



## SEPARATION AND APPLICATION OF MIXED WOOD PYROLYSED 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 separation of water from oil and application of bio-oil which was obtained from the mixed wood pyrolysis. In this workout two processes mention for removal of water from bio-oil. One is simple distillation and other is bio-oil kept in oven at 100<sup>o</sup> C till constant weight reaches. A GC-MS technique was used for both the processes to determine the families of lighter chemicals from pyrolysed oil. Karl fisher titration and calorific value characterizes bio-oil after separation of water in terms of % of water in Karl fisher and heating value in calorific value for both the processes. Eleven compounds found in the GC-MS analysis of bio-oil distillation and twelve compound obtained from oven. In application part what are the uses of this oil is given as all industrial uses, domestic uses and in this oil whatever chemical compounds useful is also given.

**Keywords:** Pyrolysis, bio-oil, distillation, GC-MS, Karl-fisher, analysis.

### I. INTRODUCTION

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<sup>o</sup> C and lasts till 450-650<sup>o</sup>C.

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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. General reaction of wood pyrolysis as:

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  $\longrightarrow$  esters + water
2. Organic acids + olefins  $\longrightarrow$  esters.
3. Aldehydes + water  $\longrightarrow$  hydrates.
4. Aldehydes + alcohols  $\longrightarrow$  hemiacetals + acetals + water.
5. Aldehydes  $\longrightarrow$  oligomers + resins.
6. Aldehydes + phenolics  $\longrightarrow$  resins + water.
7. Unsaturated compounds  $\longrightarrow$  polyolefin.

Bio-oil has a high content of carboxylic acids, so catalytic esterification is used to neutralize

these acids. Both solid acid and base catalysts display high activity for the conversion of carboxylic acids into the corresponding esters, and the heating value of the upgraded oil is thereby increased markedly. Formed this type of oil has 66.9% of water two techniques are used to remove that water %.

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. 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.[2,3]

In this work out separation of water done by two ways as:

1. Simple distillation
2. By taking oil in oven at 100 °C till constant weight occur.

And finally getting oil is characterize by calculating calorific value or heating value and karl fisher titration to show remaining % water in oil.

#### ❖ SEPARATION OF WATER FROM BIO-OIL:

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, 1996; Czernik & Bridgwater, 2004; Mortensen et al., 2011). In view of its molecular structure and functional groups, and using existing chemical processes for reference, such as hydrodesulfurization, catalytic cracking, and natural gas steam reforming, several generic bio-oil upgrading technologies have been developed, including hydrogenation, cracking,

esterification, emulsification, and steam reforming. Components with unsaturated bonds, such as aldehydes, ketones, and alkenyl compounds, influence the storage stability of bio-oil, and hydrogenation could be used to improve its overall saturation[4,5]. Hydrogenation can achieve a degree of deoxygenation and distillation and oven techniques used for removal of water from oil.

#### 2.MATERIALS AND METHODS

25 kg of mixed wood is used for pyrolysis and then mixed wood pyrolysed oil is getting.

Overall process for formation of this type of oil is mentioned in.[1]

Mainly two methods for separation of oil from water as:

1. Simple distillation
2. By Oven

Overall process description of both the methods as follows:

1. Simple distillation:

Distillation is a common separating technology in the chemical industry. This method separates the components successively according to their different volatilities, and it is essential for the separation of liquid mixtures. Atmospheric simple distillation, vacuum distillation, steam distillation, and some other types of distillation have been applied in bio-oil separation.

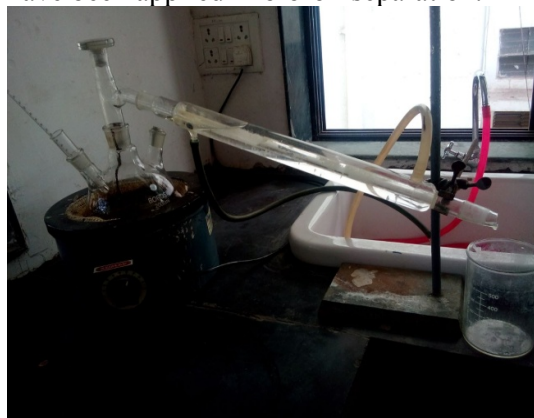


Fig.2 .1: Simple distillation assembly with oil

In this process take 300ml of oil in round bottom three joint necked flask.

At 840 C first cut getting and upto 1020 C this first cut continually getting. This distillate taken time of 2 hrs for collection. This overall process takes 3 hrs to complete distillation upto 1020 C. Final results of this process:

Oil taken=300 ml  
 Distillate=166 ml  
 Residue=70ml  
 Overall loss=64ml

GC-MS analysis of residue is done and also karl fisher and calorific value is calculated.

