

Bio-Oil Production from Pyrolysis of Coffee and Eucalyptus Sawdust in the Presence of 5% Hydrogen

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Abstract— In this paper, we have done some important analysis of bio-oil obtained from the pyrolysis of coffee and eucalyptus sawdust in the presence of 5% Hydrogen. The bio-oil was obtained in one step pyrolysis in which temperature of the system was kept 25°C and then increased up to 850°C. After pyrolysis the obtained dark sticky liquid (highly viscous bio-oil) was introduced to thermal cracking. During thermal cracking the bio-oil was condensed at two different temperatures 100°C and 5°C so we got two types of bio-oil, BHTT (bio-oil obtained at high temperature 100 °C after thermal cracking) and BLTT (bio-oil obtained at low temperature 5°C after thermal cracking). Then both types of bio-oil were distilled and analyzed in Gas chromatography and Mass spectrometry (GC-MS) technique and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detection (GC×GC/TOFMS). Agriculture residue bio-oil and its thermal cracking fractions could be effectively characterized by GC/MS and GC×GC/TOFMS, where the light fraction was composed of a wide range of lower polarity compounds while heavy fraction had higher polarity compounds.

Keywords— Chromatographic analysis, GC/MS, GC×GC/TOFMS, biomass pyrolysis, bio-oil production.

Abbreviations:

BESC: Bio-oil produced from Coffee and Eucalyptus Sawdust

BHTT: Bio-oil condensed at 100°C High Temperature after Thermal cracking

BLTT: Bio-oil condensed at 5°C Low Temperature after Thermal cracking

I. INTRODUCTION

The Bio-oil resulting from the pyrolysis process consists of a mixture of more than 300 organic compounds. In terms of environmental issue biodiesel is more adoptable compare to fossil fuel as it forms low carbon and smoke which are responsible for global warming. Among several biomass energy conversion methods, microwave assisted pyrolysis offers low temperature and energy efficient route to convert solid waste biomass resources to energy products. In United States soybean is used for the production of biodiesel. "Bio-fuels done right" must be derived from feed stocks with low greenhouse gas emissions and little or no competition with food production [1-5]. On the other hand biodiesel has higher molecular weight, density, viscosity and pour point than conventional diesel fuel [6,7]. Higher molecular weight and viscosity of biodiesel causes low volatility and poor fuel atomization, injector coking, piston ring sticking and leading incomplete combustion [8]. as well as it has cold flow property which is a barrier to use it in cold or chill weather [9]. Anyhow the best benefit of Bio-oils is that they are preparing from renewable sources like corpse, plants, trees and residues etc. Approximately 100 years ago, Rudolf Diesel tested Bio oil as the fuel for his engine that was available with him [10, 11]. According to scientists and researchers there are 350 oil containing crops and plants identified, among them only soybean, rapeseed, coffee, sunflower, cottonseed, peanut, and coconut oils are considered that they have the potential and quality of alternative fuels for Diesel engines [12, 13]. Bio oils have the capacity to substitute for a part or fraction of the petroleum Products, distillates and petroleum based petrochemicals in the future. Due to being more expensive than petroleum Bio-fuels are nowadays not petroleum competitive fuels. However, due to the misuse, high expenditure and increases in petroleum prices and the uncertainties concerning petroleum availability, there is renewed interest in using Bio-oils in Diesel engines [14]. The emergence of transesterification can be dated back as early as 1846 when Rochieder described glycerol preparation through methanolysis of castor oil and since that time, alcoholysis has been studied in many parts of the world. Scientists, researchers have also investigated the important reaction conditions and parameters on the alcoholysis of triglycerides, such as tallow, fish oils, sunflower, soybean, rapeseed, linseed oils, cottonseed, sunflower, safflower, and peanut [15,16]. Soybean oil was transesterified into ethyl and methylesters, and comparisons of the performances of the fuels with diesel were made.[17,18]. Also, methylesters have been prepared from palm oil by transesterification using methanol in the presence of a catalyst (NaOH) or (KOH) in a batch reactor. Ethan oils a preferred alcohol in the transesterification process compared to methanol because it is derived from natural agricultural products and is renewable and biologically less objectionable in the

