

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 distilled and analyzed by Gas chromatography and Mass spectrometry (GC-MS) technique and comprehensive two-dimensional 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 (C₂H₁₀O), Caustic soda (NaOH) and Hydrochloric acid (HCl) 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

Abbreviations: BAW: Bio-oil obtained from agricultural wastes; BHPT: Bio-oil obtained at high temperature (90°C) after pyrolysis; BLTP: Bio-oil obtained at low temperature (10°C) after pyrolysis.

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 bio-based 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 intensification, techno-economic analysis, molecular distillation system, environmental assessment, in addition to enterprise-wide and supply chain optimization [16-22]. Now-a-day biomass has an unignorable 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 CO₂ neutrality with low sulfur and nitrogen contents make biomass a sustainable and eco-friendly 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 CO₂, H₂ 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

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Received November 02, 2016; Accepted December 12, 2016; Published January 02, 2017

Citation: Shah Z, Renato CV, Marco AC, Rosangela DS (2017) Separation of Phenol from Bio-oil Produced from Pyrolysis of Agricultural Wastes. Mod Chem Appl 5: 199. doi: [10.4172/2329-6798.1000199](https://doi.org/10.4172/2329-6798.1000199)

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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 μm) Chromatographic conditions: Injection volume of 0.2 μL , 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).

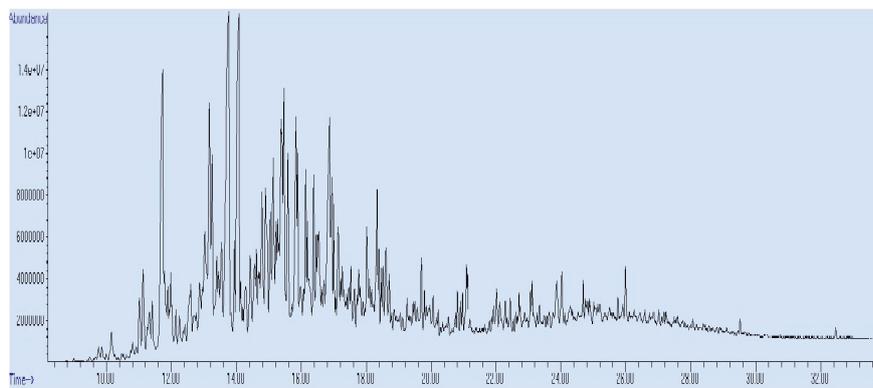
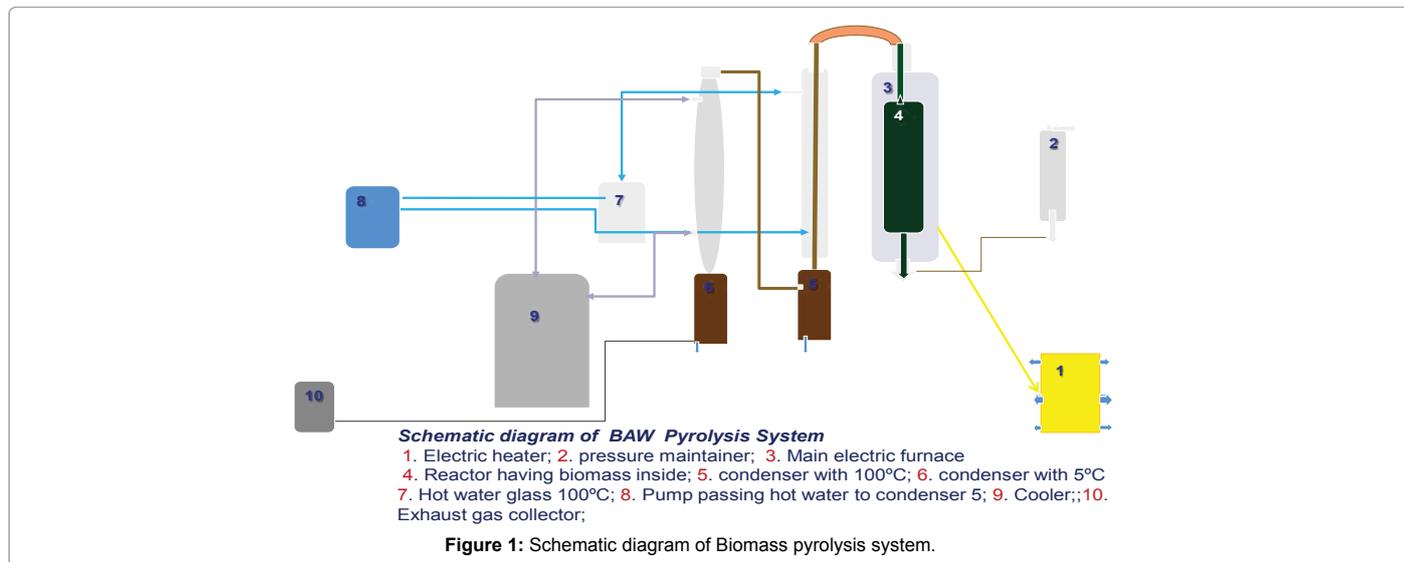


