



Slow pyrolysis of pine wood: Effect of CO₂ and N₂ atmosphere

Bijoy Biswas^a, Bhavya B Krishna^{a,b}, Rawel Singh^{a,b}, Jitendra Kumar^a, Thallada Bhaskar^{a,b*}

^aThermo-catalytic Processes Area (TPA), Bio-Fuels Division (BFD), CSIR-Indian Institute of Petroleum (IIP), Dehradun 248005, India

^bAcademy of Scientific and Innovative Research (AcSIR), New Delhi, India

ARTICLE INFO

Received : 15 August 2016
Accepted : 27 September 2016

Keywords:

pine wood, slow pyrolysis, effect of atmosphere, bio-oil, bio-char.

ABSTRACT

Biomass pyrolysis is one of the most promising approaches for effective biomass utilization. The role of N₂ and CO₂ atmosphere during slow pyrolysis of pine wood has been studied in a fixed bed reactor to understand the atmosphere effect on distribution of product yields, composition of bio-oil and conversion of biomass. The slow pyrolysis of pine wood was carried out at 300-550 °C. The maximum liquid yields obtained are as follows: 54 wt.% bio-oil obtained in CO₂ and 58 wt.% obtained in the presence of N₂. Under different atmospheres, differences in the yields of gases, liquid, char and also variations in oxygenated compounds observed. Phenols and furans were prominent in bio-oils obtained at all tested temperatures. From the GC-MS analysis showed that the phenolic compounds in the bio-oil produced from pine wood in fixed bed were significantly higher under N₂ atmosphere than the CO₂ atmosphere. These results are likely to confirm that CO₂ has role on slow pyrolysis of pinewood biomass.

© 2016 ISEES, All rights reserved

1. Introduction

Biomass is a renewable resource, whose exploitation has received great attention due to environmental considerations and the increasing demands of energy widespread (Tasi et al. 2007). Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, and aquatic plants and algae. Pyrolysis is one of the thermochemical biomass conversion methods with best industrial perspectives for biomass valorization, since the process conditions can be optimized to maximize the yields of gas, liquid and char (Czemik and Bridgwater 2004) and is defined as the chemical decomposition of organic material by heating in the absence of oxygen (Ozbay et al. 2001; Aguado et al. 2000; Huber et al. 2006). The pyrolysis behavior of lignocellulosic biomass depends on its three major building blocks: cellulose, hemicellulose and lignin. Forest biomass contains a high weight percentage of cellulose and lignin, whereas agricultural biomass contains a high weight percentage of cellulose and hemicellulose (Cendrowska 1997). Each of the components decomposes at a different temperature range. Hemicellulose and cellulose decompose at around 200-300°C and 300-400°C, respectively, and lignin decomposes from about 200°C to upwards of 500°C (Mohan et al. 2006; Yang et al. 2007).

Typically, fast pyrolysis has been used where the desired end product is liquid or bio-oil and slow pyrolysis has been used for production of bio-char. However the process condition for slow pyrolysis can be altered to produce significant quantities of bio-oil and gas in addition to the bio-

char (Williams and Besler 1996). Numbers of studies have addressed the pyrolysis of pine wood such as fast pyrolysis, slow pyrolysis and catalytic pyrolysis. Pyrolysis of pine wood biomass at different temperatures produced mostly of oxygenated compounds such as furans and phenol-type compounds (Wang et al. 2010). Highest liquid yield of 46.8% was obtained from fast pyrolysis of pine wood at 550 °C with sweep gas (N₂) flow rate of 500 ml/min (Ngo and Kim 2014). 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 (Huff et al. 2014). Hanaoka et al. carried out pyrolysis under different atmosphere and found that chars produced in a N₂/CO₂/O₂-containing atmosphere had more surface area and a higher reactivity towards pure CO₂ than under pure N₂ atmosphere (Hanaoka et al. 2012). Wei-Hsin Chen and Bo-jhih Lin has been carried out pyrolysis of oil palm fiber and its pellets under N₂ and CO₂ atmosphere and evaluate the impact of biomass pattern and carrier gas at different temperature (400-500 °C). The result showed that the liquid yield higher in CO₂ atmosphere than the N₂ atmosphere at 450 °C (Chen and Lin 2016).

Cho et al., reported the slow pyrolysis of spent coffee ground in the presence of CO₂ to understand the formation of gaseous products and morphological properties of biochar produced (Cho et al. 2015). The product distributions from the pyrolysis of biomass depend on pyrolysis parameters, such as processing temperature, heating rate, reaction atmosphere, i.e. N₂, H₂, CO₂ or H₂O (steam) and type of pyrolysis reactor (Zhang et al. 2011).

