

Formation, analysis and characterization of wood pyrolyzed oil

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Abstract. Pyrolysis of wood is the possible path for converting biomass to higher valuable products such as bio-oil, bio-char and bio-gas. Bio-oil or liquid biofuels have higher heating values so it can store and transport more conveniently. The by-products bio-char and bio-gas, which can be used to provide heat required in the process. This work focused on the formation, analysis and characterization of bio-oil which was obtained from the mixed wood pyrolysis. A GC-MS technique was used for the determination of families of lighter chemicals from pyrolyzed oil. Karl fisher titration and other analytical methods were used for the characterization of pyrolyzed oil. In all there were sixty-six compounds found in the GC-MS analysis of bio-oil and the major compound was acetic acid (19.06 wt%), formic acid (4.90 wt%) 1,2-benzenediol (4.43 wt%) and furfural (3.46 wt%). Along with this analysis, pyrolyzed oil was characterized by calculating its viscosity, density, calorific value, acid value, fire point, flash point, carbon, hydrogen, nitrogen, ash and water content in it. Most of the above mentioned properties of bio-oil matches with the properties of crude oil except it shows more water content in it.

1. Introduction

Among the different thermo chemical processes, pyrolysis is an emerging and promising route to produce bio-oil or pyrolysis oil and value added chemicals from solid biomass feed stock (Bridgwater et al., 1999; Dinesh et al., 2006). Pyrolysis is essentially the thermal decomposition of organic matter under inert atmospheric conditions or in a limited supply of air, leading to the release of volatiles and formation of char. The resulting bio-oil obtained with the yield of 70 to 80 wt. % (dry feed basis) depending upon the cellulose and lignin present in the wood material (Demirbas, 2009; Lu et al., 2009).

Bio-oils are derived primarily from depolymerization and fragmentation reactions of cellulose, hemicelluloses and lignin, resulting in its composition and properties of considerable difference from those of petroleum based fuel oils. Bio-oil appears in dark brown viscous state with little sulphur and nitrogen content, but has a high oxygen content nearly 45 wt. % including water. The lower heating value of bio-oil is only 40-45% of that exhibited by the hydrocarbon fuels. Moreover, organic acids in the bio-oils are highly corrosive to common construction materials. Even though hydrocarbon fuels cannot be replaced by bio-oil, but its industrial production focused on the manufacture of higher value chemicals and materials other than fuels (Helena and Ralph, 2001; Mckendry, 2002).



Bio-oil is an extremely complex mixture of organic components, including various types of oxygen containing organic compounds derived from pyrolysis of biomass components. Recent detailed analyses shown that pyrolysis bio-oil contain more than 400 compounds, even though it remains a challenge to identify every compound present in it. (Serdar, 2004; Jean et al., 2001).

Because of the complexity, some simplified analytical methods were used to characterize bio-oil. Chemical characterization of pyrolysis oil has generally been based on the fractionation of oil by using solvent extraction, adsorption, molecular distillation, etc. and then the different fractions obtained were further characterized using analytical methods such as GC-MS, HPLC, gel permeation chromatography, etc. with focusing on its different chemical information (Bridgwater et al., 1999; Lu et al., 2009).

The purpose of the present work is to develop an effective quantitative analysis for light weight components of bio-oils by using GC-MS techniques. Thus yields up to 40 wt. % of the bio-oils can be quantified. Another objective of the work is to carry out the fractionation of the bio-oil using distillation technique to separate the light weight and heavy weight components to further increase the yield of bio-oil.

2. Materials and methods

2.1 Materials

Three kinds of biomass feedstock such as pine, teak, neem were selected as pyrolysis materials. All these biomass used in this study were purchased from a local wooden mills in Aurangabad, India. All this feedstock were first air dried and grounded, and then sieved to a mean particle size of 0.26-0.57 mm. Ultimate analysis of the wood samples was determined by using an analyzer. The proximate analysis, the ash content and volatile matter were determined while fixed carbon was determined by difference. The results were shown in Table 1 and Table 2.

