International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 05, May-2016

Formation, Analysis and Characterization of Mixed Wood Pyrolysed Oil

Dhanashree D. Wagh, Omprakash K. Mahadwad, Prasad L. Kokil
Chemical Engineering Department,
Jawaharlal Nehru Engineering College, Aurangabad, India
Sanjay Technoplast Private Limited, Aurangabad, India

***Abstract*- Pyrolysis of wood is the possible path for converting biomass to higher valueable 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 form 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.**

Keywords: Pyrolysis, bio-oil, GC-MS, characterization, analysis.

I. INTRODUCTION-

Pyrolysis is a thermo chemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen). It involves the simultaneous change of chemical composition and physical phase, and is irreversible.

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. Pyrolysis in wood is typically initiated at 200^0 C and lasts till 450-650^0C.

Bio-oil is a complex mixture of more than 300 compounds resulting from the depolymerization of biomass building blocks, cellulose; hemi-cellulose; and lignin. (10) Typical oxygen content of bio-oil is about 40-50%, resulting in low calorific value of around 16-18 MJ kg-1 . It is also acidic in nature with pH of about 2.5. Bio-oil is highly viscous and its viscosity increases upon storage. The moisture content of bio-oil is about 25-35 wt%. Bio-oil typically contains micron sized char particles. Bio-oil is insoluble with petroleum based fuels. Due to these reasons bio-oil is a low quality fuel and cannot be used directly in a diesel or gasoline combustion engine. In this study we first develop techniques for the physical and chemical characterization of bio-oil.

Biomass is a CO_2-neutral energy source that has considerable reserve. It can replace fossil feedstock in the production of heat, electricity, transportation fuels, chemicals, and various materials. Liquid bio-fuels, which are considered to be substitutes for traditional petrol liquid fuels, can be produced from biomass in different ways, such as high-pressure liquefaction, hydrothermal pyrolysis, and fast pyrolysis.

Wood pyrolysis process is biomass pyrolysis process and it is a fast pyrolysis process. Fast pyrolysis is a technology that can efficiently convert biomass feedstock into liquid biofuels. The liquid obtained from fast pyrolysis, which is also called crude bio-oil, may be used as burning oil in boilers or even as a transportation fuel after upgrading. Fast pyrolysis is a process in which lingo cellulosic molecules of biomass are rapidly decomposed to short chain molecules in the absence of oxygen. Under conditions of high heating rate, short residence time, and moderate pyrolysis temperature, pyrolysis vapor and some char are generated. After condensation of the pyrolysis vapor, liquid product can be collected in a yield of up to 70 wt% on a dry weight basis (Bridg water et al., 1999; Lu et al., 2009). The obvious advantages of the process are as follows:

1. Low-grade biomass feedstock can be transformed into liquid biofuels with relatively higher heating value, thus making storage and transportation more convenient.

2. The by-products are char and gas, which can be used to provide the heat required in the process or be collected for sale.

3. For waste treatment, fast pyrolysis offers a method that can avoid hazards such as heavy metal elements in the char and reduce pollution of the environment.

From wood pyrolysis process we get:

solid $\longrightarrow$ char + volatile matter + gas

Following are the major reactions that can occur within the bio-oil:In analysis part we get all components which are obtained from this chemical reactions.

1. Organic acids + alcohols → esters + water
2. Organic acids + olefins → esters.
3. Aldehydes + water → hydrates.
4. Aldehydes + alcohols → hemiacetals + acetals + water.
5. Aldehydes → oligomers + resins.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 05, May-2016

6. Aldehydes + phenolics → resins + water.
7. Unsaturated compounds → polyolefins.

The composition and properties of bio-oil

The chemical composition of bio-oil is significantly different from that of petroleum fuels. It consists of different compounds derived from decomposition reactions of cellulose, hemicellulose, and lignin. The chemical composition of bio-oil varies depending on the type of biomass feedstock and the operating parameters. Generally speaking, bio-oil is a mixture of water and complex oxygen-rich organic compounds, including almost all such kinds of organic compounds, that is, alcohols, organic acids, ethers, esters, aldehydes, ketones,phenols, etc. Normally, the component distribution of bio-oil may be measured by GC-MS analysis.
In characterization various characteristics properties of oil can be calculated as its viscosity, density, calorific value, carbon content, ash content, acid value, fire point, flash point and also water content can be calculated by Karl fisher titrator present in oil. So from this entire study we get analysis of oil and characterization of oil.