Figure 2: Chromatogram operated in splitless mode.

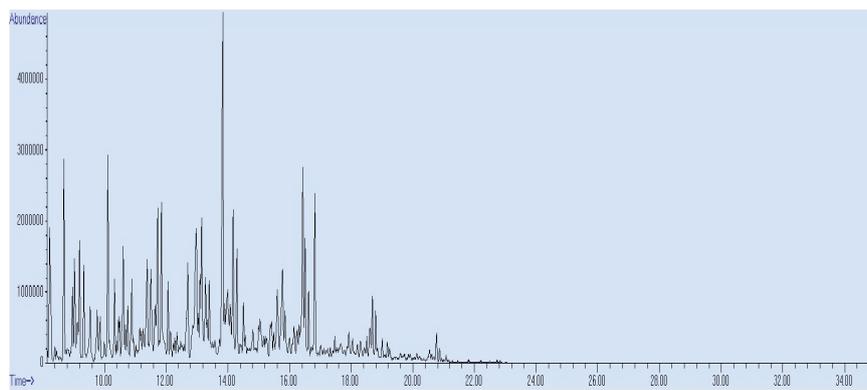


Figure 3: Chromatogram operated in split mode.

Extraction of phenols

A feasible separation route to isolate phenolic fraction from bio-oil was investigated. A certain amount of Ethyl ether ($C_4H_{10}O$) 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 ($NaOH + C_6H_5O = NaOC_6H_5 + H_2O$). 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 $NaOC_6H_5$ in solution to form NaCl and phenol ($NaOC_6H_5 + HCl = C_6H_5O + NaCl$) 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 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_8-C_{17} 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

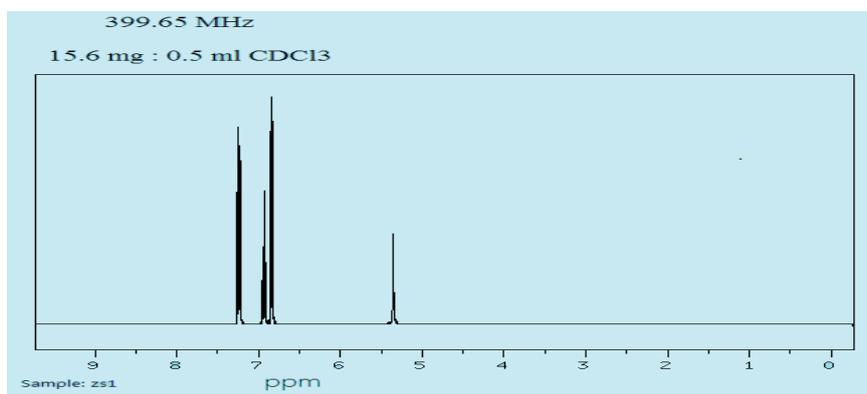


Figure 4: NMR chromatogram showing the presence of phenol.

