# Separation of Phenol from Bio-Oil Produced From Pyrolysis of Agricultural Wastes

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Abstract – The aim of this study was to separate phenol from Bio-Oil obtained from the pyrolysis of agricultural wastes (BAW). The BAW was obtained in one step catalytic pyrolysis in which temperature of the reactor was kept at 30°C and then increased up to 900°C. After pyrolysis, the BAW was distillated and analyzed by Gas chromatography and Mass spectrometry (GC-MS) technique and comprehensive twodimensional gas chromatography with time-of-flight mass spectrometry detection (GC × GC/TOFMS) Where BAW showed the presence of more than 120 other important compounds and phenol. After detection, phenol was separated by solvent extraction method, where Ethyl ether (C<sub>4</sub>H<sub>10</sub>O), Caustic soda (NaOH) and Hydrochloric acid (HCI) were used to separate phenol from BAW and then Nuclear magnetic resonance spectroscopy (NMR) was done to confirm the recovery of phenol.

Keywords: NMR; GC/MS; Biomass Pyrolysis; Bio-Oil Production; Phenol Extraction

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#### INTRODUCTION

Bio-oil is a complex mixture which contains a large number of organic compounds, including alcohol, organic acids, phenol, aldehyde, ketone, etc. Some of these chemicals, such as phenols are important industrial raw materials and additives [1-3]. The total amount of phenolic compounds in the pyrolysis oil varies from 20.0% to 30% depending on the biomass used and operating conditions [4,5]. Bio-oil contains several hundreds of chemicals as a result, it exhibits some inferior properties, such as high water content, high oxygen content, high viscosity low flash point, and strong corrosiveness [6]. These drawbacks make it difficult to be directly used as a vehicle fuel. Therefore, several upgrading technologies have been developed to improve the quality of bio-oil, including catalytic hydrodeoxygenation [7-9], catalytic cracking, steam reforming, catalytic esterification, supercritical upgrading and so on [10]. Compared with phenols derived from petroleum fuel, these phenolic compounds are renewable and easily obtained. These phenols are not only used as a replacement for phenol in phenol-formaldehyde resins but also as raw materials for developing biobased antioxidants and many other purposes [11-15]. Pyrolysis offers the cheapest route to renewable liquid fuels. Nonetheless, many aspects of the pyrolysis pathway are still under investigation. The diverse array of research into biomass pyrolysis is multi-disciplinary and multi-dimensional and includes Pyrolysis Oil (PO) characterization, kinetic studies, new distillation systems like vacuum distillations system, computational fluid dynamics, design of new reactors, new catalytic systems, microwave-assisted pyrolysis, optimizing the pyrolysis yield, process techno-economic intensification. analysis. molecular distillation system, environmental assessment, in addition to enterprise-wide and supply chain optimization [16-22]. Now-a-day biomass has an un ignorable importance in our life and in industries as an interesting renewable resource used to provide second generation of biofuels or chemicals [23-27]. Large amount and CO<sub>2</sub> neutrality with low sulfur and nitrogen contents make biomass a sustainable and ecofriendly energy source [28-32]. Recently bio-oil has been paid attention to provide fuels and chemicals and the residues of pyrolysis could be used as soil fertilizer [33-38]. Biomass is a CO<sub>2</sub>, H<sub>2</sub> and syngas neutral energy source that has considerable stockpile. It can replace fossil feedstock in the production of heat, electricity, transportation fuels, chemicals, soil fertilizers and other important materials [39-41]. Liquid bio-fuels, which are considered to be substitutes for traditional fossil fuels, can be produced from biomass in different ways, such as high-pressure liquefaction, fast pyrolysis and Hydro-thermal pyrolysis [42-45]. Pyrolysis is a technology that can efficiently convert biomass stockpile 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 [46,47]. In fast pyrolysis, lignocellulosic molecules of biomass are rapidly decomposed to short chain molecules in the absence of oxygen [48]. 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 65-75% on a dry weight basis [49,50].

#### EXPERIMENTAL

## Materials discarded sawdust and other reagents

The BAW was obtained by pyrolysis of a mixture (3:1 in mass) of sawdust (Pterocarpus, Eucalyptus and Kapok ect) and CaO. The sawdust was mixed with the water after their granulometric reduction Calcium oxide was added to this mixture. After preparation, the mixture was dried at environmental temperature for 24 hours.