* Corresponding Author: e-mail: tbhaskar@iip.res.in; thalladab@yahoo.com

Slow pyrolysis is generally carried out in an inert atmosphere but also can be carried out in the presence of other gases such as hydrogen, carbon dioxide etc. Present scenario shows that power plants are the major sources of CO₂ emission. To reduce the carbon storage in the environment, carbon capture and sequestration has been suggested as a strategy which includes geological or deep sea storage and mineralisation. Another alternative method for CO₂ utilization is it can be used as a reagent for the synthesis of chemicals such as urea, salicylic acid, polycarbonates etc. Due to the limited application of these products compared to amount of CO₂ produced from the consumption of fossil fuels and thus unlikely to make a significant impact on emission. Most of the studies so far reported only the effect of CO₂ on the solid product but there are very few publications that have discussed the liquid products and their detailed characterization. The novelty of the manuscript is to study the slow pyrolysis of pine wood biomass under different atmospheres of nitrogen and CO₂ and to understand the product distribution, and extensive analysis of pyrolysis products.

In this study, the pyrolysis of pine wood was carried out at temperature ranging from 300 to 550 °C under N₂ and CO₂ atmosphere. Slow pyrolysis of the pine wood has been performed to understand the distribution of products and effect on biomass/carbon conversion during the pyrolysis. The effect of pyrolysis temperature and the pyrolysis atmosphere on the bio-oil were discussed in detail. The feedstock and pyrolysis products were analyzed by using various analytical techniques such as TGA, ¹H NMR, FT-IR, total organic carbon etc., Identification of compounds in bio-oils was done by gas chromatography/mass spectrometry (GC-MS).

2. Materials and methodology

2.1 Materials

Pine wood biomass collected from Uttarakhand state, India was used in this experiment. The biomass was milled in a laboratory grinding machine and then sieved to 0.5–2.0 mm. The results of proximate and ultimate analysis basis of wet pinewood biomass are given in Table 1.

Table 1: Ultimate and proximate analysis of pine wood.

Ultimate analysis, wt.%		Proximate analysis, wt.%	
C	51.3	Moisture	6.3
H	5.8	Ash content	0.5
O	35.9	Volatile matter	78.5
N	0.1		
S	0.01		

2.2 Characterisation methods

The thermo gravimetric analysis was carried out in Shimadzu DTG-60 instrument under nitrogen atmosphere with a heating rate of 10 °C min⁻¹. 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 FT-IR spectrometer with the sample powder diluted in KBr. ¹H NMR of the bio-oils was carried out in Bruker Ultrashield 500 Plus instrument using CDCl₃ 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 cm³ min⁻¹. 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 minutes, followed by a heating rate of 5 °C min⁻¹ to 260 °C for 5 minutes. The injected volume was 0.4 μL in a splitless mode. TOC analysis of feed and bio-char was performed 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±50 °C for 2 minutes similar to ASTM D3175.

2.3 Experimental procedure

Slow pyrolysis of pine wood was performed in a glass reactor (length: 280 mm; i.d. 34 mm) under atmospheric pressure of nitrogen and carbon dioxide as shown in Figure 1

Briefly, 10g of pine wood was loaded into the reactor and the residual air in the reactor was purged using carrier gas nitrogen and carbon dioxide (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 25 °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

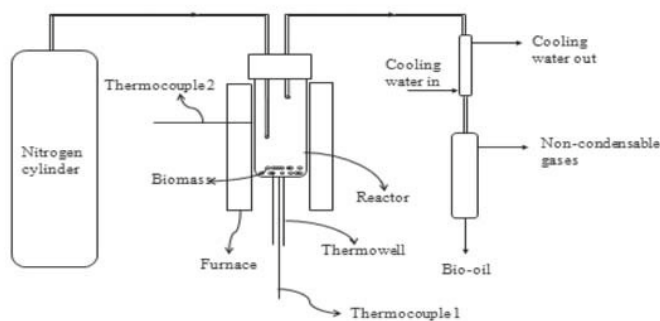


Figure 1: Schematic diagram of experimental setup

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).

Bio-char yield, wt.% = [(Weight of reactor after reaction) - (Weight of empty reactor)] / (Weight of feed) * 100

Bio-oil yield, wt.% = [(Weight of measuring cylinder with biooil) - (Weight of empty measuring cylinder)] / (Weight of feed) * 100

Gas yield, wt.% = 100 - (Bio-oil yield, wt.% + Bio-char yield, wt.%)

Conversion, % = 100 - (Bio-char yield, wt.%)

The experiments have been carried out in duplicates and the average values have been reported which are within the standard deviation of ± 1.0%. The organic fraction of the bio-oil was characterised using FT-IR, ¹H NMR and GC-MS. The solid bio-char has been characterised using FT-IR and XRD.

