

Bio-oil Production from Fast Pyrolysis of Aquatic Prostate Herb (*Achyranthes paludosa*)

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Abstract: Pyrolysis of aquatic prostate herb (*Achyranthes paludosa*) was performed in a semi-batch reactor made of Pyrex glass to determine the characteristics and yields of liquid and solid products. Pyrolysis experiments were carried out at the temperatures ranging from 400°C to 600°C at a constant heating rate of 20 °C min⁻¹. The maximum liquid product yield of 38.52 % (by weight) was obtained and had the calorific values 9.97 MJ/kg for *Achyranthes paludosa* respectively. The thermal degradation of *achyranthes paludosa* was studied in atmospheric pressure by TGA. The chemical composition of the bio-oil and bio-char was investigated using 1H-NMR, FT-IR, GC-MS and SEM-EDX. The chemical characterization showed that the bio-oil obtained from *achyranthes paludosa* can be potentially valued as a fuel and chemical feedstock or blended with diesel after upgrading.

Keywords: *Achyranthes paludosa*, Pyrolysis, Biomass, Bio-oil, Bio-char.

I. INTRODUCTION

The depletion of crude oil reserves along with the increased demand for oil and its derivatives have motivated the hunt for different routes of energy generation and of fuel and chemical production. Biomass is considered to be a carbon neutral resource because an equivalent amount of CO₂ is absorbed from the atmosphere during its growth. Biomass has cellulose, hemicelluloses and lignin as its basic building block. Biomass resources including wood and wood wastes, industrial or agricultural residues and their waste by-products, municipal solid waste, animal wastes or dedicated energy crops (e.g., fast growing trees, shrubs and grasses) are main biomass fuels. There are two processes by which biomass can be converted into fuels viz. biochemical process and thermo-chemical process. Thermo-chemical conversion processes that include combustion, gasification, liquefaction, hydrogenation and pyrolysis can convert the biomass into various energy products [1]. Bio-oils, one of the pyrolysis products, are usually dark brown organic mobile liquids which can be readily stored and transported & can be used for the production of chemicals and have potential to substitute fuel-oils in many stationary applications for heat or electricity generation [2]. However, bio-oils are low-quality fuels that cannot be used in conventional gasoline and diesel fuel engines because they are immiscible with petroleum-derived

fuels, primarily on account of their high oxygen content in the range of 35–60 wt.% (wet basis) [3]. Disadvantages of bio-oil are that they contain high water content and lower hydrocarbon ratio compared to fossil fuel. Phase separation is common while storing of bio-oil and direct use of bio-oil in engine may cause a problem due to its higher viscosity and density. They can only be used if blended with diesel or thermally processed to reduce viscosity and increase volatility. The spread of invasive species beyond their home range has many underlying mechanisms and such species are generally detrimental to native biodiversity and ecosystem functioning in the introduced regions, inflicting huge socio-economic damage [4]. Invasive non-native species inflict harmful ecological and economic impacts upon ecosystems in non native regions [5-6]. Biological invasion has emerged as the most severe one causing substantial damage with cascading effects on structural organization and functional integrity of freshwater ecosystems. Early detection and timely exclusion are the most cost effective methods of controlling and preventing invasive species. Control measures often come into play only after the alien species has spread to nuisance proportions [7]. *Achyranthes paludosa* (alligator weed) is known as an invasive species in many parts of the world having a tremendous potential for vegetative reproduction due to its short growth cycle, high growth speed and very strong nutritional intake ability. In India, the species has been reported from Assam, Bihar, West Bengal, Tripura, Manipur, Andhra Pradesh, Karnataka, Maharashtra, Delhi and Punjab [8]. Therefore proper measure needs to taken in order to stop the invasion of foreign species. Pyrolysis of aquatic duckweed was conducted in a quartz tube reactor, and 40wt% of bio-oil was obtained at a temperature of 500°C at constant argon flow rate of 60 ml/min. It was found that pyrolysis temperature had minor effect on the bio-oil product slate, but exerted major influence on the relative quantities of the individual pyrolysis products obtained [9]. The fast pyrolysis of Milkweed was conducted in a bubbling fluidized bed stainless steel pipe reactor in nitrogen atmosphere where the total liquid yield from milkweed pyrolysis was between 40.74 % and 44.19 % (wt) between 425 °C and 550 °C. The ¹³C NMR analysis of the pyrolysis oil showed a large fraction of carboxylic group and its derivatives were present in the bio-oils extracted at 425°C and 475°C, which resulted in higher oxygen content. The study of bio-oil from milkweed also showed that a large