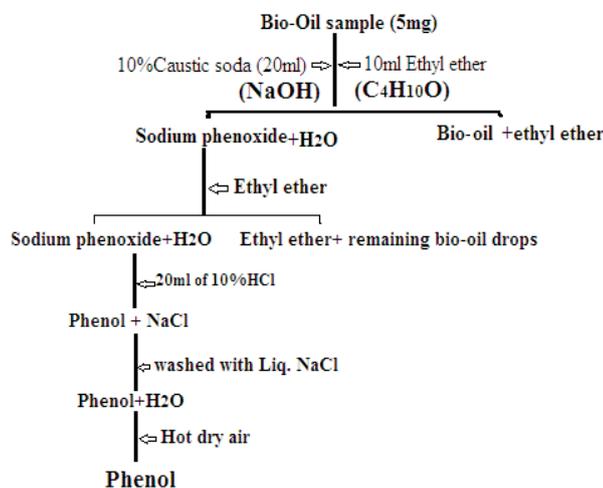
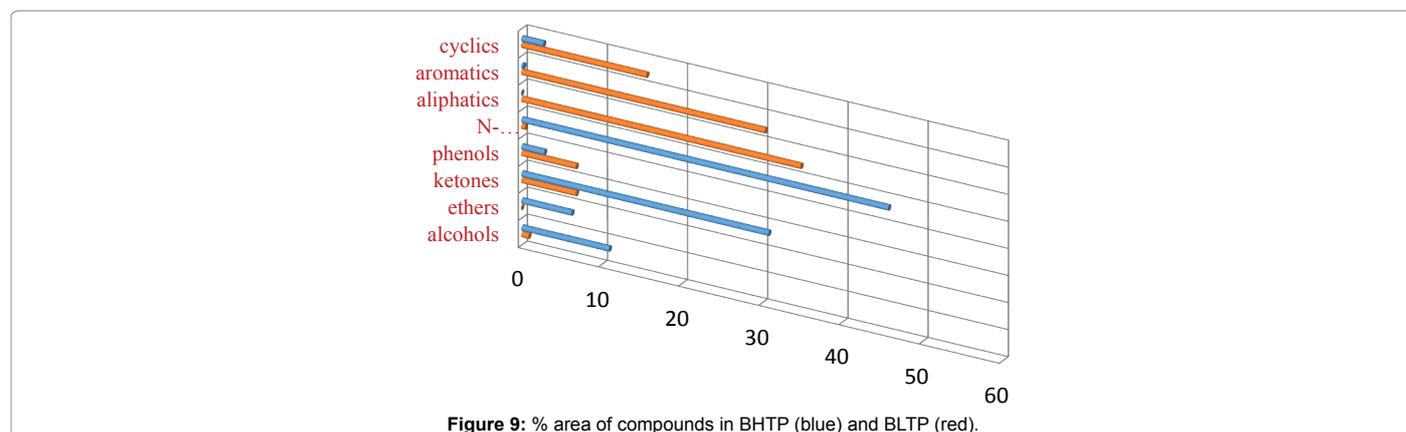
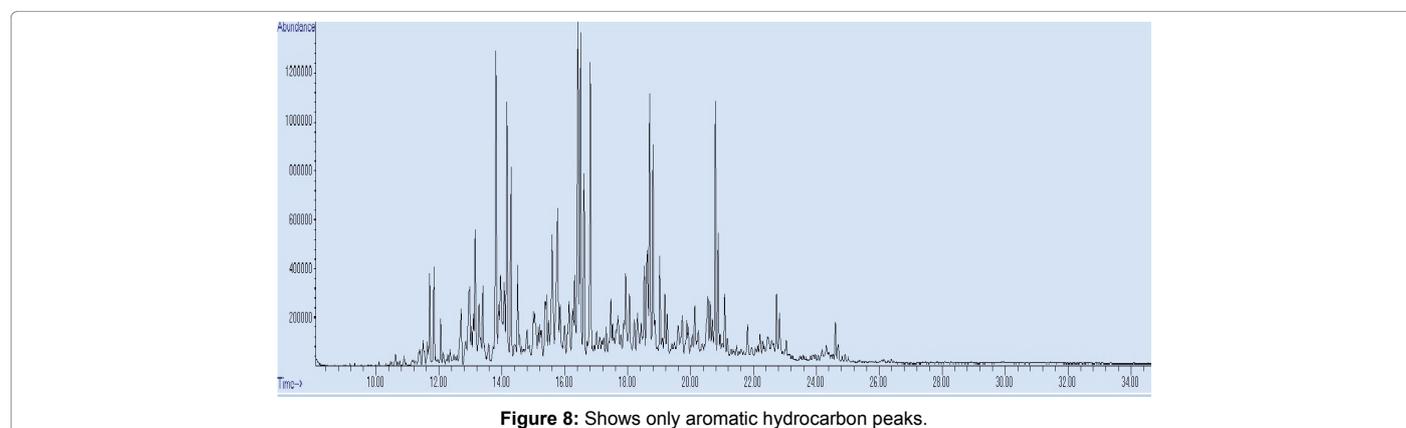