3. Results and Discussions

The ultimate analysis of pine wood was found to be as follows: carbon (51.3 wt.%), hydrogen (5.80wt.%), oxygen (35.99 wt.%), nitrogen (0.1 wt.%) and sulphur (0.01 wt.%). The gross calorific value of the feedstock was found to be 18.2 MJ Kg⁻¹. Pine wood contained 6.34wt.% moisture, 78.54wt.% volatile matter and 0.5wt.% ash. Pine wood belongs to the softwood category composed of cellulose, hemicellulose and lignin. The typical composition of pine wood as obtained from literature is as follows: hemicellulose (35.0% - 45.0%), cellulose (25.0% - 35.0%) and lignin (20.5% - 25.0%) and is of indicative nature. The thermogravimetry-differential thermogravimetry (TG-DTG) curve in Fig.2 showed that pine wood had a single significant decomposition step. From the curve, three zones for weight loss can be observed such as: first zone up to around 110 °C corresponding to loss of moisture in the feedstock, second zone there was a primary peak of mass loss at the temperature of 366 °C, and the temperature range of mass loss was from 223 °C to 440 °C

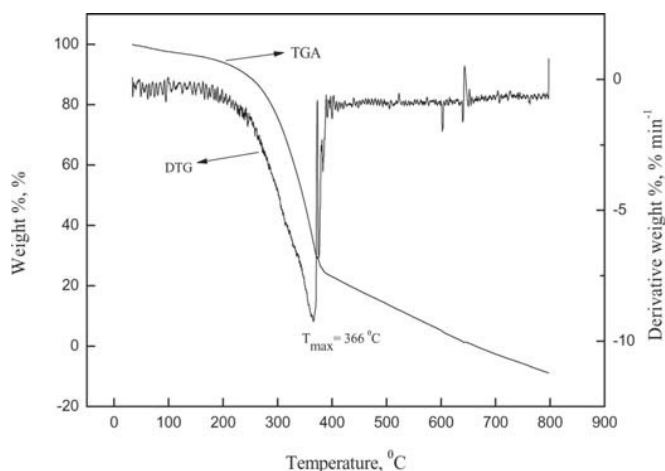


Figure 2: TG-DTG of Pine wood feed

corresponding to weight loss due to mainly the holocellulose content (Overend et al. 1985) though some portion of lignin also starts to decompose in this region and continues till 800 °C which is the last zone. Thus, the pyrolysis temperature of 450 to 500 °C was enough to make sufficient for the pine wood sample.

3.1 Product yields of pine wood biomass pyrolysis under N₂ and CO₂

Slow pyrolysis of pine wood has been carried out at from 300 to 550 °C in case of nitrogen atmosphere and from 300 to 450 °C in case of carbon dioxide atmosphere. The product distribution at various reaction temperatures and atmospheres has been provided in Table 2. Maximum bio-oil yield of 58 wt.% and 54 wt.% were obtained at 500 and 400 °C in nitrogen and carbon dioxide atmosphere respectively. With further increase in temperature, the bio-oil yield decreased. Conversion was seen to increase with increase in temperature due to the primary decomposition of biomass. The increasing temperature also had an effect on the non-condensable gases yield which increased at higher temperatures due to secondary cracking (Putun et al. 2005).

However, a decrease in solid residue is more significant for the decomposition under CO₂ atmosphere than that of N₂ atmosphere at lower temperature but at higher temperature it seems to be same decreases trend. Moreover, the less gas and more bio-oil were obtained in the presence of N₂. As bio-oil is the desired product, 500 and 400 °C has been considered as the most favourable temperature for slow pyrolysis of pine wood under N₂ and CO₂ atmosphere respectively and these two pyrolysis products have been characterized extensively to understand the role of CO₂. The decrease in the bio-oil yield with 450 °C was observed from 400 °C, hence the higher reaction temperatures such as 500 and 550 °C was not investigated in the presence of CO₂ atmosphere.

Table 2: Product yields of pyrolysis of pine wood under N₂ and CO₂ atmosphere at different temperatures

Temperature, °C	Bio-oil, wt. %		Gas, wt. %		Bio-char, wt. %		Conversion, %	
	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂
300	41.0	39.0	14.0	14.0	45.0	46.0	55.0	53.0
350	52.0	53.0	15.0	16.0	34.0	31.0	67.0	69.0
400	56.0	55.0	15.0	17.0	29.0	28.0	71.0	72.0
450	57.0	54.0	18.0	21.0	25.0	25.0	75.0	75.0
500	58.0	-	18.0	-	24.0	-	76.0	-
550	57.0	-	20.0	-	23.0	-	77.0	-

The most suitable conditions for slow pyrolysis of pine wood under N₂ and CO₂ environments have been established and the characterisation of the pyrolysis products such as bio-oil and bio-char is required for the better understanding of the effect of reaction atmosphere. The temperature conditions required for pyrolysis under nitrogen atmosphere are milder than the temperature required for pyrolysis under carbon dioxide atmosphere.

3.2. Total Organic Carbon (TOC) analysis of pine wood and bio-char

To understand the conversion on the basis of total organic carbon (TOC), TOC analysis of pine wood and bio-char obtained after pyrolysis at different temperatures was investigated and results are presented in Table 3.

Table 3: TOC analysis of bio-char obtained from pyrolysis of Pine wood at different temperatures under N₂ and CO₂ atmosphere.