fraction of aromatic and aliphatic hydrocarbons could be easily upgraded to hydrocarbon fuels [10]. Fast pyrolysis of three wetland plants (Alligator weed, *Oenanthe javanica* and *Typha angustifolia*) was conducted in a vertical drop fixed bed reactor. At different pyrolysis temperatures and the maximum bio-oil yields achieved were 42.3%, 40.2% and 43.60 % for Alligator weed, *Oenanthe javanica* and *Typha angustifolia*, respectively. The elemental composition of the bio-oil and char were analyzed, and the results show that a low temperature was appropriate for the nitrogen and phosphorus enrichment in char. GC-MS analysis shows that nitrogenous compounds, phenols and oxygenates were the main categories in the bio-oil. With an increase in pyrolysis temperature, nitrogen and phosphorus enriched in the char were continuously decreased. Average 76% of total nitrogen and 57% of total phosphorus in the char could be recovered, far more than that of the feed-stocks by leaching. Pyrolysis of wetland plants, as an effective nitrogen and phosphorus enrichment and recovery way, has a great application potential in water pollution control. [11]. In this work, pyrolysis of alligator weed (*Achyranthes paludosa*) was conducted in a semi-batch Pyrex glass reactor at an temperature ranging from 400°C to 500°C. The effect of pyrolysis temperatures on product yields was studied. The bio-oil obtained after pyrolysis was analyzed by FT-IR, 1H-NMR, GC-MS. The bio-char was analyzed by FT-IR and SEM. The elemental analysis of biomass, bio-oil and bio-char were also conducted in the study.

II. METHODS

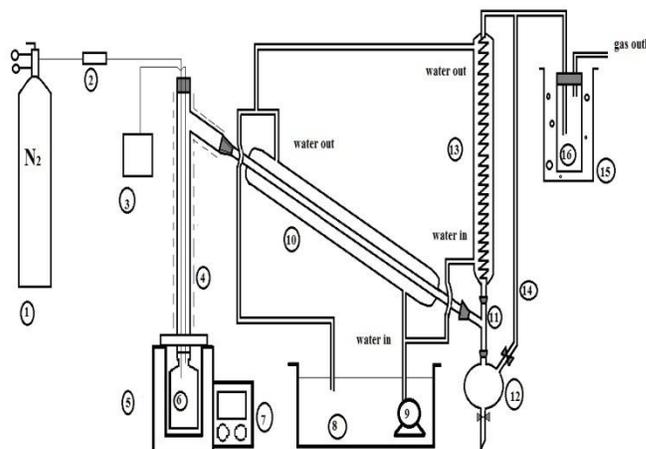
A. Raw material

The raw sample (*Achyranthes paludosa*) was collected from local pond in rural Howrah, West Bengal, India. The sun dried samples were then powdered with the help of a house hold grinder and sieved through a screen having a mesh size of 72 B.S. The screen samples were used in pyrolysis process. ASTM D3172-07a procedure was followed in order to determine moisture content, ash content, volatile matter content, and fixed carbon content. The elemental analysis of biomass (*Achyranthes paludosa*) was carried out with the help of a Perkin Elmer (2400 Series II CHN/O) to determine the carbon, hydrogen, nitrogen, sulphur and oxygen. Component analysis of biomass was done in order to find out the percentage composition of cellulose, hemi-cellulose and lignin [12]. Thermo-gravimetric analysis of the sample was performed in a TA Instruments SDT-Q600 Simultaneous TGA / DSC, V8.2 Build 100. Dried bio-mass samples were analyzed in a Ziess Evo Q800 plus in order to determine its elemental composition.