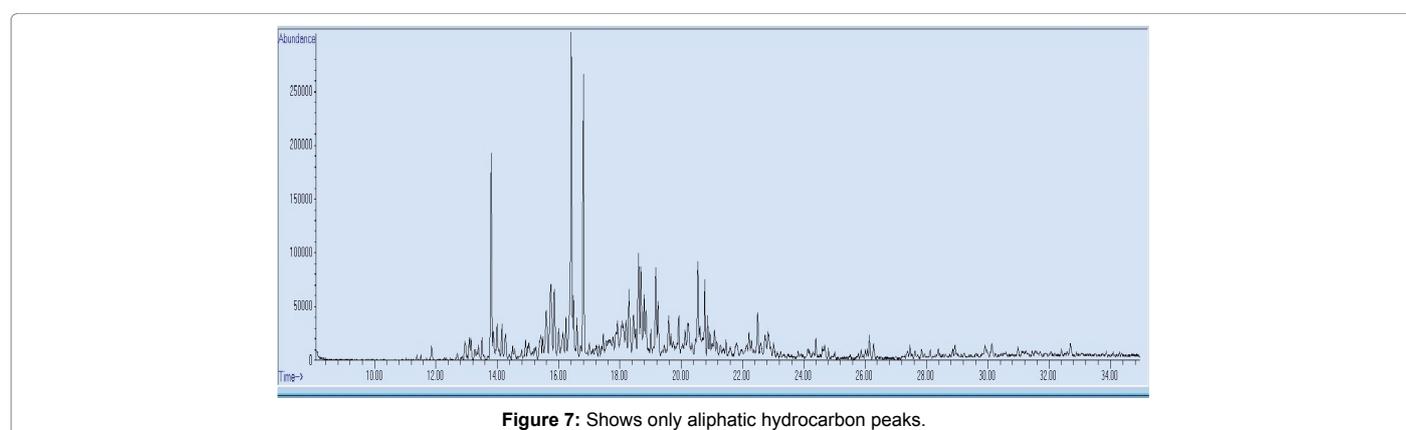
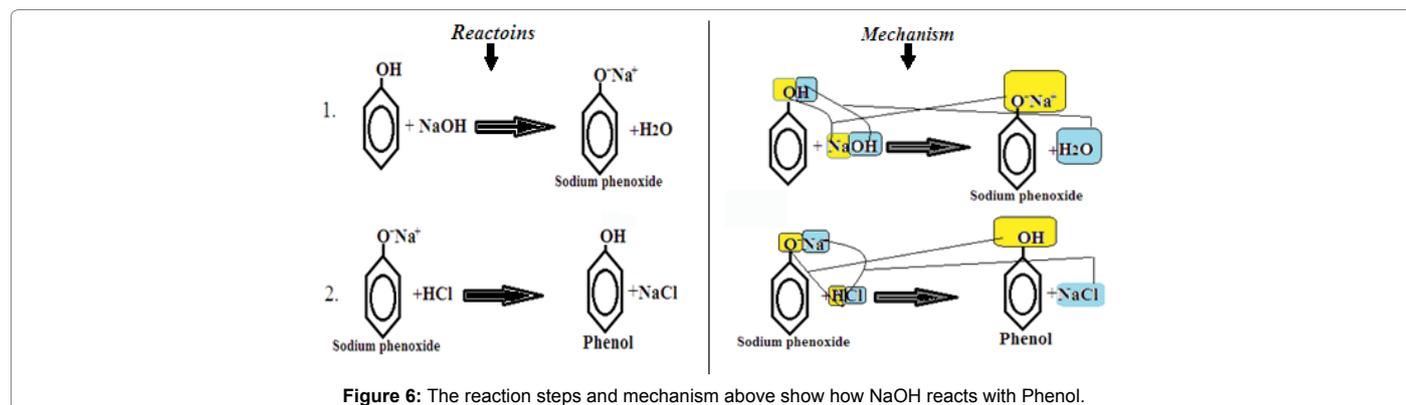


