



## Pyrolysis of *Cedrus deodara* saw mill shavings in hydrogen and nitrogen atmosphere for the production of bio-oil



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### ABSTRACT

Pyrolysis of deodar has been carried out at 350 and 400 °C at 0.1, 1, 2 and 3 MPa hydrogen pressure. Pyrolysis under nitrogen atmosphere has been carried out at 300, 350, 400 and 450 °C. The favourable process conditions under hydrogen environment were found to be 400 °C and 2 MPa pressure and in case of nitrogen environment was found to be 350 °C. The products have been characterised using GC–MS, <sup>1</sup>H NMR, FT-IR and SEM. It has been observed that the bio-oil is rich in phenolic compounds under nitrogen and hydrogen atmospheres. Selectivity towards certain compounds such as catechol, vanillin and its derivatives etc. are high under hydrogen atmosphere. Deodar has undergone decomposition significantly which is evident by the absence of most functionality in bio-char and loss of crystallinity. The products formed under hydrogen and nitrogen environments are different from each other owing to the differences in reaction mechanism.

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## 1. Introduction

Industrialisation in the past several decades has made it necessary for mankind to exploit the fossil resources at an alarming rate. This has led to the increase in greenhouse gas emissions in the atmosphere causing climate change problems. The negative effect caused by the usage of non-renewable and unsustainable sources of energy has led to the increase in research for the development of renewable and sustainable alternatives. Biomass, defined as any organic matter produced by the process of photosynthesis, is the only renewable source of organic carbon [1]. Though solar, wind, tidal energy can be used to produce electricity, only biomass can be used for the production of hydrocarbons in an environmental friendly manner [2]. But also recently CO<sub>2</sub> has been used for production of hydrocarbon [3]. Feed for the production of second generation biofuels which does not cause the food vs fuel issue is lignocellulosic biomass. It encompasses the energy crops specifically for the production of biofuels/chemicals, agricultural and forest residues [4]. The composition of lignocellulosic biomass is

mainly cellulose, hemicellulose and lignin together with a small amount of inorganic material and extractives [5].

Forest residues constitute all those residues that are obtained during the pruning of the trees or while felling it. Any small trees or branches or tops that are obtained in this process during forest clearing can also be used as feedstock for biofuel production. In addition, when these logs are processed in saw mills, huge amounts of saw dust is obtained which can be collected at regular intervals and small decentralised units can be operated using the same. Forest residues thus obtained can be used for the production of bio-fuels/chemicals [6]. Deodar belongs to the Pinaceae family and is softwood whose lignin is mainly composed of guaiacyl units [7]. It is an evergreen coniferous tree widely available in the western Himalyan region. The wood is widely used for various purposes and hence, large quantities of saw dust are available which can be valorized to hydrocarbons/chemicals.

There are various methods of conversion of biomass of which thermo-chemical methods have gained interest in the recent past [8]. Among them, the process which is seen to have the maximum potential for commercialisation in short- and medium-term for the production of valuable hydrocarbons is pyrolysis which is defined as the decomposition of any organic material in the absence of oxygen [9]. Pyrolysis can be carried out under inert atmosphere or

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in the presence of hydrogen pressure creating a reductive atmosphere. Depending upon the residence time of the feed and product vapours inside the reactor and heating rate, pyrolysis can be classified into slow, fast and flash pyrolysis. In slow pyrolysis, the residence time/reaction time for feed in the reactor is in the range of 30–60 min. Some of the products of pyrolysis include bio-oil, bio-char and non-condensable gases. Bio-oil is a source of hydrocarbons which can be used for fuel applications after upgradation or is a rich source of functional chemicals such as phenolic compounds, aromatic ethers, furans etc. Bio-char is a solid product obtained by the process of pyrolysis and can be used for soil amendment/enrichment purposes, as adsorbents, catalysts/catalyst supports, for high value applications such as super capacitors, electrodes etc.