Temperature, °C	Organic carbon in bio-char from TOC analysis, wt%		Organic carbon conversion from TOC analysis, wt. %	
	N ₂	CO ₂	N ₂	CO ₂
300	68.0	71.1	32.0	28.9
350	51.6	49.2	48.4	50.8
400	45.3	44.5	54.7	55.5
450	41.4	42.2	58.6	57.8
500	40.6	-	59.4	-
550	39.8	-	60.2	-

TOC results indicated that pine wood under CO₂ atmosphere showed better carbon conversion at 350 and 400 °C than under N₂ atmosphere. Pine wood biomass conversion on basis of organic carbon increased with increase in temperature. Higher organic carbon conversion was observed in case of CO₂ at 350 and 450 °C than N₂ atmosphere but lower at 300 and 450 °C than N₂ atmosphere. At 300 and 450 °C under CO₂ atmosphere, the CO₂ may be possibly reacted with the active volatiles or with the biomass char and enhanced the char, hence reduction of biomass conversion. From earlier reports also, the effective conversion of biomass has been reduced (Guizani et al. 2014; Jindarom et al. 2007). The similar phenomena have been observed in this investigation too. However, the temperature window for this typical feedstock is completely different and hence the lower conversions have been observed in 350 and 400 °C not in higher temperatures. As the temperature increased 450 to 550 °C the total organic conversion was faintly increased under N₂ atmosphere.

3.3 Bio-oil characterization

3.3.1 Gas chromatography-Mass spectrometry (GC-MS)

The main chemical constituents of pine wood species are carbohydrates (cellulose and hemicelluloses) and lignin. Accordingly, the pine wood pyrolysis bio-oil is derived from these components with different proportions depending on the temperature and different atmospheres used in process. GC-MS is a very powerful analytical technique that is used to identify the products formed by the reaction with the help of difference in retention time in a column followed by difference in molecular mass of the compound. The identified compounds have been classified into various groups such as phenolic derivatives and aromatic ethers which are majorly derived from the lignin component of lignocellulosic biomass, furans, acids/ esters, hydrocarbons, carbonyl compounds (Table 4).

Table 4: Compounds identified by GC-MS: pine wood biomass slow pyrolysis bio-oil obtained in N₂ and CO₂ atmosphere

Name of the compounds	Area, %	
	Under CO ₂ atmosphere	Under N ₂ atmosphere
Furfural	2.7	2.2
2-Furanmethanol	2.6	1.3
2(5H)-Furanone	-	0.6
2,4-Hexadiene, 2,5-dimethyl	1.3	-
2(3H)-Furanone, 5-methyl-	-	0.9
2-Furancarboxaldehyde, 5-methyl-	2.2	1.7
Phenol	1.4	1.6
1,2-Cyclopentanedione	1.5	-
1,2-Cyclopentanedione, 3-methyl-	2.8	1.5
Phenol, 2-methyl-	-	1.9
p-Cresol	-	2.2
Phenol, 2-methoxy-	5.6	8.2
Phenol, 2,4-dimethyl-	-	1.6
Benzeneethanol, 4-hydroxy-	1.3	-
Phenol, 2,5-dimethyl-	0.3	-
Phenol, 3,5-dimethyl-	1.4	-
Phenol, 2-methoxy-3-methyl-	-	1.8
Creosol	6.5	12.0
Catechol	3.6	0.8
5-Hydroxymethylfurfural	1.0	0.9
3,4-Dimethoxytoluene	-	0.6
Phenol, 4-ethyl-2-methoxy-	5.4	6.3
2-Methoxy-4-vinylphenol	5.4	3.8
Phenol, 2-methoxy-3-(2-propenyl)-	-	2.6
3-Allyl-6-methoxyphenol	2.9	-
Phenol, 2-methoxy-4-propyl-	1.9	0.5
Vanillin	1.8	1.5
trans-Isoeugenol	6.5	1.9
Longifolene	1.5	1.5
Phenol, 2-methoxy-4-propyl-	1.9	0.6
Apocynin	1.3	8.6
4-Hydroxy-2-methoxycinnamaldehyde	2.2	-
1-(4-methylthiophenyl)-2-propanone	-	1.3
Phenol, 4-(3-hydroxy-1-propenyl)-2-methoxy-	-	2.2
Homovanillic acid	3.0	0.5
Ethyl homovanillate	1.4	-
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)-	-	1.5

Bio-oils under nitrogen and carbon dioxide environment were majorly composed of cyclopentanedione (e.g., 1,2-Cyclopentanedione, 1,2-Cyclopentanedione, 3-methyl-), furans (e.g., Furfural, 2-Furanmethanol, 2-Furancarboxaldehyde, 5-methyl-, 5-Hydroxymethylfurfural), phenols (e.g., Phenol, Phenol, 2-methoxy-, p-Cresol, Catechol, Phenol, 3,5-dimethyl-, Phenol, 2,5-dimethyl-), guaiacols (e.g., Phenol, 4-ethyl-2-methoxy-, Phenol, 2-methoxy-, Phenol, 2-methoxy-3-methyl-, 2-Methoxy-4-vinylphenol, Vanillin, trans-Isoeugenol).