## Production of BAW

The BAW was produced from the pyrolysis of sawdust in the presence of 25% CaO as catalyst. The biomass sample was kept inside a stainless steel reactor of pyrolysis system which was connected to two other glass chambers as shown in Figure 1. The temperature of the chamber which had biomass was increased from 30°C to 900°C with the help of electric heater, temperature controller cabinet, and two condensers. In this system through biomass was converted to biogas and then condensed to bio-oil at temperatures 90°C and 10°C respectively. The two condensed fractions BHTP and BLTP were collected and introduced for further analysis (Figure 2).

## GC-MS analysis of BHTP and BLTP (BAW)

The bio-oil identification were performed on a GC Agilent series 6890 with an Agilent mass selective detector of series 5973, a capillary polar wax column, polyethylene glycol (PEG)-coated (length of 30 m, internal diameter of 0.25 mm, and film thickness of 0.25  $\mu$ m) Chromatographic conditions: Injection volume of 0.2  $\mu$ L, oven at 40°C (1 min) 6°C min–1 up to 300°C (10/Min) split mode with a ratio of 100:1 and injection temperature of 290°C. Time taken was 54.3 minutes, He (helium) as carrier gas with a flow rate of 2.9 mL min-1 (Figure 3).





Figure 2: Chromatograph operated in splitless mode.



Figure 3: Chromatograph operated in split mode.

## Extraction of phenols

A feasible separation route to isolate phenolic fraction from bio-oil was investigated. A certain amount of Ethyl ether (C<sub>4</sub>H<sub>10</sub>O) and 20 ml of 10% solution of Caustic soda (NaOH) was added to bio-oil to separate the water and phenol from the bio-oil by reacting with phenol to form Sodium phenoxide (NaOH+C<sub>6</sub>H<sub>6</sub>O=NaOC<sub>6</sub>H<sub>5</sub>+H<sub>2</sub>O). The phase splitting was initiated and two phases occurred, a bottom aqueous layer which was a little bit clear and transparent brown compared to an upper layer that was very viscous and dark. The formed bottom layer was separated and 20 ml of 10% solution of HCl was added to it, to react with NaOC<sub>6</sub>H<sub>5</sub> in solution to form NaCl and phenol (NaOC<sub>6</sub>H<sub>5</sub>+HCl=C<sub>6</sub>H<sub>6</sub>O+NaCl) and after pH test, the water was evaporated through hot air and the remaining compound (phenol) was washed with liquid NaCl and introduced to NMR to confirm the recovery of phenol from bio-oil as shown in Figure 4 and a simple sketch in Figure 5. While reactions and mechanisms are shown in Figure 6.

## **RESULTS AND DISCUSSION**

#### **Chemical composition of BAW**

BAW was a dark and sticky liquid mixture of more than 120 of organic compounds. The compounds detected in BAW can be classified into hydrocarbons, alcohols, phenol, ethers, aldehydes, ketones, carboxylic acids, and other esters. But large peaks of GC/ MS mostly showed aromatic, aliphatic, and cyclic hydrocarbons while small peaks showed other groups, Library match was used for identification of compounds based

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on probability score and each compound was detected very clearly and with a high probability value. According to GC/MS analysis summarized in Tables 1 and 2, mostly aromatics and aliphatic groups were enriched in the sample. After GC/MS analysis, each peak of chromatogram was matched with library one by one, where different peaks showed different Aliphatic and Aromatic compounds as well as other important compounds like phenol and ketone (Figures 7 and 8).

#### Hydrocarbons in BAW

Tables 2 and 3 show C<sub>8</sub>–C<sub>17</sub> hydrocarbons and other classes were enriched in the BAW. As shown in Table 1. Aliphatic and aromatic hydrocarbons with  $C_8$ – $C_{17}$  are predominant in the BAW sample with a % area of 53.99

Alcohols, Aldehydes, Ketones, Ethers, Esters, Phenols, and Nitrogenous compound also present in BAW while in these classes, Phenols and ketones occupied more space compared to others as shown in Table 4 and 5. Above Figure 9 is the graphical representation of both fractions BHTP (blue) and BLTP (red) Show % area of all groups present in BAW.

## **Catalytic optimization**

Numerous reaction were carried out in which the amount of







Figure 5: The simple sketch above shows how to recover phenol from bio-oil step by step.



Figure 6: The reaction steps and mechanism above show how NaOH reacts with Phenol.



Figure 7: Shows only aliphatic hydrocarbon peaks.



Figure 8: Shows only aromatic hydrocarbon peaks.



Figure 9: % area of compounds in BHTP (blue) and BLTP (red).

