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Value addition to rice straw through pyrolysis in hydrogen and nitrogen environments

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HIGHLIGHTS

- Rice straw is a potential biomass for production of high value chemicals.
- Pyrolysis of rice straw under hydrogen atmosphere has been reported for first time.
- Higher selectivity to phenolics at 400 °C and 30 bar hydrogen atmosphere.
- Higher bio-oil yield under nitrogen atmosphere compared to hydrogen atmosphere.

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ABSTRACT

Pyrolysis of rice straw has been carried out under hydrogen atmosphere at 300, 350, 400 and 450 °C and pressures of 1, 10, 20, 30 and 40 bar and in nitrogen atmosphere, experiments have been carried out at the same temperatures. It has been observed that the optimum process conditions for hydrolysis are 400 °C and 30 bar pressure and for slow pyrolysis, the optimum temperature is 400 °C. The bio-oil has been characterised using GC-MS, ¹H NMR and FT-IR and bio-char using FT-IR, SEM and XRD. The bio-oil yield under hydrogen pressure was observed to be 12.8 wt.% (400 °C and 30 bar) and yield under nitrogen atmosphere was found to be 31 wt.% (400 °C). From the product characterisation, it was found that the distribution of products is different for hydrogen and nitrogen environments due to differences in the decomposition reaction mechanism.

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1. Introduction

The necessity to move towards the utilisation of renewable sources of energy has increased over the past decade due to rise in greenhouse gas emissions and questions over the availability of fossil based resources. Renewable sources such as solar, wind, tidal energy can be used to produce electricity which can also be used to run electric bikes, cars etc. The heavy duty transportation sector, chemicals and the petrochemical industries are still heavily dependent on liquid hydrocarbons. Biomass is the only source of organic carbon which can be used for producing hydrocarbons in a renewable and sustainable manner. Biomass is defined as any organic matter that is produced by the process of photosynthesis. First generation bio-fuels have the disadvantage of causing the food vs. fuel issue. The second generation bio-fuels are obtained from non-edible lignocellulosic biomass (agricultural residues,

forest residues or energy crops) which are composed of cellulose (crystalline polymer of glucose monomeric units), hemicellulose (monomer units are mostly C₅ sugars such as xylose, arabinose etc), lignin (coumaryl alcohol, sinapyl alcohol and coniferyl alcohol are its monomers) and a small amount of extractives and inorganic matter (Stöcker, 2008).

Rice (*Oryza sativa*) is the staple food of many countries and hence is one of the most cultivated crops in the world. Rice is a semi-aquatic annual grass plant that includes approximately 22 species of the genus *Oryza*. China and India account for the major rice production in the world. Some of the other countries where rice is cultivated are Thailand, Philippines, Japan, Pakistan, Cambodia, Republic of Korea, Nepal, Sri Lanka, Brazil, the United States, Egypt, Madagascar and Nigeria (Muthayya et al., 2014). The forecast for world rice production stands at 496.3 million tonnes for the year 2014 [<http://www.fao.org/worldfoodsituation/csdb/en/>]. For 1 ton of rice paddy, 290 kg of rice straw is generated as the rice straw to paddy ratio ranges from 1 to 4.3 [<http://www.bioenergyconsult.com/tag/rice-straw/>]. Hence, a huge amount of rice straw is generated all over

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the world every year. Some of the rice straw is diverted for fodder purpose [<http://www.fao.org/docrep/004/X6512E/X6512E07.htm>] while the rest is burnt in some parts of the world.

Value addition of rice straw to valuable hydrocarbons and chemicals can be carried out instead of burning the same. Biochemical methods of conversion can be used to produce bioethanol from rice straw and till now under the optimum conditions, ethanol concentration of 29.1 g L^{-1} and ethanol yield of 61.3% has been produced (Binod et al., 2010). Thermo-chemical methods of conversion have more advantages than biochemical methods and among them, pyrolysis is seen to have the maximum potential for commercialisation. It is defined as the decomposition of any organic matter in the absence of oxygen and can be carried out under inert atmosphere of nitrogen/helium or under reductive atmosphere of hydrogen. Depending on the heating rate and residence time, pyrolysis can be classified into slow, fast and flash pyrolysis. Slow pyrolysis is generally carried out at slow heating rates of $5\text{--}40 \text{ }^\circ\text{C min}^{-1}$ and has a residence time of minimum 30–60 min. The products obtained are solid bio-char, liquid bio-oil and non-condensable gases. The concept of hydrolysis followed by hydrodeoxygenation has arisen due to the disadvantages of fast pyrolysis bio-oil such as high total acid number, low miscibility with crude/crude fractions, low instability etc. In this concept, hydrolysis has been carried out under high pressures of hydrogen (5–40 bar) and the vapours are in-situ hydrodeoxygenated to produce fuels (Marker et al., 2014).