GC/MS of bio-oil obtained at optimum condition under different atmosphere (N_2 at 500 °C and CO_2 at 400 °C) are shown in table 4. Furan ring-containing compounds were present in both case, under CO_2 atmosphere, higher area percentage of 2-Furanmethanol was observed than in N_2 atmosphere. In N_2 atmosphere relatively higher percentage content of phenols were obtained, as compared to obtained under CO_2 atmosphere. The relative content of Creosol was twice greater under N_2 atmosphere with respect to that obtained under CO_2 atmosphere, but under CO_2 atmosphere produced less Phenol and more Catechol. The total area percentage of methoxy-containing compounds (guaiacols) was obtained high in N_2 atmosphere than the CO_2 atmosphere. The compounds Phenol, 2-methoxy-, Phenol, 4-ethyl-2-methoxy-, Apocynin were present in a higher area percentage in N_2 atmosphere than CO_2 atmosphere but compounds 2-Methoxy-4-vinylphenol and vanillin were present more in CO_2 atmosphere than N_2 atmosphere. Phenolic compounds in bio-oil were derived majorly from the degradation of the lignin component in biomass. Selectivity of apocynin and creosol is higher in N_2 than CO_2 atmosphere. The creosol and apocynin are mainly formed from lignin decomposed by pyrolysis without severe breakdown of the structural lignin present in the biomass. It has been established from our earlier investigations on the use of pure lignin as a feedstock (Biswas et al. 2016). Table 4 shows that the overall contributions of phenolic compounds in the bio-oil produced from pine wood in fixed bed were significantly higher under N_2 atmosphere than the CO_2 atmosphere. Hence, it can be observed that the bio-oil produced by pyrolysis of pine wood under nitrogen and carbon dioxide environments is different. To understand further the structure of bio-oil, 1H NMR and FT-IR of bio-oil was carried out which is discussed in the following sections.

3.3.2 1H Nuclear magnetic resonance (NMR) of bio-oil

NMR spectra are used to get information regarding the various types of protons present in the bio-oil. A summary of integrated peak area regions assigned to different functional group classes present in the bio-oil obtained from pyrolysis of pine wood at temperatures of 300, 350, 400, 450, 500 and 550 °C under N_2 atmosphere and temperatures of 300, 350, 400 and 450 °C under CO_2 atmosphere is shown in Fig.3 respectively. In case of pyrolysis bio-oil under N_2 (at 300, 350, 400, 450, 500 and 550 °C) and CO_2 (at 300, 350, 400 and 450 °C) proton percentage in the region from 0.5 to 1.5 ppm was 24, 20, 17, 17, 19 and 17% respectively that corresponds to protons on aliphatic carbon atoms at least two bonds away from $C=C$ or heteroatom. The next region from 1.5 to 3 ppm, proton percentage was higher under CO_2 pyrolysis bio-oil than under N_2 pyrolysis bio-oil, and this is corresponds to protons on aliphatic carbon atoms which are bonded to $C=C$ either aromatic or olefinic or are two bonds away from a heteroatom. In the next region 3-4.4 ppm, proton percentage under N_2 was higher than under CO_2 . These protons correspond to protons that are attached to carbon atoms next to an aliphatic alcohol or ether or a methylene group which bonds two aromatic rings. The region from 4.4-6.0 ppm, proton percentage resonating in this region was almost negligible at 300, 400 and 450 °C but at 350 °C proton percentage 6% in case CO_2 and in case of N_2 at all temperature protons were observed, that is represents aromatic ether protons (i.e., lignin derived methoxyphenols) and hydrogen atoms of carbohydrate-like molecules (Mullen et al. 2009; Biswas et al. 2016). The region of the spectrum between 6.0 and 8.5 ppm corresponds to the aromatic region. Proton percentage resonating in this region in case of CO_2 was higher than that of N_2 . The downfield spectrum regions (8.5-10 ppm) of the bio-oils arise from carboxylic acids and aldehydes. The proton percentage resonating in this region was almost negligible in case of N_2 and CO_2 .

3.3.3 Fourier transform-Infrared spectroscopy (FT-IR) of bio-oil

FTIR spectra representing functional group compositional analysis from pine wood biomass and bio-oils from pinewood biomass pyrolysis products provided in Fig.4. The broad absorbance band between 3,050 and 3,600 cm^{-1} are attributed to (O-H) vibrations of hydroxyl groups which indicate the presence of alcohols, phenols, and water in the bio-oil. The presence of the O-H absorbance peak together with the presence of