environment. The success of rapeseed ethylester production would mean that biodiesel's two main raw materials would be agriculturally produced, renewable and environmentally friend [19, 20]. Methyl, ethyl, 2-propyl and butyl esters were prepared from canola and linseed oils through transesterification using KOH and/or sodium alkoxides as catalysts. In addition, methyl and ethylesters were prepared from rapeseed and sunflower oils using the same catalysts [21- 24]. In the last few decades, the significant global warming problems caused by CO₂ have been magnified by the continued and increasing use of petroleum in diesel engines. Reducing CO₂ emission has become an explicit goal of policy measures to support the use of biofuels. For example, European Union mandates 10% share for biofuels in the EU (European Union) total energy mix by 2020 [25] and United States sets a total of 36 billion-gallon target for biofuels production by 2022 [26]. Therefore, alternative renewable biofuels have been investigated to partly or completely replace diesel fuel to overcome the emission problems [27-30].

II. EXPERIMENTAL

2.1 Materials: coffee, eucalyptus sawdust and other reagents

The bio-oil was obtained by pyrolysis of a mixture (1:1 in mass) of coffee grounds and eucalyptus sawdust. Coffee grounds and eucalyptus sawdust were mixed after their granulometric reduction (till 0.21 mm). Calcium oxide (CaO) was added to this mixture (at 20% in mass) and sufficient amount of water to produce a malleable mixture that could be fixed and conformed in cylinders. After building the cylinders, they were dried at environmental temperature during 3 days. Before the pyrolysis, the system was purged during 20 minutes with Argon and with 5% of hydrogen (100 mL/min).

2.2 Production of BESC

The bio-oil was produced from the pyrolysis of coffee grounds and eucalyptus sawdust in the presence of 5% hydrogen. A round block shaped structure of sample was made inside the filter paper from (filter paper as side wall of the sample block to keep the biomass tight) biomass, while the weight of this sample was kept 300grams, after preparation of this sample block it was kept inside a stainless steel reactor of pyrolysis system which is further connected to two other chambers which are shown in diagram in figure, 1. The temperature of reactor was increased from 25°C - 850°C with help of heater, temperature controller cabinet, and two condensation chambers, through which biomass was converted to biogas and then the biogas was condensed in other two chambers, which condensed fractions of biogas to bio-oil on temperature 100°C and 5°C after pyrolysis and thermal cracking. The two condensed fractions from these chambers (BHTT & BLTT) were collected and introduced to further analysis.

