\%$. Various equations to calculate the yield of various fractions are given below.

$$\text{Conversion(\%)} = \frac{W_{\text{RS}} - W_{\text{residue}}}{W_{\text{RS}}} \times 100 \quad (1)$$

$$\text{Bio - oil1 Yield(wt\%)} = \frac{W_{\text{ethersoluble}}}{W_{\text{RS}}} \times 100 \quad (2)$$

$$\text{Bio - oil2 Yield(wt\%)} = \frac{W_{\text{acetonesoluble}}}{W_{\text{RS}}} \times 100 \quad (3)$$

$$\text{Gas Yield(wt\%)} = \frac{W_{(\text{vessel}+\text{feed}+\text{water})\text{beforeHTU}} - W_{(\text{vessel}+\text{feed}+\text{water})\text{afterHTU}}}{\text{Amount of feed taken (g)} + \text{Amount of water added (g)}} \times 100 \quad (4)$$

$$\text{solid residue Yield(wt\%)} = \frac{W_{\text{Solidresidue}}}{W_{\text{RS}}} \times 100 \quad (5)$$

$$\text{Other Yield(wt\%)} = 100 - (\text{bio - oil1} + \text{bio - oil2} + \text{solidresidue} + \text{gas})\text{Yield} \quad (6)$$

W_{RS} is the weight of rice straw; W_{residue} is the weight of bio-residue; $W_{\text{ethersoluble}}$ is the weight of ether soluble bio-oil (bio-oil1); $W_{\text{acetonesoluble}}$ is the weight of acetone soluble bio-oil (bio-oil2). All yields were calculated on a dry basis of material. Others correspond to the water soluble oxygenated hydrocarbons and some losses.

2.3. Analysis of feed and reaction products

Rice straw was analyzed using thermogravimetric analysis, powder XRD, SEM and FTIR. The liquid products were analyzed using FTIR, NMR (^1H NMR, ^{13}C NMR) and GC/MS. Powder XRD patterns of bio-residues were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a $\text{Cu K}\alpha$ radiation source. Diffraction patterns in the 2–80° region are recorded with a 0.04 step size (step time = 4 s). SEM images have been collected on a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB_6) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for SEM has been subjected to disperse on a carbon paper coated adhesive followed by gold coating. TG-DTG of rice straw was carried out on Shimadzu DTG-60 under N_2 flow. The ^{13}C NMR and ^1H NMR spectra of the liquid samples have been recorded in Bruker Avance 500 plus instrument using CDCl_3 as a solvent. The FTIR spectra were recorded on Nicolet 8700 FTIR spectrometer. The liquid products were analyzed via 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 ($25 \text{ m} \times 0.32 \text{ mm} \times 0.17 \mu\text{m}$) was used for the separation. An oven isothermal program was set at 50 °C for 2 min, followed by a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ –260 °C for 5 min. The injected volume was $0.4 \mu\text{L}$ in a split less mode. TOC analysis of rice straw, aqueous fraction and bio-residue was performed using Shimadzu TOC-L unit with solid sample module SSM-5000A.

3. Results and discussion

3.1. Analysis of rice straw

Rice straw kinetic studies carried out using non-isothermal thermogravimetric analysis in nitrogen atmosphere at six different heating rates of $5\text{--}40 \text{ }^\circ\text{C min}^{-1}$ using several model free kinetic methods have been presented in our earlier communication and the results indicated that the decomposition process exhibited two zones of constant apparent activation energies [16]. FTIR and powder XRD of rice straw has been discussed in our earlier communication [9]. Rice straw FTIR showed various peaks corresponding to lignocellulosic biomass components viz. hemicellulose, cellulose and lignin. Various peaks/bands observed in FTIR of rice straw were broad band of the CH, CH_2 stretching at 2920 cm^{-1} and the CH_2 shearing at 1427 cm^{-1} , 1640, 1427, and 899 cm^{-1} corresponding to C=C stretching, CH_2 bending, and C–H in-plane bending, respectively that indicate the possible presence of lignin in rice straw [17]. Bands at 3428 and 1513 cm^{-1} corresponds to H-bonded OH stretch and aromatic C–H respectively. Aromatic compound group peaks were observed between 900 and 650 cm^{-1} . Powder XRD of rice straw showed the peaks observed at $2\theta = 16^\circ$ and 22° that corresponds to cellulose I crystal and (1 1 0), and (2 0 0) planes of cellulose [8,18].

3.2. Effect of reaction parameters on product distribution

Hydrothermal liquefaction of rice straw was performed at 280, 300 and 320 °C at 15 min residence time and biomass: H_2O ratio of 1:6 under various reaction environments of N_2 , O_2 and CO_2 . Product distribution from hydrothermal liquefaction of rice straw under different reaction environments viz., N_2 , O_2 and CO_2 is shown in Table 1.

In case of hydrothermal liquefaction using N_2 at 280 °C, bio-oil1 yield was 5 wt% and bio-oil2 yield was 12 wt% yielding total bio-oil yield of 17 wt% and gas yield was 6 wt%. The yield of bio-residue

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