B. Apparatus

The experimental set-up is shown in Fig.1. The pyrolysis experiments were performed both in air atmosphere and N₂

atmosphere using a semi-batch reactor made of quartz glass with an internal diameter of 2 inches and a length of 6 inches. The reactor was heated externally by an electric muffle furnace.



1. N₂ cylinder. 2. Rotameter. 3. K-type thermocouple.
4. Pyrex glass tube. 5. Electric muffle furnace. 6. Pyrex glass reactor. 7. PID controller. 8. Water tank. 9. Mini pump. 10. Straight condenser. 11. Glass union. 12. Thermo-gravimetric bottle. 13. Spiral condenser. 14. Reflux tube. 15. Five litres glass beaker. 16. Sealed glass beaker.

Fig.1. Pyrolysis setup using Pyrex glass reactor

The pyrolysis temperature and heating rate were controlled with a PID controller. The carrier gas nitrogen with a purity of 99.99% was used for the pyrolysis experiment and the N₂ flow rate was measured by a rotameter. The reactor outlet was insulated with glass wool to minimise heat loss or pre-condensation of hot pyrolytic vapours. The hot pyrolytic vapours entered into a set of condensers where all the vapours condensed into pyrolysis condensate. The condensers were maintained at 10 °C by chilled water with the help of dry ice. The condensate was collected in a thermo gravimetric bottle attached at the bottom of the condensers. The uncondensed vapours were passed through a sealed beaker, which was kept cold by dry ice and water. The uncondensed vapours were collected in Tedlar bag for further analysis.

C. Experimental procedure

The experiment was carried out in two stages. The aim of the first stage was to determine the effect of pyrolysis temperature in air atmosphere at a constant heating rate of 25 °C/min. The sample was heated to a final pyrolysis temperature of 400, 425, 450, 500, 525, 550, 575, 600 °C & held at that temperature for 40 minutes until no significant release of gas was observed. The volatile product was condensed by the set of condensers & the liquid product was collected in thermo-gravimetric bottle. The condensed liquid

consists of pyrolysed oil and oily water. Oily water contains mainly dissolved hydrocarbons and mostly water [13].

The second stage was conducted in a sweep gas (N_2) flow rates of 0.1, 0.2, 0.3, 0.4, 0.5 L/min with the optimum pyrolysis temperature of $500\text{ }^\circ\text{C}$ to obtain the effect of sweeping gas (N_2) flow rate on pyrolysis product yield. All the liquid products were collected in a measuring cylinder and were weighed. After the reactor was cooled to room temperature, the solid char was collected, weighed & recorded.

D. Characterization of *Achyranthes paludosa* bio-oil

Physical characterization of bio-oil such as density, specific gravity, kinematic viscosity, pour point, cloud point, fire point, flash point, calorific value, and distillation range were determined using standard testing techniques for petroleum products. The elemental analysis of bio-oil was carried out with the help of a Perkin Elmer (2400 Series II CHN/O) to determine the carbon, hydrogen, nitrogen, sulphur and oxygen. FTIR of the bio-oil obtained at $500\text{ }^\circ\text{C}$ was conducted by thermo fisher scientific Nicolet i35 (iD3 ATR) with a resolution of 4cm^{-1} at a range of 4000 to 600cm^{-1} . The functional group composition was determined on the basis of the IR-charts available. Agilent 6890 series plus GC-MS analyzer, equipped with flame ionization and mass spectrometry detection (GC-FID-MS) was used to determine the chemical compounds present in the oil. A capillary column coated with a $0.25\text{ }\mu\text{m}$ film of HP-5 with length of 30 m and diameter 0.25 mm was used. The GC was equipped with a split injector at $200\text{ }^\circ\text{C}$ with a split ratio of 1:10. Helium gas of 99.995% purity was used as carrier gas at flow rate of 1.51 ml min^{-1} . The oven initial temperature was set to $70\text{ }^\circ\text{C}$ for 2 min and then increased to $300\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C/min}$ and maintained for 7 min. NIST library was used to identify the compounds. Mass spectrometer was operated at an interface temperature of $250\text{ }^\circ\text{C}$ with ion source temperature of $230\text{ }^\circ\text{C}$ of range 40-800 m/z.