Figure 5: The simple sketch above shows how to recover phenol from bio-oil step by step.



NO	Compound's Name	Formula	Retention time
1	Benzene, 1-ethyl-3-methyl	C ₉ H ₁₂	8.18
2	Benzene, 1,2,3-trimethyl	C ₉ H ₁₂	9.00
3	Decane	C ₁₀ H ₂₂	9.15
4	2-Decene, (Z)	C ₁₀ H ₂₀	9.32
5	cis-3-Decene	C ₁₀ H ₂₀	9.52
6	Benzene, 1,2,3-trimethyl	C ₉ H ₁₂	9.72
7	Benzene, 2-propenyl	C ₉ H ₁₀	9.82
8	Indane	C ₉ H ₁₀	10.17
9	Indene	C ₉ H ₈	10.30
10	Benzene, butyl	C ₁₀ H ₁₄	10.52
11	Benzene, 1,2-diethyl	C ₁₀ H ₁₄	10.72
12	Benzene, 1-methyl-4-(1-methylethyl)	C ₁₀ H ₁₄	11.30
13	Undecane	C ₁₁ H ₂₄	11.65
14	5-Undecene, (Z)	C ₁₁ H ₂₂	11.80
15	Benzene, 4-ethenyl-1,2-dimethyl	C ₁₀ H ₁₂	12.65
16	1H-Indene, 2,3-dihydro-5-methyl	C ₁₀ H ₁₂	12.90
17	7-Methyl-1,2,3,5,8,8a-hexahydronaphthalene	C ₁₁ H ₁₆	13.00
18	2-Methylindene	C ₁₀ H ₁₀	13.10
19	Benzene, pentyl	C ₁₁ H ₁₆	13.13
20	Naphthalene, 1,2,3,4-tetrahydro	C ₁₀ H ₁₂	13.25
21	Benzene, (1-methylbutyl)	C ₁₁ H ₁₆	13.38
22	Naphthalene	C ₁₀ H ₈	13.75
23	3-Dodecene, (Z)	C ₁₂ H ₂₄	13.90
24	3-Dodecene, (Z)	C ₁₂ H ₂₄	14.05
25	Dodecane	C ₁₂ H ₂₆	14.15
26	3-Dodecene, (E)	C ₁₂ H ₂₄	14.25
27	3-Dodecene, (Z)	C ₁₂ H ₂₄	14.50
28	2-Ethyl-2,3-dihydro-1H-indene	C ₁₁ H ₁₄	14.95
29	Benzene, hexyl	C ₁₂ H ₁₈	15.55
30	Benzene, (1-methylpentyl)	C ₁₂ H ₁₈	15.70
31	2-Tridecene, (Z)	C ₁₃ H ₂₆	16.30
32	Naphthalene, 1-methyl	C ₁₁ H ₁₀	16.35
33	Tridecane	C ₁₃ H ₂₈	16.45
34	3-Tridecene, (E)	C ₁₃ H ₂₆	16.55
35	1H-Indene, 1-ethylidene	C ₁₁ H ₁₀	16.75
36	Benzene, heptyl	C ₁₃ H ₂₀	17.90
37	1-Methyl-2-n-hexylbenzene	C ₁₃ H ₂₀	18.00
38	Naphthalene, 2-ethyl	C ₁₂ H ₁₂	18.60
39	3-Tetradecene, (E)	C ₁₄ H ₂₈	18.50
40	Tetradecane	C ₁₄ H ₃₀	18.65
41	3-Tetradecene, (E)	C ₁₄ H ₂₈	19.00
42	Naphthalene, 1,7-dimethyl	C ₁₂ H ₁₂	19.15
43	Pentadecane	C ₁₅ H ₃₂	20.72
44	n-Nonylcyclohexane	C ₁₅ H ₃₀	21.80
45	Hexadecane	C ₁₆ H ₃₄	22.70
46	Cyclopentane, undecyl	C ₁₆ H ₃₂	22.80
47	Heptadecane	C ₁₇ H ₃₆	24.58

Table 1: Aliphatic and Aromatic hydrocarbons identified in BAW.