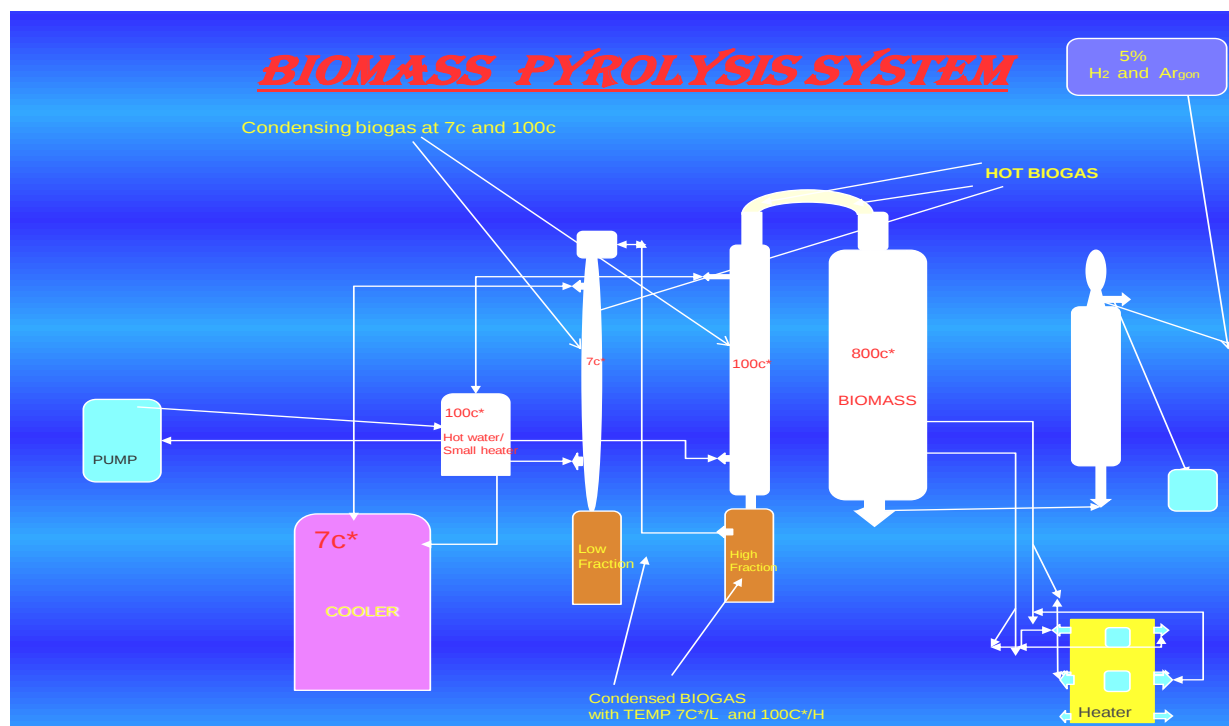


FIG.1. BIOMASS PYROLYSIS SYSTEM.

2.3 GC-MS Analysis of BHTT & BLTT

The bio-oil identification and composition determination were performed on a GC Agilent series 6890 with a 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 were as follows:

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

III. GC-MS CHROMATOGRAMS OF BESC

Below fig 2. And fig 3. Are different chromatograms of BHTT and BLTT respectively which show different peaks for different compounds in both cases.