II. MATERIALS AND METHOD

Materials used is mixed wood of 25 Kg. The ultimate in table (a) and proximate analysis in table(b) of softwood and hardwood as follows:

Table no.2(a)-Ultimate analysis.

Type of wood	Volatile Matter	Fixed Carbon	Ash
Hardwood	77.3	19.4	3.2
Softwood	77.2	22	1.6

Type of wood	C	H	N	O	Ash
Hardwood	50.8	6.4	0.4	41.8	0.9
Softwood	52.9	6.3	0.1	39.7	1.0

Table no.2(b)-Proximate analysis **.**

In my report I have used both or combination of above materials.
Method used is pyrolysis of mixed wood to obtain wood pyrolyzed oil.
This process includes five main parts that shown in flow diagram as follows.

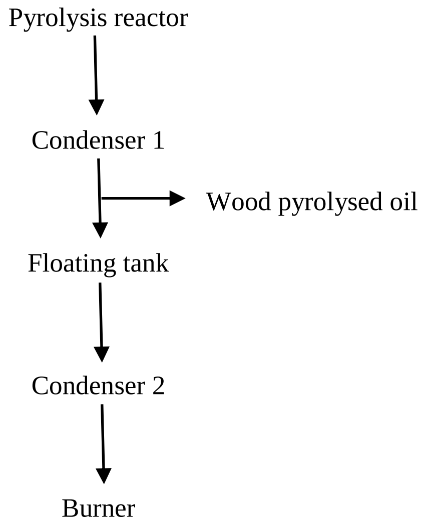

FIG.2.1-Flow diagram of formation of wood pyrolysed oil

First we take mixed type of wood from market then cut it into small pieces. Keep it in oven at 140 for 4 hr for reducing moisture content. Then 20 kg of wood is entered into pyrolyserreactor.The reactor is openable at top side as well as bottom side.The top side is for inserting wood inserting wood into annular space of reactor.The bottom side is for remove ash.

Firstly bottom side is closed and from top side wood is inserted.The top cover and bottom cover is closed by clamp.In combustion chamber 500 gm of wood is inserted then ignition is start .This pyrolysis process is initiated at 200 and lasts till 450-650^{0}C as providing insulating material as rockwool to pyrolysis reactor.After 10 min feeding rate of 140 gm per 5 min wood blocks are added to combustion chamber.

The heat which is coming out through the burning of wood is absorbed by combustion chamber and give it to annular space.Then pyrolysis is start in reactor.After15 min gas(smoke) is coming from reactor and give it to condenser 1.That gas is condensed due to decreasing temperature.then tar is settled down at the bottom of condenser 1.If the temperature of water in condenser 1 reach 40 c then water is change for good condensation purpose and again water is filled.Because of this non condensable hot gas is travel upper side of inner cylinder and condensed gas that is liquid tar is collect at bottom side of condenser 1 that liquid is "pyrolysis oil".That can be collected every 5 min.
Then hot gas travel through the pipe to collect into floating tank.After 20 min floating tank is lifted.Floatingtank contains 2/3 rd of water.It has two cylinders one is upper which collect hot gas and another is lower has 2/3 rd of water.Upper and lower cylinders are adjustable according to pressure of the gas in upper cylinder.

The gas in upper cylinder creates pressure due to limited volume of tank.That pressure lifted upper cylinder in vertical direction.Then we put 50 kg weight on upper tank to get the more pressurized gas.Then exit valve of floating tank is open to give pressurized gas to condenser 2.Condenser 2 is filled with water at ¾ thlevel.In this gas inlet deep 100 mm below the water level.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 05, May-2016

Then pressurized gas comes directly in contact of water where again condensable gas is settled down and non condensable gas is separated and it give to burner that finally lightens the burner.Burners are light up continuously till the pyrolysis reaction ends.Then after some time reactor temperature is decreases charcoal is collected from annular space of reactor.

Therefore in this way we get wood pyrolysed oil .charcoal and non condensable gas.

Fig.2.1:Overall assembly at plant location.

III. RESULT AND DISCUSSION

Below results shows overall process results.