Pyrolysis of rice straw has been carried out by several researchers using various reactors and process conditions. Park et al. used around 100 g of feedstock and carried out slow pyrolysis at 300, 400, 500, 600 and $700 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ (Park et al., 2014). Almost same yields of bio-oil and bio-char have been obtained at higher temperatures above $500 \text{ }^\circ\text{C}$. Wu et al. carried out the slow pyrolysis of rice straw at 300, 400, 500, 600 and $700 \text{ }^\circ\text{C}$ with residence time of 1, 2, 3 and 5 h to produce bio-chars that can be used for soil amendment. They observed that bio-chars at $400 \text{ }^\circ\text{C}$ had high alkalinity and cation exchange capacity (Wu et al., 2012). Pyrolysis of rice straw has also been carried out by Pütün et al. (2004) with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ at 400, 500, 550 and $700 \text{ }^\circ\text{C}$. Maximum bio-oil yield of 27.77% was observed at $550 \text{ }^\circ\text{C}$ with a particle size of $0.425 < D_p < 0.85 \text{ mm}$ and 200 ml min^{-1} nitrogen flow. Hydrolysis (fluidised bed reactor) followed by hydrodeoxygenation (fixed bed reactor) of poplar biomass has been studied and fuel range hydrocarbon recovery of around 32% has been observed (Venkatakrishnan et al., 2015). In addition, co-pyrolysis of rice straw has been carried out with Shenfu coal and it was observed that addition of biomass promoted tar decomposition (Li et al., 2014).

The various products of the first step of integrated hydrolysis concept have to be understood in detail to design catalysts for the upgradation step and rice straw hydrolysis has not been carried out so far in the open literature.

The objective of this study is to understand the role of reaction environment and product distribution during the pyrolysis of rice straw. Hydrolysis of rice straw at 300, 350, 400 and $450 \text{ }^\circ\text{C}$ and pressures of 1, 10, 20, 30 and 40 bar and slow pyrolysis at the same temperatures have been carried out for the same.

2. Methods

2.1. Materials

Rice straw has been obtained from a local agricultural farm in Dehradun, Uttarakhand, India and has been crushed and sieved to obtain particle size between 0.5 and 2 mm.

2.2. Characterisation methods

The thermogravimetric analysis was carried out in Shimadzu DTG-60 instrument. The trace metal analysis of rice straw was carried out using DRE, PS-3000 UV, Leeman Labs Inc., Inductively Coupled Plasma-Atomic Emission Spectroscopy. The gross calorific value of the feed has been found out using Parr 6300 Bomb Calorimeter. The ultimate analysis has been carried out using Elemental vario micro cube unit. Powder X-ray diffraction patterns 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. The FT-IR spectra were recorded on a Nicolet 8700 FTIR spectrometer with the sample powder diluted in KBR. SEM images have been collected on 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 analysis has been dispersed on a carbon coated adhesive followed by gold coating. $^1\text{H NMR}$ of the bio-oils was carried out in a Bruker Avance III NMR spectrometer using CDCl_3 as solvent. The liquid products were analyzed via gas chromatography–mass spectrometry (GC–MS, Agilent 7890B). The carrier gas was He and column flow rate was 1 mL min^{-1} . A HP-1 column ($25 \text{ m} \times 0.32 \text{ mm} \times 0.17 \text{ }\mu\text{m}$) was used for the separation. An oven isothermal program was set at $50 \text{ }^\circ\text{C}$ for 2 min, followed by a heating rate of $5 \text{ }^\circ\text{C/min}$ to $260 \text{ }^\circ\text{C}$ for 5 min. The injected volume was $0.4 \text{ }\mu\text{L}$ in a splitless mode.

2.3. Experimental procedure

The schematic diagram of the prototype hydrolysis unit has been provided in an earlier communication (Balagurumurthy et al., 2013). In brief, oven dried rice straw is weighed (10 g) and loaded into the reactor. The reactor is purged with hydrogen to remove the inside air and then pressurized using hydrogen till the desired pressure is reached. It is heated in an electrical furnace which is controlled by a temperature programmed controller. The thermocouples are placed in the skin and in the heart of the reactor inside the thermowell provided. The gas from the hydrogen cylinder is passed into the reactor bottom. The required final temperature and heating rate are set and the final temperature is maintained for 1 h. The pressure is maintained constant by intermittently removing the products from the system. The product stream from the reactor is passed through a shell and tube heat exchanger with water in the shell side at $4 \text{ }^\circ\text{C}$ and liquid product is collected separately. Conversion (%) is calculated as 100-char (wt.\%) .

Slow pyrolysis of rice straw has been performed in a fixed bed glass reactor (length: 280 mm; i.d. 34 mm) under atmospheric pressure of nitrogen. The same particle size feedstock has been used in this study as well. At first, 5 g of rice straw was loaded into the reactor and the desired temperature was set. The residual air in the reactor is purged using nitrogen and the carrier gas (nitrogen) flow rate for the experiment was set to 50 ml min^{-1} . The final temperature was maintained for 60 min. The nitrogen flow was then cut off. Bed temperature has been taken as the pyrolysis temperature. The vapours formed during pyrolysis were condensed using water condenser maintained at $4 \text{ }^\circ\text{C}$ and liquid products were collected. The difference between the reactor weight before and after reaction was used to calculate the weight of bio-char. Yield of gas is calculated as $100 - (\text{bio-char} + \text{bio-oil})$ and conversion as $100 - \text{biochar, wt.\%}$.

In both cases, the organic fraction of the bio-oil was characterised using FT-IR, $^1\text{H NMR}$ and GC–MS. The solid bio-char has been characterised using FT-IR, SEM and XRD.

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