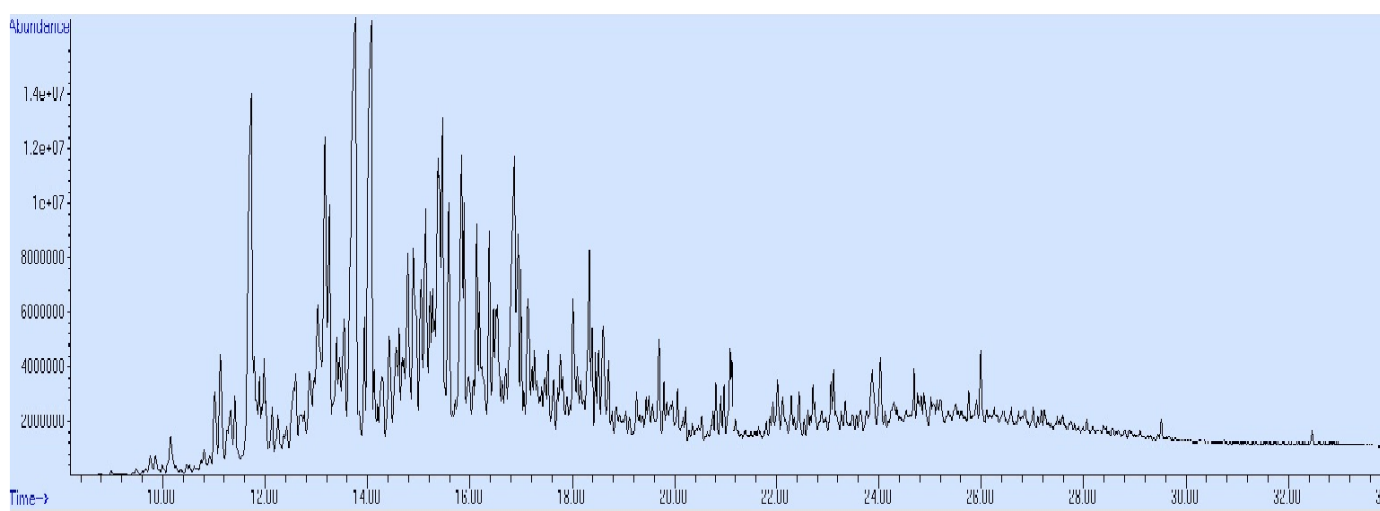


FIG.2. DONE WITH SPLITLESS MODE WHERE DIFFERENT PEAKS SHOW DIFFERENT COMPOUNDS IN BHTT AT DIFFERENT RETENTION TIME

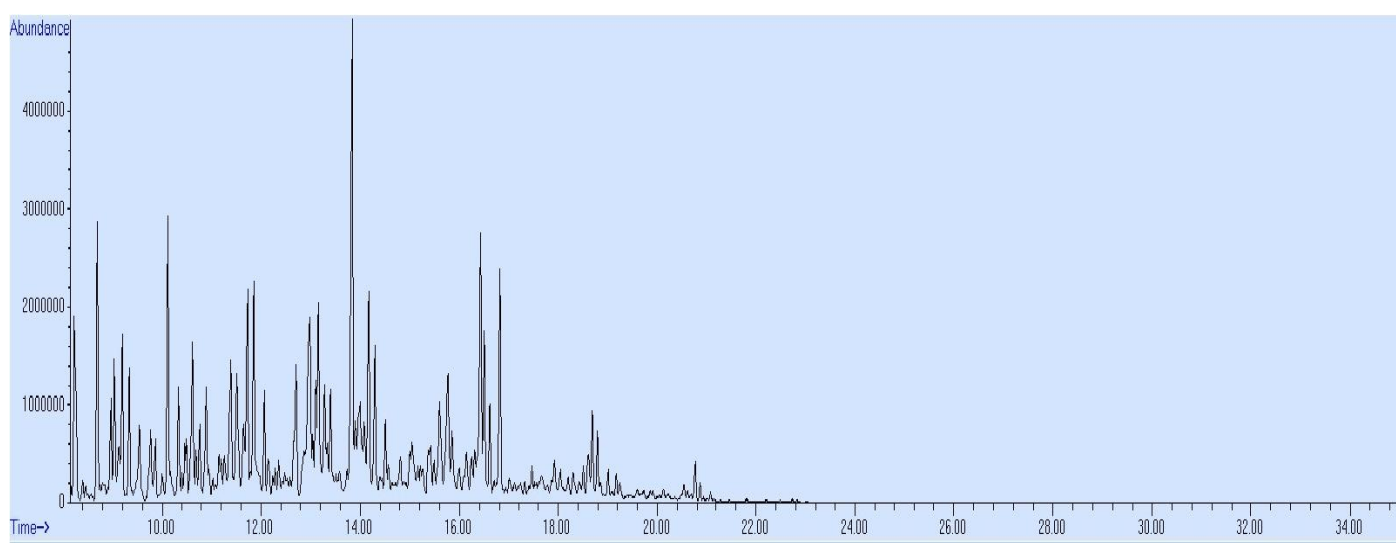


FIG.3. DONE WITH SPLIT MODE WHERE DIFFERENT PEAKS SHOW DIFFERENT COMPOUNDS IN BLTT AT DIFFERENT RETENTION TIME

TABLE 1
ALIPHATIC & AROMATIC HYDROCARBONS DETECTED IN BLTT WITH THEIR RETENTION TIME

NO	NAME OF COMPOUND	FORMULA	RETENTION TIME
1	3-Undecene, (Z)-	C ₁₁ H ₂₂	11.45
2	Undecane	C ₁₁ H ₂₄	11.65
3	5-Undecene, (Z)-	C ₁₁ H ₂₂	11.80
4	Benzene, 4-ethenyl-1,2-dimethyl-	C ₁₀ H ₁₂	12.65
5	1H-Indene, 2,3-dihydro-5-methyl-	C ₁₀ H ₁₂	12.90
6	7-Methyl-1,2,3,5,8,8a-hexahydronaphthalene	C ₁₁ H ₁₆	13.00
7	2-Methylindene	C ₁₀ H ₁₀	13.10
8	Benzene, pentyl-	C ₁₁ H ₁₆	13.13
9	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	13.25
10	Benzene, (1-methylbutyl)-	C ₁₁ H ₁₆	13.38
11	Naphthalene	C ₁₀ H ₈	13.75
12	3-Dodecene, (Z)-	C ₁₂ H ₂₄	13.90
13	Dodecane	C ₁₂ H ₂₆	14.15
14	2-Ethyl-2,3-dihydro-1H-indene	C ₁₁ H ₁₄	14.95
15	Benzene, hexyl-	C ₁₂ H ₁₈	15.55
16	Benzene, (1-methylpentyl)-	C ₁₂ H ₁₈	15.70
17	2-Tridecene, (Z)-	C ₁₃ H ₂₆	16.30
18	Naphthalene, 1-meth yl-	C ₁₁ H ₁₀	16.35
19	Tridecane	C ₁₃ H ₂₈	16.45
20	3-Tridecene, (E)-	C ₁₃ H ₂₆	16.55
21	1H-Indene, 1-ethylidene-	C ₁₁ H ₁₀	16.75
22	Benzene, heptyl-	C ₁₃ H ₂₀	17.90
23	1-Methyl-2-n-hexylbenzene	C ₁₃ H ₂₀	18.00
24	Naphthalene, 2-ethyl-	C ₁₂ H ₁₂	18.60
25	Tetradecane	C ₁₄ H ₃₀	18.65