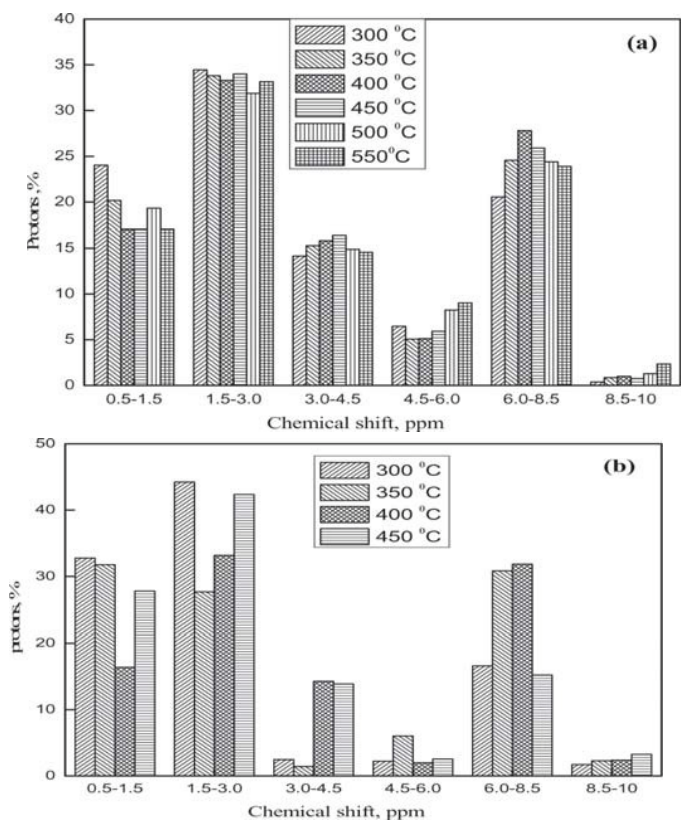


Figure 3: 1H Nuclear magnetic resonance (NMR) of Pine wood bio-oil under (a) N_2 and (b) CO_2 atmosphere at different temperature

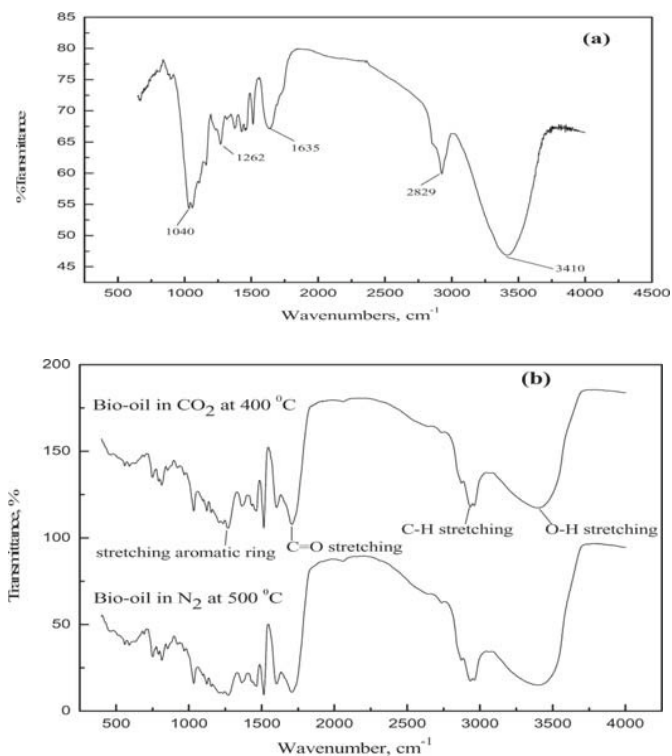


Figure 4: Fourier transform- infrared spectroscopy (FT-IR) of (a) pine wood feed and (b) bio-oil from slow pyrolysis of Pine wood at optimal temperature

C=O stretching vibrations between 1,650 and 1,750 cm^{-1} indicates the presence of carboxylic acids and their derivatives. In addition, the presence of the peaks between 1,650 and 1,750 cm^{-1} may also indicate the presence of ketones, quinones, and aldehyde groups (Putun 2002). The absorbance peak of C-H stretching vibrations between 2,800 and 3,000 cm^{-1} and the C-H deformation vibrations between 1,350 and 1,470 cm^{-1} indicates the presence of methyl and methylene groups of alkanes in pyrolysis oil. The C-H stretching vibrations band for alkanes was more pronounced in case of bio-oil than pine wood feed, which indicates more hydrocarbon compounds in those bio-oils. Increase in the absorbance for alkenes compounds was associated with shrinking of the hydroxyl group absorbance band. The presence of alkenes in the pyrolysis oil may be indicated by the absorbance of stretching vibration of C=C peaks between 1,680 and 1,580 cm^{-1} ; this absorbance peak is also indicative for aromatics. Absorbance peaks between 700–900 cm^{-1} may be related to out of plane C-H bending of mono, polycyclic, and substituted aromatic groups present in bio-oil but absent in pine wood feed (Gercel 2002). The peaks between 950 and 1,300 cm^{-1} are due to the presence of primary, secondary, and tertiary alcohols (Das et al. 2004), 1040 cm^{-1} peak were more well-defined in pine wood feed but absent in the case of bio-oil. The preliminary studies in this investigation confirmed the participatory role of CO_2 and variations in the products distributions. Further studies to understand the synergistic interactions with the solid biomass and/or vapors in the presence of thermal and catalytic studies are in progress.

3.4 Bio-char characterization by Powder X-Ray diffraction and FT-IR

The stacked powder XRD patterns of feed pine wood and biochar at optimal final temperatures have been shown as Fig. 5. The significant reduction of cellulose peak is evidence in the presence of CO_2 atmosphere than in N_2 atmosphere. From the figure, it can also be observed that the pine wood 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 (Wu et al. 2012). These are in confirmation with the results of FT-IR which indicates the conversion of feed cellulose into products. The biochars are seen to be amorphous in nature but rich in carbon content.