Slow pyrolysis of barks of *Pinus brutia* were carried out under nitrogen atmosphere and maximum bio-oil yield of 33.25% was obtained at 450 °C and a heating rate of 40 °C min<sup>-1</sup>. Bio-oil obtained was mostly composed of oxygenated components with low quantities of hydrocarbons [10]. Huff et al., compared the bio-chars derived from pinewood by the process of pyrolysis in the presence of nitrogen and hydrothermal conversion. The bio-char yields at 300, 400 and 500 °C were 32.89, 27.26 and 26.47% respectively [11]. Mixed wood samples have been pyrolysed in the presence of hydrogen and proprietary catalyst in a continuous reactor with fast heating rates. At 396 °C, 2.24 MPa pressure and weight hourly space velocity of 1.52, bio-oil yield of 25.1% was obtained [12]. It was observed that reducing environment had a pronounced effect on the pyrolysis of biomass. Venkatakrishnan et al., used poplar feed to carry out fast hydrolysis and vapour-phase catalytic hydrodeoxygenation and observed 32% hydrocarbon yield in the liquid fuel range [13]. With other feedstocks as well, hydrogen pressure was seen to play an important role in the quality of the products obtained [13–20]. It has been observed that in the presence of hydrogen, no undesirable polynuclear aromatics, olefins, or reactive free radicals are formed [12,15].

The originality of the present investigation is to understand the effect of environment on pyrolysis of *Cedrus deodara* saw mill shavings and product distribution for obtaining more bio-oil yield. The compositional differences in the bio-oil at different reaction parameters have been established for the first time. When the reaction environment is changed, the products obtained are different owing to the differences in the reaction mechanism that the feed undergoes and hence, is an important process parameter to be optimised. To establish this, experiments have been carried out at 350 and 400 °C and 0.1, 1, 2 and 3 MPa under hydrogen pressure and at temperatures of 300, 350, 400 and 450 °C in case of nitrogen atmosphere and products such as bio-oil and bio-char have been obtained. The liquid and solid products have been characterised using various analytical techniques such as Fourier Transform-Infrared Spectroscopy (FT-IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Gas Chromatography- Mass Spectrometry (GC-MS) and Scanning Electron Microscopy (SEM).

## 2. Materials and methodology

### 2.1. Materials

Deodar (*Cedrus deodara*) shavings have been obtained from a saw mill in Dehradun, Uttarakhand, India and have been sieved using standard mesh 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 under nitrogen atmosphere with a heating rate

of 10 °C min<sup>-1</sup>. The trace metal analysis of deodar 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 obtained using the Parr 6300 Bomb Calorimeter. The ultimate analysis has been carried out using Elementar vario micro cube unit. 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 a FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB<sub>6</sub>) 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. <sup>1</sup>H NMR of the bio-oils was carried out in Bruker Ultrashield 500 Plus instrument using CDCl<sub>3</sub> as solvent. The liquid products were analysed via gas chromatography-mass spectrometry (GC-MS, Agilent 7890B). The carrier gas was He and column flow rate was 1 cm<sup>3</sup> min<sup>-1</sup>. A HP-1 column (25 m × 0.32 mm × 0.17 μm) was used in GC-MS. An oven program was set at 50 °C for 2 min, followed by a heating rate of 5 °C min<sup>-1</sup> to 260 °C for 5 min. The injected volume was 0.4 μL in a splitless mode.

### 2.3. Experimental procedure

The schematic diagram of the prototype hydrolysis unit has been provided in an earlier communication [21]. In brief, oven dried deodar 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. The required final temperature and heating rate (20 °C min<sup>-1</sup>) are set and the final temperature is maintained for 1 h. The pressure is maintained constant by the means of a needle valve. The product stream from the reactor is passed through a shell and tube heat exchanger with water in the shell side at 4 °C. Slow pyrolysis of deodar has been performed in a fixed bed glass reactor (length: 28 cm; i.d. 3.4 cm) under atmospheric pressure of nitrogen as shown in Fig. 1. The same particle size feedstock has been used in this study as well. At first, 5 g of the feed was loaded into the reactor and the reactor was purged with nitrogen to remove the inside air. The nitrogen flow rate during pyrolysis was 50 cm<sup>3</sup> min<sup>-1</sup>. The starting temperature was the ambient room temperature at 25 °C and the heating rate to reach the pyrolysis final temperature (300, 350, 400 and 450 °C) was set at around 20 °C min<sup>-1</sup>. 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 as indicated using thermocouple 1 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.

Water in the bio-oil was removed by the addition of anhydrous sodium sulphate and acetone was used to recover the organic fraction. The experiments have been carried out in duplicates and average results have been reported. The remaining solid after the reaction left in the reactor is termed as bio-char.

$$\text{Bio - char yield, wt.}\% = \left[ \frac{(\text{Weight of reactor after reaction}) - (\text{Weight of empty reactor})}{(\text{Weight of feed})} \right] * 100$$

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