2. Bio-oil taken in oven at 1000C



Fig.2.2: Assembly of Bio-oil taken in oven  
 Weight of crucible=80gm  
 Weight of oil with crucible=180gm

Time(hr)	Measuring weight
1	168
2	160
3	148
4	138
5	118
6	114
7	108
8	92
9	92

Weight of oil taken=100gm  
 Table 1-Weight analysis of Bio-oil.

In this process 100 gm of bio-oil taken into oven at 100<sup>0</sup> C. And at interval of 1 hr. weight if oil is checked till the constant weight occur. at 100<sup>0</sup>C. -

According to table for reaching constant weight at 100<sup>0</sup>C in oven for this oil take 9 hrs. And finally out of 100 gm of oil after 9 hrs. Only 12 gm of oil is remain in crucible. This 12 gm of oil's GC-MS analysis and karl fisher and calorific value is calculated.

**3.RESULTS AND DISSCCUSION:**

In result part GC-MS analysis of both the processes mentioned. And also for characterise % of water karl fisher titration and calorific value is calculated.

1. GC-MS analysis of simple distillation residue as follows:

ON AGILENT 7890 B GC-MS.  
 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 GC-MS analysis in this processed oil 10 components are remaining.

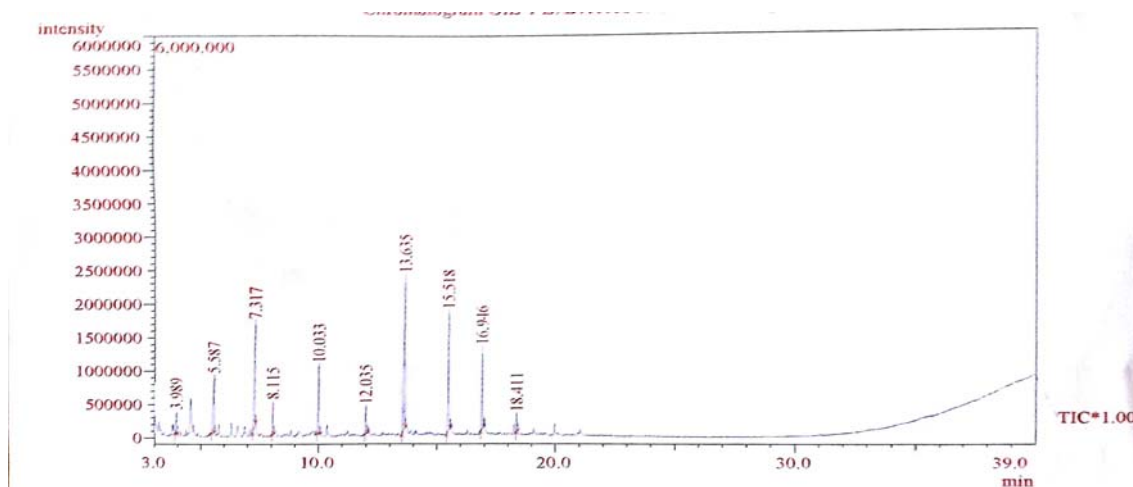


Fig.3.1-TIC of simple distillation residue

Peak No.	Retention Time	Area %	Component Name
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	18.411	2.25	2,4-Hexadienedioic acid,3,4-diethyl,dimethyl ester(z,z)
		100.0	

TABLE 2:Peak Analysis of TIC of simple ditillation (residue)

➤ By using karl fisher titration in this oil  
 41.44% of water is present.  
 Calorific value=2025.86 Cal/°C

2.GC-MS analysis of bio-oil taken in oven(12gm):  
 ON AGILENT 7890 B GC-MS.  
 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 GC-MS analysis in this processed oil 12 components are remaining.