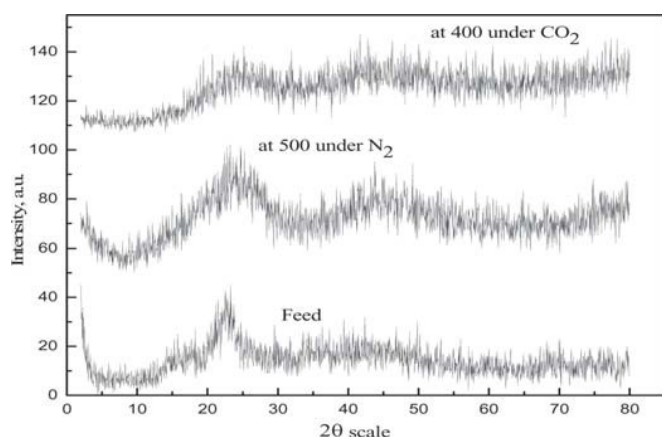


Figure 5: Powder XRD of Pine wood feed and bio-char obtained at optimal temperature under N_2 and CO_2 atmosphere

The FT-IR spectra of feed and bio-chars at optimal pyrolysis conditions under nitrogen and carbon dioxide environments are shown in the Fig 6. The pinewood biomass spectra as discussed earlier shows several vibrations corresponding to O-H stretching, C-H stretching, C=O stretching, aromatic ring vibration, C-H in plane deformation, O-H in plane bending, aromatic ring vibrations, C-O-C asymmetrical stretching and C-O, C-C-O stretching due to cellulose, hemicellulose and lignin moieties. The bio-char spectra show the absence of most functionalities indicating maximum conversion of bio-char. The presence of single peak at 1590 cm^{-1} attributed to the C=C stretching indicates the formation of aromatic bio-char (Krishna et al. 2016). The results obtained are in line with those observed in literature for forest biomass where high degree of aromatic functionality is observed in bio-chars derived by pyrolysis (Wang et al. 2008).

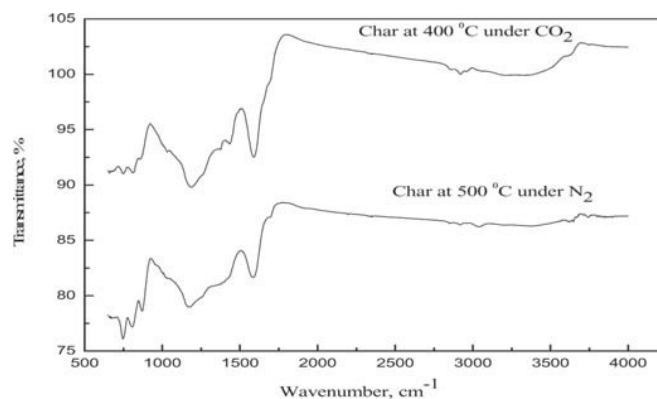


Figure 6: FT-IR of pine wood bio-char obtained at optimal temperature under N_2 and CO_2 atmosphere

4. Conclusions

The role of reaction atmospheres (N_2 and CO_2) on slow pyrolysis of pinewood biomass indicated that the biooil yields are higher with N_2 compared to CO_2 atmosphere. Total organic carbon (TOC) analysis char confirms that the conversion of biomass at 300 °C and above 400 °C is higher in N_2 atmosphere than CO_2 atmosphere. The conversion of biomass is higher in CO_2 atmosphere at 350 and 400 °C than N_2 atmospheres. Selectivity of apocynin and creosol is higher in N_2 than CO_2 atmosphere. The extensive analysis of liquid product further confirms that there is no significant incorporation of CO_2 in the biomass conversion products under the experimental conditions. It has been confirmed from XRD that the significant reduction of cellulose in CO_2 atmosphere than N_2 atmosphere.

Acknowledgements

The authors thank the Director, CSIR-Indian Institute of Petroleum, Dehradun, for his constant encouragement and support. RS thanks Council of Scientific and Industrial Research (CSIR), New Delhi, India, for providing Senior Research Fellowship (SRF). The authors thank the Analytical Science Division (ASD) of CSIR-IIP for NMR, FT-IR, and XRD analysis. The authors thank CSIR in the form of XII Five Year Plan project (CSC0116/BioEn) and Ministry of New and Renewable Energy for providing financial support.