NO	Compound's Name	Formula	Retention time (Min)
1	pentanol	C ₅ H ₁₂ O	9.50
2	pentanone	C ₅ H ₁₀ O	7.63
3	hexanone	C ₆ H ₁₂ O	9.50
4	octanone	C ₈ H ₁₆ O	20.83
5	heptanone	C ₇ H ₁₄ O	15.77
6	Hexenol	C ₆ H ₁₂ O	13.89
7	cyclopentanone	C ₅ H ₈ O	11.23
8	cyclopentanone, C ₁	C ₆ H ₁₀ O	13.63

9	cyclopentanone, C ₂	C ₇ H ₁₂ O	16.03
10	cyclohexenone, C ₁	C ₇ H ₁₀ O	19.77
11	heptanone	C ₇ H ₁₄ O	15.77
12	cyclopentenone, C ₃	C ₈ H ₁₂ O	22.57
13	acetophenone	C ₈ H ₈ O	24.97
14	cyclohexenyl, ethanone	C ₈ H ₁₂ O	26.03
15	cyclopentenone, C ₄	C ₉ H ₁₄ O	26.83
16	cyclohexanone, ethylidene	C ₈ H ₁₂ O	28.17
17	cyclopentenone, C ₃ methylene	C ₉ H ₁₂ O	31.50
18	indenone, hexahydro	C ₉ H ₁₂ O	37.50
19	ethane, diethoxy	C ₆ H ₁₄ O ₂	9.23
20	furanmethanol	C ₆ H ₆ O ₂	17.37
21	furan, C ₂	C ₆ H ₈ O	22.97
22	phenol	C ₆ H ₆ O	23.37
23	phenol, C ₁	C ₇ H ₈ O	24.97
24	pyrrole	C ₄ H ₅ N	9.63
25	pyrrole, C ₁	C ₅ H ₇ N	10.43
26	piperidine, C ₁	C ₆ H ₁₃ N	11.37
27	piperidine, C ₁	C ₆ H ₁₃ N	11.50
28	piperidine, C ₂	C ₇ H ₁₅ N	15.37
29	pyridine, C ₁	C ₆ H ₇ N	15.50
30	pyridine, C ₃	C ₈ H ₁₁ N	21.10
31	imidazole, C ₄	C ₇ H ₁₂ N ₂	15.77
32	pyrazine, C ₂	C ₆ H ₈ N ₂	16.43
33	pyrazine, C ₃	C ₇ H ₁₀ N ₂	21.23
34	pyrazine, C ₄	C ₈ H ₁₂ N ₂	25.37
35	pyrazine, C ₅	C ₉ H ₁₄ N ₂	29.50
36	pyrazine, C ₆	C ₁₁ H ₁₈ N ₂	29.90
37	pyrrolidinone, C ₂	C ₆ H ₁₁ NO	26.83
38	piperidinone, C ₄	C ₉ H ₁₇ NO	27.23
39	pentanamide, C ₁	C ₆ H ₁₃ NO	28.30
40	pyrazine, C ₆	C ₁₀ H ₁₆ N ₂	33.37
41	imidazole, C ₃	C ₆ H ₁₀ N ₂	31.23
42	pyrazole, C ₃	C ₆ H ₁₀ N ₂	33.23
43	pyrazole, C ₄	C ₇ H ₁₂ N ₂	33.37
44	imidazole, C ₄	C ₇ H ₁₂ N ₂	33.50
45	pyridine, C ₁ propenyl	C ₁₀ H ₁₃ N	34.97
46	pyrrolidinone, C ₂ methylidene	C ₇ H ₁₁ NO	36.18

Table 2: Compounds of other groups detected in BAW.

NO	Name	Formula	Retention time (Min)
1	Undecane	C ₁₁ H ₂₄	11.65
2	5-Undecene, (Z)	C ₁₁ H ₂₂	11.80
3	3-Dodecene, (Z)	C ₁₂ H ₂₄	13.90
4	3-Dodecene, (Z)	C ₁₂ H ₂₄	14.05
5	Dodecane	C ₁₂ H ₂₆	14.15
6	3-Dodecene, (E)	C ₁₂ H ₂₄	14.25
7	3-Dodecene, (Z)	C ₁₂ H ₂₄	14.50
8	2-Tridecene, (Z)	C ₁₃ H ₂₆	16.30
9	Tridecane	C ₁₃ H ₂₈	16.45
10	3-Tridecene, (E)	C ₁₃ H ₂₆	16.55
11	3-Tetradecene, (E)	C ₁₄ H ₂₈	18.50
13	Tetradecane	C ₁₄ H ₃₀	18.65
14	3-Tetradecene, (E)	C ₁₄ H ₂₈	19.00
15	Pentadecane	C ₁₅ H ₃₂	20.72
16	Hexadecane	C ₁₆ H ₃₄	22.70

Table 3: Shows Aliphatic compounds identified in BAW.