Table 1. Ultimate analysis of three biomasses

Sample	C	H	N	O
Pine	50.8	6.4	0.3	42.5
Teak	51.3	6.1	0.2	42.4
Neem	53.9	6.3	0.1	39.7

Table 2. Proximate analysis of three biomasses

Sample	Volatile Matter	Fixed Carbon	Ash Content
Pine	85.3	12.4	2.3
Teak	80.2	18.4	1.4
Neem	77.2	22	1.6

2.2 Preparation of Bio-oils

Direct fast pyrolysis of biomass was carried out in a self designed annular packed bed reactor in Sanjay Techno Plast Pvt. Ltd. The schematic drawing is shown in Figure 1(a).



Figure 1(a). Schematic representation of experimental setup.

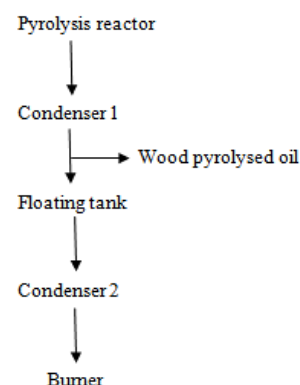


Figure 1(b). Flow diagram of formation of wood pyrolysis oil.

The annular fixed bed reactor was used to carry out the pyrolysis reaction, which can be made open from top and bottom to add and remove the content in it. The inner part of the annular reactor was used as a combustion chamber and outer part was used for the pyrolysis reaction. In combustion chamber 500 gm of wood was inserted with equal amount of all three type of wood. The heat which was generated through the burning of wood was absorbed by combustion chamber and gives it to annular space where pyrolysis reaction was carried out. The pyrolysis reaction was initiated at 200 °C in the annular reactor and continued till 650 °C. After 15 min of the reaction the gas (smoke) generated in reactor chamber was fed to the condenser-1, where tar (pyrolysis oil) get settled at the bottom of the condenser and non-condensable gases were fed to the floating tank. Floating tank was used to hold and create the high pressurized gas. Condenser-2 was filled with $\frac{3}{4}$ th level of water and gases coming out from the floating tank were left 100 mm deep inside the water level. Then pressurized gas comes directly in contact with water where again the condensable gases get settled down and the non-condensable gases were feed to burner. Burners were light up continuously till the pyrolysis reaction ends. This process includes five main parts that are shown in flow diagram as follows (Figure. 1(b)).

3. Results and discussion

3.1 Experimental operating conditions and results obtained

Different experiments were conducted to set the parameter values and to obtain the best results. Following Table 3 shows the optimized parameter values used in the experiments to obtain the pyrolysis oil.

Table 3. Process parameters and its values

Parameters	Results
Wood in Annular Space (gm)	20
Initial wood for Burning (gm)	500
Feed rate used for Burning (gm/min)	28
Total Wood for Burning (gm)	4120
Pyrolysis Oil (gm)	4950
Charcoal wt (gm)	7800
Residue Wt (gm)	1450
Tank Lifting Start Time (min)	30
Weight on Tank (kg)	50
Flame Start Time after all Set up Start (min)	58
Burner -1(min)	81
Burner-2 (min)	79
Burner-3 (min)	80

3.2 Qualitative analysis

The main component of the bio-oil is a verity of small molecules with oxygen containing functional groups such as aldehydes, ketones, carboxylic acids, furans, phenols, carbohydrates, etc. (Dobele et al., 2007; Hyeon et al., 2010). Figure 2 shows the total ion chromatogram of bio-oil from mixed wood pyrolysis at 650 °C and the main compositions corresponding labels in Figure 2 were identified and listed in Table 4. Levoglucosan, a typical pyrolysis product from cellulose pyrolysis, represents incomplete cracking of carbohydrates. A large no of methylated or methoxylated phenolic compounds such as 2-methoxy-phenol, 2-methoxy-4-methyl phenol, 2,6-dimethoxy phenol, that derived from lignin pyrolysis were also detected. Ketones mainly composed of 2-hydroxy-2-cyclopenten, and large no of cyclopentadiones.