NO	Compound's Name	Formula	Retention time
1	Benzene, 1-ethyl-3-methyl	C981Z	8.18
2	Benzene, 1,2,3-trimethyl	C9H12	9.00
3	Decane	C10822	9.15
4	2-Decene, (Z)	F10H20	9.32
5	cis-3-Decene	C10820	9.52
6	Benzene, 1,2,3-trimethyl	09#12	9.72
7	Benzene, 2-propenyl	C9H10	9.82
3	Indane	09#10	10.17
¥	Indene	C <sub>9</sub> H <sub>8</sub>	10.30
10	Benzene, butyl	C10H14	10.52
11	Benzene, 1,2-diethyl	C10 <sup>II</sup> 14	10.72
12	Benzene, 1-methyl-4-(1-methylethyl)	C10H14	11.30
13	Undecane	C11H24	11.65
4	5-Undecene, (Z)	C11#22	11.80
15	Benzene, 4-ethenyl-1,2-dimethyl	¢10#12	12.65
16	1H-Indene, 2.3-dihydro-5-methyl	C10H12	12.90
17	7-Methyl-1.2.3.5.8.8a-hexahydronaphthalene	C11H16	13.00
18	2-Methylindene	F10#10	13.10
19	Benzene, pentyl	C11H16	13.13
20	Nanhthalene, 1.2.3.4-tetrahydro	E10H12	13.25
21	Benzene (1-methylbutyl)	F11#16	13.38
22	Naphthalene	C10 <sup>8</sup> 8	13.75
23	3-Dodecene (Z)	C12H24	13.90
24	3-Dadecene (Z)	C12H24	14.05
25	Dodecane	C12826	14.15
26	3-Dodecene (F)	C12H24	14.75
27	3-Dodecene (Z)	E12824	14.50
R	2.Ethyl,2.3.dihydro-1H-indepe	E11814	14.95
20	Renzene hevul	C12818	15.55
30	Renzene (1-methylnentyl)	C12818	15.70
21	2.Tridorene (7)	C13126	1630
22	Nanhthalene, Limeth vi	E11810	16.35
22	Tridacana	C13879	16.45
24	3.Tridecene (F)	E13826	16.55
25	1H-Indene, 1. athulidana	C11810	16.75
26	Romana hastul	C12H20	17.98
27	1. Mathul, 7. n. havelbanzana	C13820	18.00
10	Nanhthalene 2 athul	C12812	18.66
20	Rapidualene, 2-etby	C14H39	18.50
10	Tetraducana	C14820	10.30
11	2. Tatradacana (F)	C14830	10.03
12	Nankthalana, 1.7. dimathul	C12812	10.15
12	Proprioration of the second	C15/022	20.72
1.1	r entauetane	-15°32	21.00
19	n-ivonyicyconexane	15'30	21.80
16	flexadecane Contamentame and and	-10-34	22.70
10	Nyciopentane, undecyi	10"32	22.00
11	neptagetane	11/030	124.38

NO	Formula	Retention time (Min)
1	C5H12O	9.50
2	C5H100	7.63
3	C6H12O	9.50
4	C8H160	20.83
5	C7H14O	15.77
6	C6H12O	13.89
7	C5H8O	11.23
8	C6H100	13.63
9	C7H120	16.03
10	C2H100	19.77
11	C7H140	15.77
12	C8H120	22.57
13	CoHoO	24.97
14	CoHeaO	26.03
15	CoHO	26.83
16	CoH-0	20.05
17	C0H120	21.50
10	COH120	27.50
10	CCH1402	37.50
19	CENC02	9.23
20	c5n602	17.37
21	C6H80	22.97
22	C6H60	23.37
23	C7H8O	24.97
24	C <sub>4</sub> H <sub>5</sub> N	9.63
25	C <sub>5</sub> H <sub>7</sub> N	10.43
26	C <sub>6</sub> H <sub>13</sub> N	11.37
27	C6H13N	11.50
28	C7H15N	15.37
29	C <sub>6</sub> H <sub>7</sub> N	15.50
30	C <sub>8</sub> H <sub>11</sub> N	21.10
31	<sup>c7H</sup> 12 <sup>N</sup> 2	15.77
32	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>	16.43
33	<sup>c7H</sup> 10 <sup>N</sup> 2	21.23
34	<sup>c</sup> 8 <sup>H</sup> 12 <sup>N</sup> 2	25.37
35	с9н14 <sup>N</sup> 2	29.50
36	C11H18N2	29.90
37	C <sub>6</sub> H <sub>11</sub> NO	26.83
38	C <sub>9</sub> H <sub>17</sub> NO	27.23
39	C <sub>6</sub> H <sub>13</sub> NO	28.30
40	C10H16N2	33.37
41	C6H10N2	31.23
42	<sup>c</sup> 6 <sup>H</sup> 10 <sup>N</sup> 2	33.23
43	C7H12N2	33.37
44	C7H12N2	33.50
45	C10H13N	34.97
46	C7H11NO	36.18