Parameters	Results
Wood in Annular Space(gm)	20
Initial wood for Burning (gm)	500
Feed rate used for Burning (gm/5min)	140
Total Wood for Burning (gm)	4120
Pyrolysed 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

➢ **Analysis** of wood pyrolysed oil by GC-MS-

GC-MS - ON AGILENT 7890 B GCMS.

OVEN TEMPT -60 DEG
ISO TIME - NIL
RAMP RATE - 10 DEG
OVEN TEMP 2.-280 DEG
HOLD TIME - 20 MIN
CARRIER - HELIUM - 1 ML PER MIN

By using this specification get the following TIC of oil with 66 component.

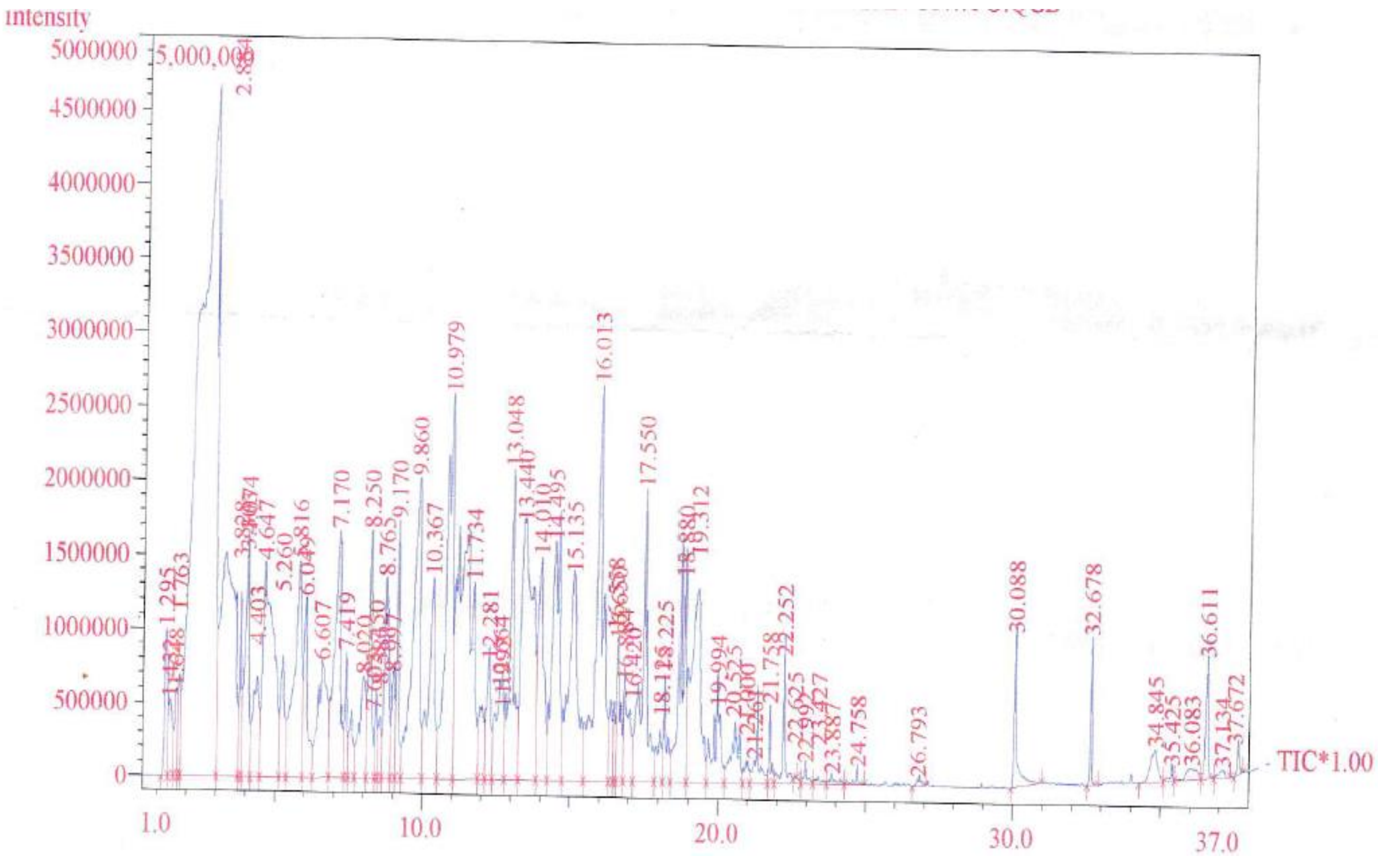

Fig.3.1:TIC of wood pyrolysed oil

Peak	Retention Time	Area %	Height	Component Name
1	1.295	0.68	1000729	Methyl alcohol
2	1.432	0.45	520779	Glycoaldehyde dimer
3	1.648	0.39	593929	2,3-butanedione
4	1.763	0.36	692297	Acetic acid
5	2.884	19.06	4673304	Acetic acid
6	3.303	4.90	1515246	Formic acid ethyl ester
7	3.828	0.51	1196402	Pyridine
8	4.074	1.57	1616216	1-hydroxy-2-butanone
9	4.403	0.95	678090	2-furanol,tetrahydro
10	4.647	3.46	1456912	Furfural
11	5.260	0.81	821807	2-cyclopenten-1-one
12	5.816	2.52	1461753	Butanal
13	6.049	1.15	1198235	2-propanone,1-(acetyloxy)-
14	6.607	1.62	795817	4,4-dimethyl-2-cyclopenten-1-one
15	7.170	2048	1662359	Butyrolactone
16	7.149	0.42	812571	2,5-hexanedione
17	7.605	0.39	452305	2(5H)-furanone,3-methyl-
18	8.020	1.04	690162	2-furancarboxaldehyde,5-methyl-
19	8.250	1.31	1638915	2-cyclopenten-1-one,3-methyl
20	8.450	0.25	572823	2(5H)-furanone,3-methyl
21	8.586	0.31	417803	Phenol
22	8.765	0.37	1355492	Phenol
23	8.997	0.59	727940	Etganone,1-cyclopentyl-
24	9.170	0.87	1734404	2-furanmethanol,tetrahydro-
25	9.860	3.44	2031865	1,2-cyclopentanedione,3-methyl
26	10.367	1.93	1289208	Phenol,2-methyl
27	10.979	3.92	2595338	Phenol,2-methoxy
28	11.734	5.69	1265667	2-cyclopenten-1-one,3-ethyl-2-hydroxy
29	11.992	0.60	482359	Phenol,2,3-dimethyl
30	12.281	0.86	828316	Phenol,2,5-dimethyl
31	12.664	1.17	648474	Phenol,3-ethyl