Based on an overall consideration of the qualitative results of the bio-oil from mixed wood raw material pyrolysis, following 16 compounds out of 66, were indentified and present in considerable amount i.e. acetic acid, formic acid, furfural, butanal, butyrolactone, 3-methyl-1,2-cyclopentane, 2-methyl-phenol, 2-methoxy phenol, 3-ethyl-2-hydroxy-2cyclopenten, 2-methoxy-4methyl-phenol, 1,2-

benzenediol, 3-methoxy-1,2-benzenediol, 3-methyl-1,2-benzenediol, 2,6-dimethoxy-phenol, 1,2,3-trimethoxy-benzene, levoglucosan.

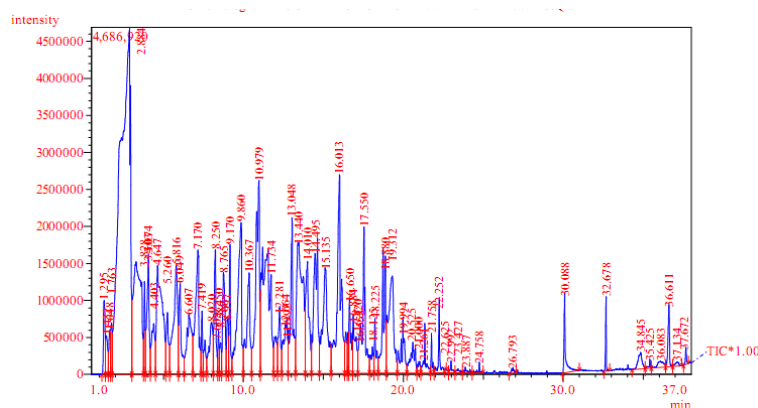


Figure 2. Total ion chromatogram of bio-oil from mixed wood pyrolysis at 650 °C.

Table 4. Identification of the main components

Peak	RT/min	Area %	Library ID
5	2.884	19.06	Acetic acid
6	3.303	4.90	Formic acid ethyl ester
10	4.647	3.46	Furfural
11	5.260	0.81	2-cyclopenten-1-one
15	7.170	2.48	Butyrolactone
25	9.860	3.44	1,2-cyclopentanedione,3-methyl
26	10.367	1.93	Phenol,2-methyl
27	10.979	3.92	Phenol,2-methoxy
28	11.734	5.69	2-cyclopenten-1-one,3-ethyl-2-hydroxy
32	13.048	2.14	Phenol,2-methoxy-4-methyl
33	13.440	4.43	1,2-benzenediol
35	14.495	2.93	1,2-benzenediol,3-methoxy
36	15.135	2.91	1,2-benzenediol,3-methyl
37	16.013	4.30	Phenol,2,6-dimethoxy
42	17.550	2.40	1,2,3-trimethoxybenzene
46	19.312	2.97	1,6-anhydro-beta-D-glucopyranose (levoglucosan)

3.3 Characterization of wood pyrolysis oil

Moisture content of the pyrolysis oil was calculated by using Karl fisher titration and it was found that mixed wood pyrolysis oil contain 66.9 % of the moisture. Along with the moisture content some of the other important properties of the bio-oil required for its characterization was also calculated and presented in Table 5.

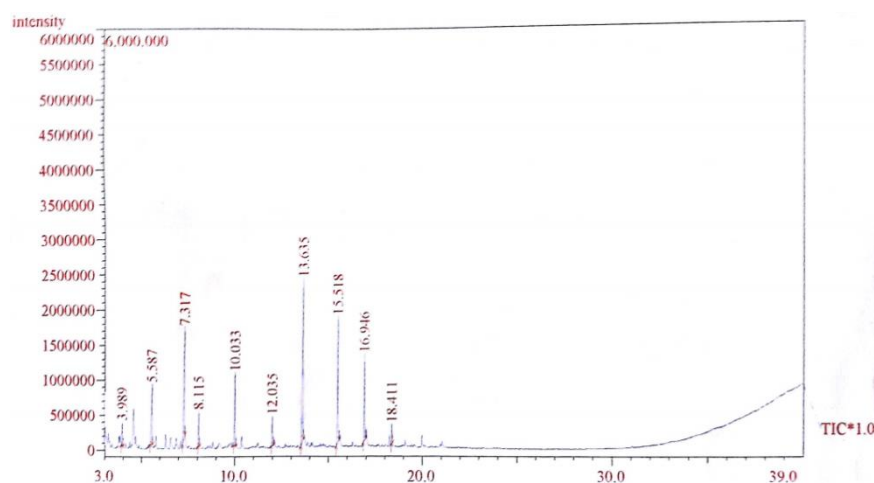
Bio-oil obtained from pyrolysis of mixed wood is highly acidic and low dense in nature. Calorific value of the bio-oil is very less compare to petroleum based fuel oils however, bio-oil is denser than petroleum oil and contain 10-15% more energy by volume. Flash and fire value of the bio-oil is also high compared with petroleum fuels, moreover it contain high ash and sulphur contain. Bio-oil cannot be replaced with the petroleum oils but can be used to obtain the different high value chemicals (Yang et al.2007).