E. Characterization of bio-char

The elemental analysis of biochar obtained after pyrolysis, was carried out with the help of a Perkin Elmer (2400 Series II CHN/O) to determine the carbon, hydrogen, nitrogen, sulphur and oxygen. FTIR of the bio-char was conducted by thermo fisher scientific Nicolet i35 (iD3 ATR) with a resolution of 4cm^{-1} at a range of 4000 to 600cm^{-1} . The SEM (scanning electron microscope) images of the biomass & bio-char were taken with the help of Ziess Evo Q800 plus microscope with an acceleration voltage of 20 KV.

III. RESULTS AND DISCUSSION

A. Effect of temperature on the pyrolysis yield at air atmosphere

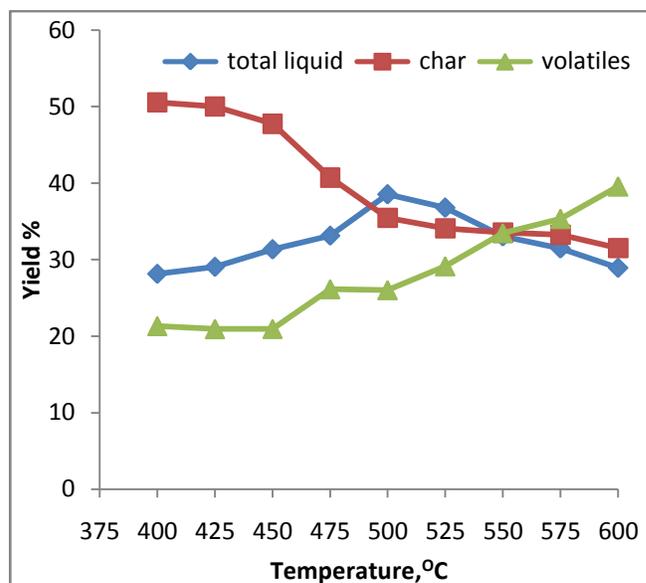


Fig.2. Yield of pyrolysis products at various temperatures.

Fig 2 shows the pyrolysis of *Achyranthes paludosa* at a heating rate of $25\text{ }^\circ\text{C/min}$, and yield of different pyrolysis products at various temperatures. With the increase in pyrolysis temperature from $400\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$, the yield of bio-oil increased from 28.13% to 38.52%. The yield of pyrolysed char also decreased from 50.56% to 35.31% as the pyrolysis temperature increased from $400\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$, due the decomposition of original cellulose and lignin at elevated temperatures. The increased in pyrolysis temperature up to $600\text{ }^\circ\text{C}$, was mainly responsible for the decomposition of char. As the temperature was increased up to $600\text{ }^\circ\text{C}$ the yield of pyrolysed char and bio-oil were also decreased to 31.51 % and 28.93 % respectively, but the yield of pyrolysed gas increased to 39.56 % at $600\text{ }^\circ\text{C}$, due to the degradation of lignin. With the increase pyrolysis temperature, both yields of liquid and gaseous products were increased because of either greater primary decomposition of the raw material or secondary decomposition of char residue [14]. So, $500\text{ }^\circ\text{C}$ is the suitable temperature at which maximum bio-oil can be extracted from *Achyranthes paludosa* at a reaction time of 18 minutes.

B. Effect of flow rate on pyrolysis product yield

The experiment was conducted at a fixed temperature of $500\text{ }^\circ\text{C}$ at a constant heating rate of $25\text{ }^\circ\text{C/min}$ by varying N_2 gas flow rate. The sweeping gas flow rate during the pyrolysis process was adjusted to 0.1, 0.2, 0.3, 0.4 and 0.5 L/min. The effects of sweeping gas flow rate on the yield of pyrolysis products were shown in Fig 3.