26	3-Tetradecene, (E)-	C ₁₄ H ₂₈	19.00
27	Naphthalene, 1,7-dimethyl-	C ₁₂ H ₁₂	19.15
28	Pentadecane	C ₁₅ H ₃₂	20.72
29	n-Nonylcyclohexane	C ₁₅ H ₃₀	21.80
30	Hexadecane	C ₁₆ H ₃₄	22.70

TABLE 2
ALIPHATIC & AROMATIC HYDROCARBONS DETECTED IN BHTT WITH THEIR RETENTION TIME

NO	NAME	FORMULA	RETENTION TIME
1	Decane	C ₁₀ H ₂₂	9.15
2	2-Decene, (Z)-	C ₁₀ H ₂₀	9.32
3	Cis-3-Decene	C ₁₀ H ₂₀	9.52
4	Benzene, 1,2,3-trimethyl-	C ₉ H ₁₂	9.72
5	Benzene, 2-propenyl-	C ₉ H ₁₀	9.82
6	Indane	C ₉ H ₁₀	10.17
7	Indene	C ₉ H ₈	10.30
8	Benzene, butyl-	C ₁₀ H ₁₄	10.52
9	Benzene, 1,2-diethyl-	C ₁₀ H ₁₄	10.72
10	2,4-Dimethylstyrene	C ₁₀ H ₁₂	11.30
11	Undecane	C ₁₁ H ₂₄	11.70
12	3-Undecene, (Z)-	C ₁₁ H ₂₂	12.05
13	Benzene, 4-ethenyl-1,2-dimethyl-	C ₁₀ H ₁₂	12.67
14	1H-Indene, 2,3-dihydro-4-methyl-	C ₁₀ H ₁₂	12.95
15	Benzene, pentyl-	C ₁₁ H ₁₆	13.15
16	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	13.25
17	Benzene, (1-methylbutyl)-	C ₁₁ H ₁₆	13.35
18	Azulene	C ₁₀ H ₈	13.75
19	Dodecane	C ₁₂ H ₂₆	14.15
20	6-Dodecene, (Z)-	C ₁₂ H ₂₄	14.25
21	3-Dodecene, (Z)-	C ₁₂ H ₂₄	14.50
22	Benzene, hexyl-	C ₁₂ H ₁₈	15.55
23	Benzene, (1-methylpentyl)-	C ₁₂ H ₁₈	15.70
24	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	16.35
25	Tridecane	C ₁₃ H ₂₈	16.47
26	3-Tridecene, (E)-	C ₁₃ H ₂₆	16.57
27	1H-Indene, 1-ethylidene-	C ₁₁ H ₁₀	16.75
28	Naphthalene, 2-methyl-	C ₁₁ H ₁₀	16.85
29	1-Isopropenyl naphthalene	C ₁₃ H ₁₂	16.95
30	Tetradecane	C ₁₄ H ₃₀	18.65