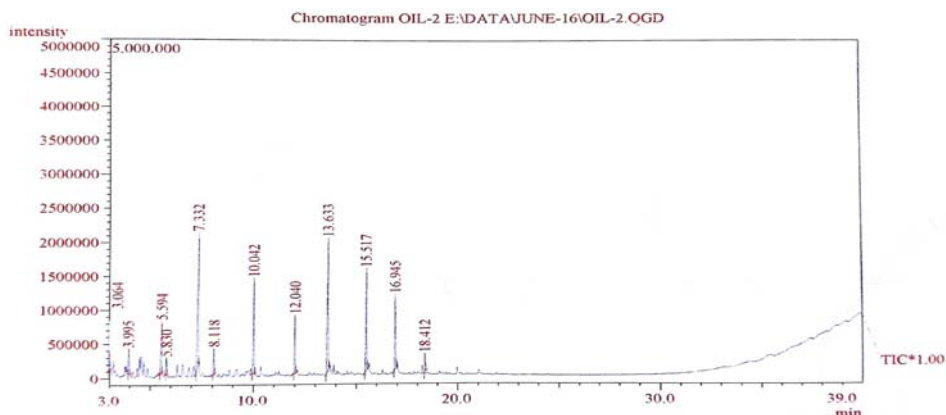


Fig.3s.2-TIC of oven bio-oil

Peak	Retention time	Area %	Component Name
1	3.064	2.08	1-(3H-Imidazol-4-yl)-ethanone
2	3.995	2.77	2-cyclopenten-1-one,3-methyl-
3	5.594	7.76	1,2-cyclopentanedione,3-methyl-
4	5.830	1.86	2-cyclopenten-1-one,2,3-dimethyl-
5	7.332	20.17	Phenol,2-methoxy
6	8.118	2.86	2-cyclopenten-1-one
7	10.042	12.35	Phenol,2-methoxy-4-methyl
8	12.040	7.50	Phenol,4-ethyl-2-methoxy
9	13.633	18.16	Phenol,2,6-dimethoxy
10	15.571	13.23	1,2,3-trimethoxybenzene
11	16.945	9.24	5-tert-Butylpyroallol
12	18.412	2.04	2,4-Hexadienedioic acid
		100.01	

TABLE 3:Peak Analysis of TIC of Oven process oil

• By using karl fisher titration in this oil 24.48% of water is present.  
 Calorific value=3206.85 Cal/°C

❖ APPLICATION OF MIXED WOOD BIO-OIL:

Bio-oil produced from this pyrolysis has a wide range of applications. The major applications include heat and power generation, liquid fuels, and raw chemical products. The oils produced can be used directly in energy production by combustion, although the heating value of bio-oil is lower than that of fossil fuels (about 40% less than diesel fuel). Basic modifications on boilers to handle the viscosity of the bio-oil are needed to accommodate the material as a burning fuel. Bio-oil produces lower emissions of nitrogen oxide and sulfur gases when burned, especially when compared to fossil fuel emissions (Czernik et al. 2004). While emissions of greenhouse gases are lower in bio-oils than in fossil fuels, particulates are higher. Overall, bio-oil used for heat generation through combustion is considered carbon-neutral because all the carbon dioxide released in combustion is captured by the plants and trees during the photosynthesis process. Chemicals extracted from bio-oil are used as food flavorings, resins, adhesives, agrichemicals, and fertilizers (Czernik et al. 2004). Table 1 (adapted from Garcia-Perez et al. 2011b) lists the potential uses of the chemical compounds from the pyrolysis of biomass.

Industrial raw chemicals	Products
Acetic acid	Adhesives
Aldehydes and ketones	Asphalt paving substitution
Alkylaromatics	Bio-carbon electrodes
5-hydroxymethyl furfural	Coal dust suppression
Levoglucofan	Fertilizer
Methanol	Antioxidants
Glucose	Food additives Pesticides Impermiabilizer Road de-icer Surfactants Wood preservatives

Table 4- The potential uses of the chemical compounds from the pyrolysis of biomass

While bio-oil has many applications, it is not suitable as a transportation fuel because of its problematic and unfavorable properties: corrosiveness, high viscosity, low energy density, and low thermal stability. Given these

challenges, bio-oil from fast pyrolysis needs to be upgraded in a secondary reactor in order to be used as a transportation fuel and realize the market value of the oil.

While transportation fuel upgrades and hydrogen upgrades are possible, economics and industrial constraints have historically limited the advancement. The recent increase in attention to the conversion of bio-fuels has caused rapid development of technologies to upgrade bio-oil in order to accommodate it into existing fuel production facilities (Bridgewater 2012). Matching the production method and biomass sources to the appropriate or logical use will further overcome many of the obstacles present today.

**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<sub>2</sub>, CH<sub>4</sub> and negligible amount of ash. And from literature survey it is clear that each product is useful. In this oil water % is excess so two separation techniques are used as for separation of water as simple distillation and oil taken in oven.

Analysis of this both processes gives 10 components in simple distillation GC-MS and more component phenol, 2,6-dimethoxy (23.30wt%) is present and 12 components in oil taken in oven. In this oil more component phenol, 2-methoxy (20.7wt%) present.

Characterizing the both oil calorific value is calculated. Caloric value of oven oil is more than distillation oil, and also water % of distillation oil is more than oven sample. It is clear that oven oil separated from water is more than distillation oil. Oven is convenient technique for reducing water % and increasing calorific value of this type of oil. In application of bio-oil it is useful in domestic, industry level, heat and power generation and also it has potentially usefulness of its compounds.

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