32	13.048	2.14	1988083	Phenol,2-methoxy-4-methyl
33	13.440	4.43	1755974	1,2-benzenediol
34	14.010	2.04	1443505	1,4:3,6-dianhydro-alpha-d-glucopyranose
35	14.495	2.93	1609551	1,2-benzenediol,3-methoxy
36	15.135	2.91	1411678	1,2-benzenediol,3-methyl
37	16.013	4.30	2670932	Phenol,2,6-dimethoxy
38	16.420	0.45	549849	2-acetyl-4,4-dimethyl-cyclopent-2-enone
39	16.558	0.27	464177	1,3-propanediol,2-methyl-,dipropanoate
40	16.650	0.76	963346	1,3-benzenediol,4-ethyl
41	16.884	0.89	708705	Phenol,2-methoxy-5-(1-propenyl)-,(E)-
42	17.550	2.40	1873968	1,2,3-trimethoxybenzene
43	18.125	0.37	241674	3,5-dimethyl-2-furyl methyl ketone
44	18.225	0.49	624230	Ethanone,1(4-hydroxy-3-methoxyphenyl)-
45	18.880	1.85	1368383	2-propanone,1(4-hydroxy-3-methoxyphenyl)
46	19.312	2.97	1299302	1,6-anhydro-beta-D-glucopyranose(levoglucosan)
47	19.994	0.92	658239	4-oxo-beta-isodamascol
48	20.525	0.71	249684	Alpha-D-mannofuranoside,1-O-heptyl
49	21.000	0.15	146302	Acetic acid,3-(5,5-dimethyl-spirol[2.5]oct-4-yl)-1-methyl-propenyl ester
50	21.261	0.44	154266	Butanoic acid,2,2-diethyl
51	21.758	0.22	401192	Ethanone,1(4-hydroxy-3,5-dimethoxyphenyl)
52	22.252	0.56	836697	3,5-dimethoxy-4-hydroxyphenlacetic acid
53	22.625	0.01	15292	1,4:3,6-dianhydro-alpha-d-glucopyranose
54	22.993	0.11	144731	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)
55	23.427	0.07	48022	
56	23.887	0.09	65479	Phenol,4-methoxy-3-(methoxymethyl)
57	24.758	0.08	120824	Eicosanoic acid
58	26.793	0.06	50522	9,12-octadecadienoic acid(Z,Z)
59	30.088	0.66	1004090	4-amnobenzanilide
60	32.678	0.32	748736	2-(2-cyanophenyl)oxazole
61	34.845	0.37	216474	Dotriacontane
62	35.425	0.07	110116	Heptasiloxane,hexadecamethyl
63	36.083	0.21	81396	Tetraentacontane,1,54-dibrome
64	36.611	0.51	750503	Tetracontane
65	37.134	0.09	54131	Sulfurous acid,octadecyl 2-propyl ester
66	37.672	0.10	184226	Heptsiloxane,hexadecamethyl
		100.00	62441796	