IV. RESULTS AND DISCUSSIONS

4.1 Chemical composition of BESC:

BESC was a dark and sticky liquid the compounds detected in BESC can be classified into hydrocarbons, alcohols, phenol, ethers, aldehydes, ketones, carboxylic acids, and other esters. but large peaks of GC/MS mostly shows aromatic, aliphatic and cyclic hydrocarbons while small peaks show other groups, Library match used for identification of compounds based on probability score and each compound was detected very clearly and with high probability value. According to GC/MS analysis summarized in table 2 and 3, 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.

4.2 Enrichment of chemicals in CSSB sample

According to GC/MS analysis summarized in Tables 1-2, C₁₀–C₁₆ alkanes, Alkenes, Cyclic hydrocarbons and aromatic hydrocarbons were enriched in the CSSB sample

4.2.1 Enrichment of C₁₀–C₁₆ aliphatic hydrocarbons (alkane, alkenes, cyclic).

As Table 2 and 4 shows, aliphatic hydrocarbons with C₁₀–C₁₆ are predominant in the sample with a % area of 51.255 and 31.204 in BLTT and BHTT respectively

Fig.4. and Table.3 show only aliphatic hydrocarbons in BESC

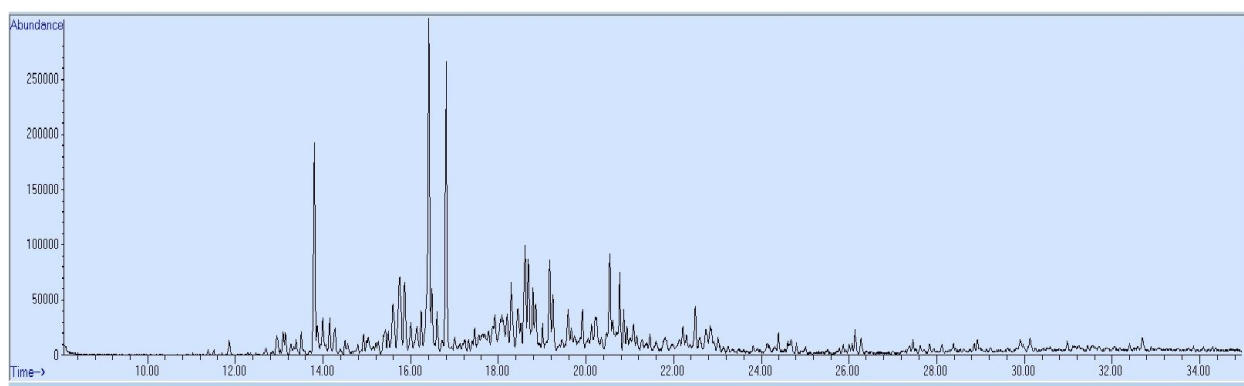


FIG.4. SHOWS ONLY ALIPHATIC HYDROCARBONS PEAKS

TABLE 3
MAIN ALIPHATIC COMPOUNDS DETECTED IN BESC AND ITS RETENTION TIME AND FORMULAS.

NO	NAME	FORMULA	RETENTION TIME
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
12	Tetradecane	C ₁₄ H ₃₀	18.65
13	3-Tetradecene, (E)-	C ₁₄ H ₂₈	19.00
14	Pentadecane	C ₁₅ H ₃₂	20.72
15	Hexadecane	C ₁₆ H ₃₄	22.70

4.2.2 Enrichment of aromatic hydrocarbons

As Table.4 and Fig.5. show only aromatic hydrocarbons detected in BESC and also occupied large part of the BESC within the sample with a % area of 24.892 and 30.008 in BHTT and BLTT respectively.