References

- Aguado R, Olazar M, Jose MJS, Aguirre G, Bilbao J, 2000, Pyrolysis of saw dust in a conical spouted bed reactor, Yields and product composition. *Ind Eng Chem Res* 39, 1925–1933
- Biswas B, Singh R, Kumar J, Khan AA, Krishna BB, Bhaskar T, 2016, Slow pyrolysis of prot, alkali and dealkaline lignins for production of chemicals, *Bioresource Technology*, 213,3 19-326.
- Cendrowska A, 1997, Hydrolysis kinetics of cellulose of forest and agricultural biomass, *Eur J Wood Wood Prod.*, 55,195–196
- Chen WH, Lin BJ, 2016, Characteristics of products from the pyrolysis of oil palm fiber and its pellets in nitrogen and carbon dioxide atmospheres, *Energy*, 94, 569-578
- Cho DW, Cho SH, Song H, Kwon EE, 2015, Carbon dioxide assisted sustainability enhancement of pyrolysis of waste biomass: A case study with spent coffee ground, *Bioresource Technology* 189, 1-6
- Czernik S, Bridgwater A, 2004 Overview of applications of biomass fast pyrolysis oil, *Energy Fuels*, 18,590–598
- Das P, Sreelatha T, Ganesh A (2004) Bio oil from pyrolysis of cashew nut shell-characterisation and related properties. *Biomass and Bioenergy* 27: 265–275
- Gercel HF, 2002, The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake, *Biomass and Bioenergy*, 23, 307–314.
- Guizani C, EscuderoSanz F J, Salvador S, 2014, Effects of CO_2 on biomass fast pyrolysis: Reaction rate, gas yields and char reactive properties, *Fuel*, 116, 310-320.
- Hanaoka T, Sakanishi K, Okumura Y, 2012, The effect of $\text{N}_2/\text{CO}_2/\text{O}_2$ 953 content and pressure on characteristics and CO_2 gasification behavior of biomass-derived char. *Fuel Process Technol*, 104, 287–94
- Huber GW, Iborra S, Corma A, 2006, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem Rev* 106, 4044-4098
- Huff MD, Kumar S, Lee JW, 2014, Comparative analysis of pinewood, peanut shell, and bamboo biomass derived bio-chars produced via hydrothermal conversion and pyrolysis, *J Environ Manage*, 146, 303-308.

13. Jindarom C, Meeyoo V, Rirksomboon T, Rangsunvigit P, 2007, Thermochemical decomposition of sewage sludge in CO₂ and N₂ atmosphere, *Chemosphere*, 67, 1477-1484.
14. Krishna BB., Biswas B, Kumar J, Singh R, Bhaskar T, 2015, Role of Reaction Temperature on Pyrolysis of Cotton Residue. *Waste and Biomass Valorization*, 7, 71-78
15. Krishna BB., Biswas B, Kumar J, Singh R, Bhaskar T, 2016, Slow pyrolysis of jatropha seed de-oiled cake and estimation of kinetic parameter, *Journal of Energy and Environmental Sustainability*, 1, 34-39
16. Mohan D, Pittman Jr CU, Steele PH, 2006, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, *Energy Fuels*, 20, 848-889
17. Mullen CA, Strahan GD, Boateng AA, 2009, Characterization of Various Fast-Pyrolysis Bio-Oils by NMR Spectroscopy, *Energy & Fuels*, 23, 2707-2718
18. Ngo TA, Kim J, 2014, Fast Pyrolysis of Pine Wood Chip in a Free Fall Reactor: The Effect of Pyrolysis Temperature and Sweep Gas Flow Rate, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 36, 1158-1165
19. Overend RP., Milne TA, Mudge L. (Eds.), 1985, *Fundamentals of Thermochemical Biomass Conversion*, Elsevier applied science, London
20. Ozbay N, Putun AE, Uzun BB, Putun E, 2001, Biocrude from biomass: pyrolysis of cottonseed cake, *Renew Energy*, 24, 615-625
21. Putun AE, 2002, Biomass to bio-oil via fast pyrolysis of cotton straw and stalk, *Energy sources*, 24, 275-285
22. Putun AE, Ozbay N, Onal EP, Putun E, 2005, Fixed-bed pyrolysis of cotton stalk for liquid and solid products, *Fuel Process Technol*, 86, 1207-1219.
23. Tsai WT, Lee MK, Chang YM, 2007, Fast pyrolysis of rice husk: product yields and compositions, *Bioresour Technol*, 98, 22-28
24. Wang C, Pan J, Li J, Yang Z, 2008, Comparative studies of products produced from four different biomass samples via deoxy-liquefaction, *Bioresour Technol* 99, 2778-2786
25. Wang Z, Wang F, Cao J, Wang J, 2010, Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst, *Fuel Processing Technology*, 91, 942-950
26. Williams PT, Besler S, 1996, The influence of temperature and heating rate on the slow pyrolysis of biomass, *Renewable energy*, 7, 233-250
27. Yang H, Yan R, Chen H, Lee DH, Zheng C, 2007, Characteristics of hemicellulose, cellulose and lignin pyrolysis, *Fuel* 86, 1781-1788
28. Zhang H, Xiao R, Wang D, He G, Shao S, Zhang J, Zhong Z, 2011, Biomass fast pyrolysis in a fluidized bed reactor under N₂, CO₂, CO, CH₄ and H₂ Atmospheres, *Bioresour Technol*, 102, 4258-4264
29. Wu W, Yang M, Feng Q, McGrouther K, Wang H, Lu H, Chen Y, 2012, Chemical characterization of rice straw-derived biochar for soil amendment, *Biomass Bioenergy*, 47, 268-276