Table 5. Properties of wood pyrolysis oil

Property Name	Specification	Values Obtained
pH	Ph probe	2.2
Density	Specific gravity Bottle	1.02 kg/litter
Viscosity	Glass viscometer	2.1 cP
Acid Value	Titration with 0.1N KOH.	128.80 mg/KOH
Calorific Value	Calorimeter	6.113 MJ/kg
Fire value	Pensky Martin Closed Cup Apparatus	Does not catch fire up to 90 °C
Flash value	Pensky Martin Closed Cup Apparatus	Above 90 °C sample extinguishes
Ash Content	Heated in muffle furnace up to 800° C	1.63%
Carbon content	By chromatogram	10.943%
Hydrogen content	By chromatogram	10.416%
Nitrogen content	By chromatogram	0.883%

3.4 Separation of bio-oil for refinement

Bio-oil cannot be directly applied as a high-grade fuel because of its inferior properties, such as high water and oxygen contents, acidity, and low heating value. Thus, it is necessary to upgrade bio-oil to produce a high-grade liquid fuel that can be used in engines (Bridgwater et al., 1996).

**Figure 3.** Total ion chromatogram of bio-oil separated by distillation process.

In view of its molecular structure and functional groups, conventional column separation technique such as laboratory distillation was used to upgrade the content of bio-oil. Due to its complex composition, the boiling of bio-oil starts below 100 °C, and then the distillation continues up to 250 °C, whereupon 35% of residue was left. The obtained residue was again analysed by using GC-MS technique and components were identified and listed in Table 6. The ion chromatogram of the residue is shown in Figure 3. Qualitative analysis of the distillate residue gives 10 major components listed in Table 6. The components presents in the residue are having the boiling points higher than 250 °C.

4. Conclusions

Overall wood pyrolysis process gives the pyrolysis oil, charcoal and gas which usually contain H₂, CH₄ and negligible amount of ash. Qualitative and chemical characterization of bio-oil is important for designing pyrolysis reaction and to find extended range of applicable fuels and chemicals. In GC-MS analysis of bio-oil in all 66 components were indentified out of which 16 components (listed in Table

4) were found in major concentration. Characterizing the properties of bio-oil like calorific value, density, viscosity, acid value, fire value and ash content one can use bio-oil as alternate source of fuel for boiler, burner, and many other uses. Distillation operation was able to separate the ten major heavy components from the complex mixture of the bio-oil.

Table 6. Identification of components present in residue

Peak	RT/ min	Area %	Library ID
1	3.989	2.77	2-cyclopenten-1-one,3-methyl-
2	5.587	9.26	1,2-cyclopentanedione,3-methyl-
3	7.317	16.54	Phenol,2-methoxy-
4	8.115	4.14	2-cyclopenten-1-one,3-ethyl-2-hydroxy-
5	10.033	9.36	Phenol,2-methoxy-4-methyl-
6	12.035	4.07	Phenol,4-ethyl-2-methoxy-
7	13.635	23.30	Phenol,2,6-dimethoxy
8	15.518	17.42	1,2,3-Trimethoxybenzene
9	16.946	10.89	Benzene,1,2,3-Trimethoxy,5-methyl-
10	18.41	2.25	2,4-Hexadienedioic acid,3,4-diethyl,dimethyl ester (z,z)

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