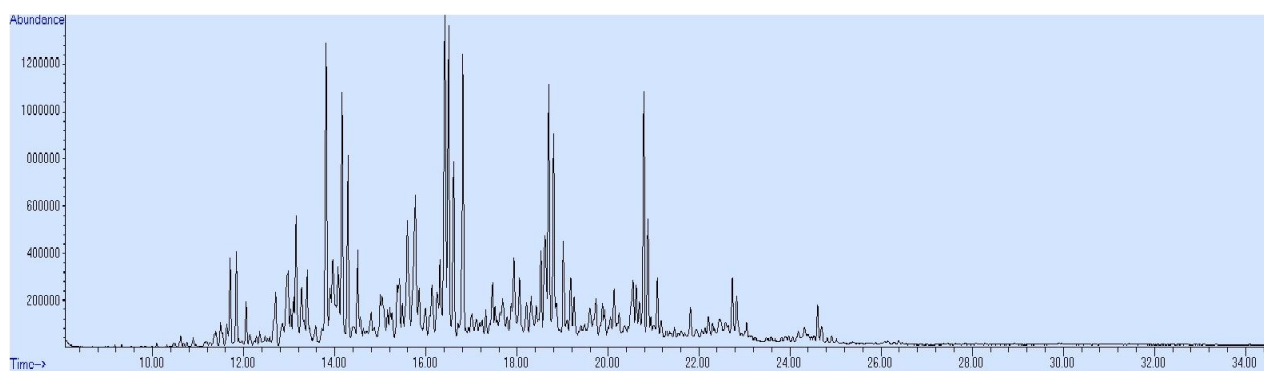


FIG.5. SHOWS ONLY AROMATIC HYDROCARBONS PEAKS

TABLE 4
MAIN AROMATIC COMPOUNDS DETECTED IN BESC AND ITS RETENTION TIME AND FORMULAS

NO	NAME	FORMULA	RETENTION TIME
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
4	2-Methylindene	C ₁₀ H ₁₀	13.10
5	Benzene, pentyl-	C ₁₁ H ₁₆	13.13
6	Naphthalene, 1,2,3,4-tetrahydro-	C ₁₀ H ₁₂	13.25
7	Benzene, (1-methylbutyl)-	C ₁₁ H ₁₆	13.38
8	Naphthalene	C ₁₀ H ₈	13.75
9	2-Ethyl-2,3-dihydro-1H-indene	C ₁₁ H ₁₄	14.95
10	Benzene, hexyl-	C ₁₂ H ₁₈	15.55
11	Benzene, (1-methylpentyl)-	C ₁₂ H ₁₈	15.70
12	Naphthalene, 1-methyl-	C ₁₁ H ₁₀	16.35
13	1H-Indene, 1-ethylidene-	C ₁₁ H ₁₀	16.75
14	Benzene, heptyl-	C ₁₃ H ₂₀	17.90
15	1-Methyl-2-n-hexylbenzene	C ₁₃ H ₂₀	18.00
16	Naphthalene, 2-ethyl-	C ₁₂ H ₁₂	18.60
17	Naphthalene, 1,7-dimethyl-	C ₁₂ H ₁₂	19.15
18	n-Nonylcyclohexane	C ₁₅ H ₃₀	21.80

4.2.3 Enrichment of other compounds

Alcohols, Aldehydes, Ketones, Ethers, Esters, Phenols, and Nitrogenous also contained some part of the BESC while in these classes Phenols and ketones were occupied more space as compared to others as shown in Table 4.

TABLE 5
% AREA OF DEFERENT COMPOUNDS DETECTED IN FRACTIONS (BHTT & BLTT) OF BESC AND ITS GRAPHICAL REPRESENTATION

Deferent Classes of compounds	% Area	
	BHTT	BLTT
Alcohols	n.d	0.168
Aldehydes	n.d.	1.289
Ketones	9.088	6.526
Ethers	1.459	0.468
Esters	0.921	n.d.
Phenols	4.018	4.458
Nitrogenous	n.d.	n.d.
Aromatics hydrocarbons	24.892	30.008
Cyclic hydrocarbons	28.319	5.829
Aliphatic hydrocarbons	31.304	51,255