Table 2: Compounds of other groups detected in BAW

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NO	Name	Formula	Retention time (Min)
1	Undecane	F11H24	11.65
2	5-Undecene, (Z)	C11H22	11.80
3	3-Dodecene, (Z)	C12H24	13,90
4	3-Dodecene, (Z)	C12H24	14.05
5	Dodecane	E12H26	14.15
6	3-Dodecene, (E)	C12H24	14.25
7	3-Dodecene, (Z)	F12H24	14.50
8	2-Tridecene, (Z)	E13H26	16.30
9	Tridecane	C13H28	16.45
10	3-Tridecene, (E)	E13H26	16.55
11	3-Tetradecene, (E)	C14H28	18.50
13	Tetradecane	F14H30	18.65
14	3-Tetradecene, (E)	C14H28	19.00
15	Pentadecane	C15H32	20.72
16	Hexadecane	F16H34	22.70

Table 3: Shows Aliphatic compounds identified in BAW



Figure 10: Distillation curve for BLTP.



Figure 11: Distillation curve for BHTP.

NO	Name	Formula	Retention time (min)
1	Benzene, 4-ethenyl-1,2-dimethyl	10*12	12.65
Z.	1H-Indene, 2,3-dihydro-5-methyl	c10#12	12.90
3	7-Methyl-1,2,3,5,8,8a-hexahydronaphthalene	11116	13.00
5	Z-Methylindene	c10#10	13.10
6	Benzene, pentyl	c11#16	13.13
7	Naphthalene, 1,2,3,4-tetrahydro	×10 <sup>#</sup> 12	13.25
8	Benzene, (1-methylbutyl)	c11#16	13.38
9	Naphthalene	c10#8	13.75
10	2-Ethyl-2,3-dihydro-1H-indene	c11#14	14.95
11	Benzene, hexyl	c12"18	15.55
12	Benzene, (1-methylpentyl)	c12º18	15.70
13	Naphthalene, 1-methyl	c11#10	16.35
14	1H-Indene, 1-ethylidene	C11H10	16.75
15	Benzene, heptyl	c13#20	17.90
16	1-Methyl-2-n-hexylbenzene	£13#20	18.00
17	Naphthalene, 2-ethyl	F12#12	18.60
18	Naphthalene, 1,7-dimethyl	C12H12	19.15
19	n-Nonylcyclohexane	C15H30	21.80

## Table 4: Shows Aromatic compounds identifiedin BAW.

Biomass was remained the same while catalyst (CaO) was varying to choose a suitable ratio of catalyst with biomass at which maximum pyrolysis yield while less amount of residue is obtained. At different ratio of CaO and biomass the pyrolysis reactions were carried out, finally 3:1 of biomass and CaO respectively were found proper for a good pyrolysis yield (Figures 10-12).

#### Table 5: % area of deferent classes of compounds identified in BAW

	% Area		
Different Classes of compounds	BLTP	BHTP	
Alcohols	0.889	11.110	
Aldehydes	0.501	1.123	
Ketones	7.02	25.827	
Ethers	n.d.	6.263	
Esters	n.d.	1.923.	
Phenols	7.109	4.858	
Nitrogenous	0.354	40.779	
Aromatics hydrocarbons	33.001	2.246	
Cyclic hydrocarbons	17.420	3.096	
Aliphatic hydrocarbons	35.121	0.101	

#### CONCLUSIONS

After different process and analyzing techniques, more than 120 compounds were detected in the BAW. Among them, aromatic, aliphatic and cyclic hydrocarbons, especially alkanes, alkenes and benzene containing compounds were dominant but other important compounds like phenol were also present. A laboratory scale effort is made in this work to recover phenol from BAW, however, to improve efficiency, this process can be successfully applied in large-scale operations because phenol is an important compound used in the preparation of resins, dyes, explosives, lubricants, pesticides and plastics. It is indirectly useful in the preparation of plywood. Phenol



Figure 12: BAW H.NMR spectra.



Figure 13: PhenoIs H.NMR spectra.

Is also used as an organic solvent to dissolve other alcohols as well as for medicinal purposes. Future work is going to test light fraction (80-160°C) in diesel engine and heavy fraction (160-240°C) in a jet engine by mixing them in normal diesel fuels and aviation fuels respectively (Figure 13).

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