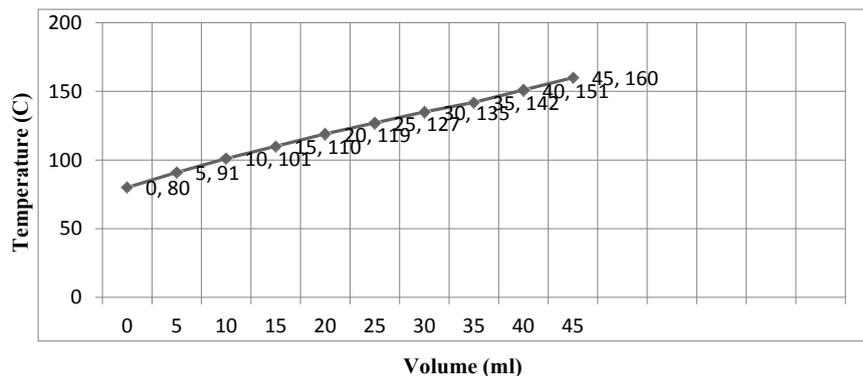


Figure 10: Distillation curve for BLTP.

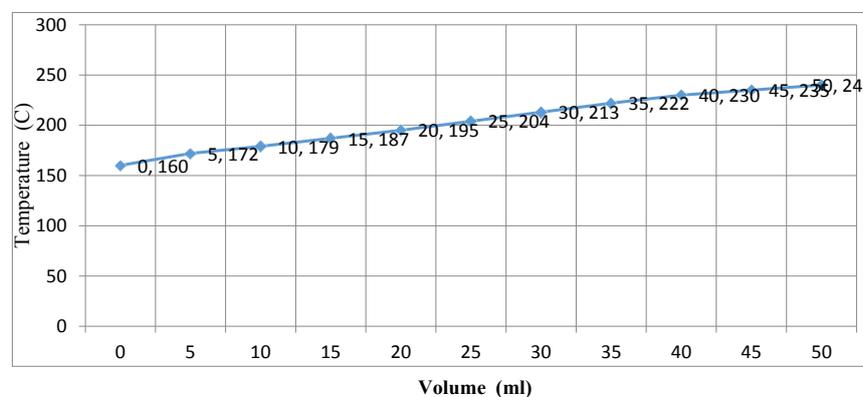


Figure 11: Distillation curve for BHTP.

NO	Name	Formula	Retention time (min)
1	Benzene, 4-ethenyl-1,2-dimethyl	C ₁₀ H ₁₂	12.65
2	1H-Indene, 2,3-dihydro-5-methyl	C ₁₀ H ₁₂	12.90
3	7-Methyl-1,2,3,5,8,8a-hexahydronaphthalene	C ₁₁ H ₁₆	13.00
5	2-Methylindene	C ₁₀ H ₁₀	13.10
6	Benzene, pentyl	C ₁₁ H ₁₆	13.13
7	Naphthalene, 1,2,3,4-tetrahydro	C ₁₀ H ₁₂	13.25
8	Benzene, (1-methylbutyl)	C ₁₁ H ₁₆	13.38
9	Naphthalene	C ₁₀ H ₈	13.75
10	2-Ethyl-2,3-dihydro-1H-indene	C ₁₁ H ₁₄	14.95
11	Benzene, hexyl	C ₁₂ H ₁₈	15.55
12	Benzene, (1-methylpentyl)	C ₁₂ H ₁₈	15.70
13	Naphthalene, 1-methyl	C ₁₁ H ₁₀	16.35
14	1H-Indene, 1-ethylidene	C ₁₁ H ₁₀	16.75
15	Benzene, heptyl	C ₁₃ H ₂₀	17.90
16	1-Methyl-2-n-hexylbenzene	C ₁₃ H ₂₀	18.00
17	Naphthalene, 2-ethyl	C ₁₂ H ₁₂	18.60
18	Naphthalene, 1,7-dimethyl	C ₁₂ H ₁₂	19.15
19	n-Nonylcyclohexane	C ₁₅ H ₃₀	21.80

Table 4: Shows Aromatic compounds identified in 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).

Different Classes of compounds	% Area	
	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

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

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

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