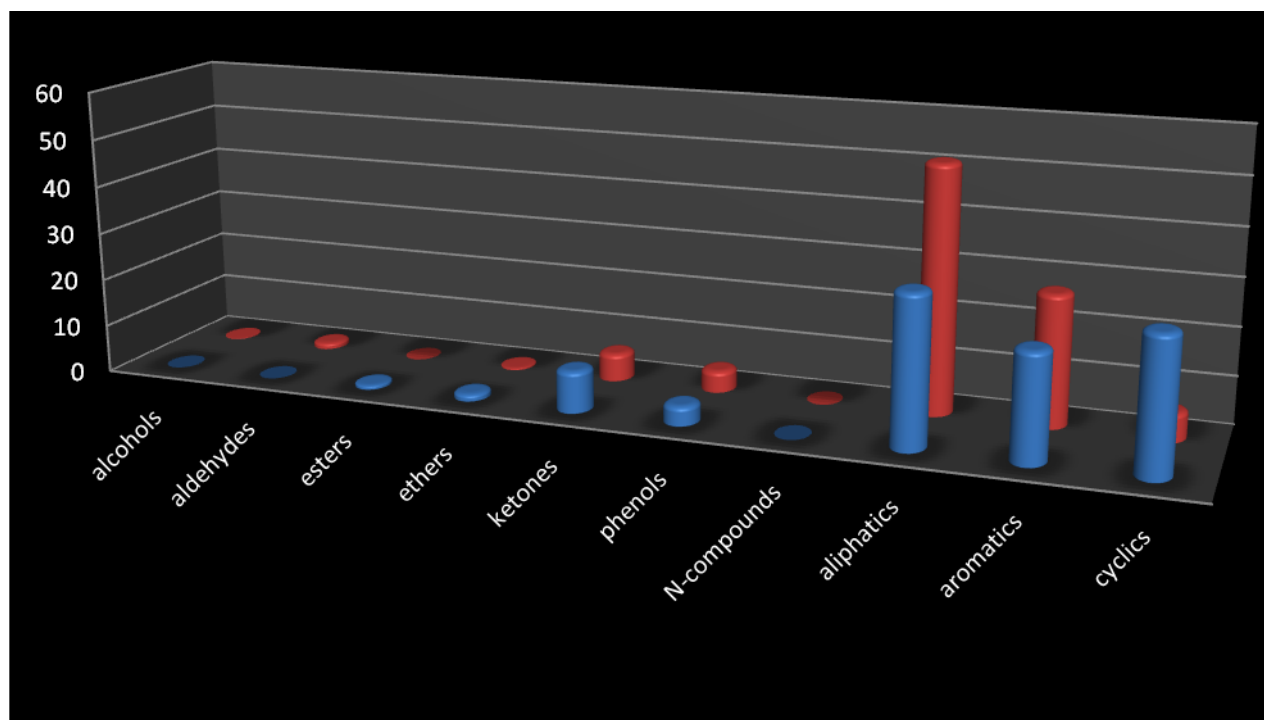


FIG.6. % AREA OF COMPOUNDS IN BHTT (BLUE) AND BLTT (RED)

Fig 6. Shows % area of alcohols , ethers , ketones , phenols , N-compounds, aliphatic, aromatic and cyclic compounds in BHTT (blue) and BLTT (red) and their detail is also given in Table 5.

V. CONCLUSION

BESC was a dark sticky liquid which contained more than 120 compounds. Among them, aromatic, aliphatic and cyclic hydrocarbons, especially alkanes, alkenes and benzene containing compounds were dominant. A laboratory scale effort is made in this work however to improve efficiency and process thus, this process can be successfully applied in large-scale operations because the demand for liquid transportation fuels is increasing day by day, and bio-fuels might be one of the best solutions for this problem. Technologies for converting biomass to biodiesel also are at various stages of development. Which include the pretreatment of biomass, although cost of biomass may be high or the costs of processing can be high but for the time being it may be an alternative for fossil fuels. Future work is going to improve the recovery of phenols, ketones and other chemicals from the BESC and formulation of BESC (10% & 20%) with normal diesel fuel to check its input and output efficiency, characteristics and particulate matter (PM) emission.

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