Table no.1:TIC information of GC-MS analysis

- **Characterization** of wood pyrolysed oil:

1.Moisture content:Moisture content of oil can be calculated by Karl fisher titrator and get the value as 66.9 %.

Property Name	**Specification**	**Values obtained**
pH	Ph probe	2.2
Density	Specific gravity Bottle	1.02g/ml
Viscosity	Glass viscometer	2.1cP
Acid Value	Titration with 0.1N KOH.	128.80 mg/KOH
Calorific Value	Bomb Calorimeter	1461.8 cal/^{0}C
Fire value	Pensky Martin Closed Cup Apparatus	Does not catch fire upto 90^0 C
Flash value	Pensky Martin Closed Cup Apparatus	Above 90^0 C sample extinguishes
Ash Content	Heated in muffle furnace upto 800^0 C	1.63%
Carbon content	By chromatogram	10.943%
Hydrogen content	By chromatogram	10.416%
Nitrogen content	By chromatogram	0.883%

Table no.2-Calculated properties of wood pyrolysed oil.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 5 Issue 05, May-2016

IV.CONCLUSION:

Overall wood pyrolysis process gives the pyrolysed oil that is obtained from mixed type of wood as a feed we also called that as heavy oil,then charcoal and gas which usually contains H_2, CH_4 and negligible amount of ash.And from literature survey it is clear that each product is useful.

Analysis of this wood pyrolysed oil which is obtained from mixed wood pyrolysis process by GC-MS analyzer gives 66 components that are light weight components from which more copmponent is acetic acid(19.06 wt%) as illustrated above all these components are useful and important .

Characterizing the properties as like calorific value, density, viscosity, acid value, fire value, ash content of this pyrolysed oil it can be used as alternate source of fuel for boiler, burner, and many other uses.

ACKNOWLEDGEMENT:

This work was supported by Chemical Engineering department my guide Prof.O,K,Mahadwad of my Institute and sincere thanks to Mr.Prasad Kokil as my industrial guide of Sanjay Technoplast pvt ltd. Aurangabad.

Very grateful thanks to Shraddha analytical services Mumbai for providing Instrumental service for project work

REFERENCE:

[1] Zaror C.A. and Pyle D.L. 1982. The Pyrolysis of Biomass: A General Review. Proc. Indian Acad. Sci. (Eng. Sci). 5: Part 4, 269-285.

[2] Krishna Prasad K., Sangen E. and Visser P. 1985. WoodburningCookstoves. Advances in Heat Transfer 17: 159-310.

[3] Papadikis,K:Gu,S:Bridge water, A.V Eulerian model for thevcondensation of pyrolysis vapors in water condenser .Energy fuels,25 1859-212(2011)

[4] Babu,B.V,:Chaurasia,A.S.Modeling,simulation and estimation of optimum parameters ofin pyrolysis of biomass.Energy Convers.Manag.,44,2135-2158(2003)

[5] Thunman,H.,:Leckner,B.Thermal conductivity of wood –Models for different stages of combustion Biomass Bioenergy 2002,23,47-54.215(2002).

[6] S.sinha,A.Jhalani,M.R.Ravi&A.Ray Department of mechanical engineering,Indian Institute of technology Journal of analytical and applied pyrolysis,New Delhi-110016,India(1982).

[7] Papadikis,K.,:Gu,S.,:Bridgewater,A.V.3D Simulation of the effects of sphericity on char entrainment in fuidisedbeds,Fuel Proc.Technol.91,749-758.(2011)