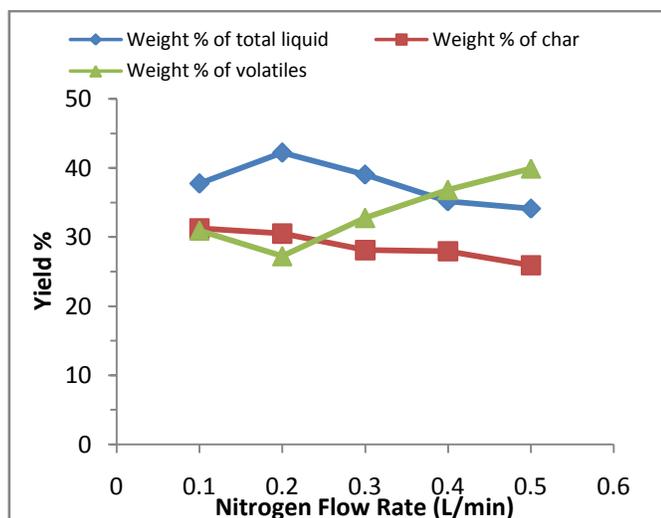


Fig.3. Effect of sweeping gas flow rate on product yield

The total yield of liquid increased from 37.76 % to 42.22 % (wt) with the increase in sweeping gas flow rate from 0.1L/min to 0.2 L/min. But with increase in sweeping gas rate from 0.2 L/min to 0.5 L/min the yield of liquid decreased from 42.22 % to 34.14 % (wt). However the yield of char decreased slightly with increasing sweeping gas flow rate. The volatile matter content increased from 30.97 % to 39.9341 % (wt.) with increase in the sweeping gas flow rate from 0.1 L/min to 0.5 L/min. This effect was due to the quenching of the hot vapours of pyrolysis by N₂ gas which helped in reducing the secondary reactions.

C. Characterization of *Achyranthes paludosa* biomass and bio-char

a. Proximate and ultimate analysis of *Achyranthes paludosa* biomass and bio-char

As seen in the Table 1, the *achyranthes paludosa* had a higher volatile matter content of 58.79% which was reduced to 24.89% after pyrolysis. High volatile content indicates that the material is more volatile than solid fuels whereas loss in fixed carbon content during pyrolysis should be less [13]. The decrease in char yield with increasing temperature could be either due to greater primary decomposition of volatiles at higher temperatures or may be due to secondary decomposition of the char residue [15]. The gaseous yield decreased initially then increased with increase in temperature. This may be due to secondary cracking of the pyrolysis vapours or the formation of some non-condensable gaseous products during secondary decomposition of the char at higher temperatures [16]. The ultimate analysis of the biomass and bio-char showed that carbon content before pyrolysis was 40.41% which later increased to 59.36 % after pyrolysis whereas the percentage of oxygen decreased from 46.95 % to 29.68 %. Biochar obtained after pyrolysis can be

potentially used as a source of fuel due to lower oxygen content and higher percentage of carbon content.

Table.1.

Proximate Analysis of *achyranthes paludosa* & *achyranthes paludosa* bio-char

	(<i>Achyranthes paludosa</i> biomass)	(<i>Achyranthes paludosa</i> bio-char)
Proximate Analysis		
Volatile Matter	58.79	24.89
Ash	18.15	34.66
Moisture	3.47	2.89
Fixed Carbon	19.59	37.56
Ultimate Analysis		
C	40.41	59.36
H	6.63	3.27
N	5.27	6.26
P ^a	0.74	1.43
O ^b	46.95	29.68
H/C	1.97	0.661
O/C	0.87	0.375
Empirical Formula	CH _{1.97} N _{0.112} O _{0.87} P _{0.0071}	CH _{0.661} N _{0.09} O _{0.37} P _{0.0093}
High Heating Value (MJ/kg) ^c	16.65	22.80
Compositional Analysis		
Extractive Analysis	32.4875	----
Hemi-cellulose Analysis	23.015	----
Cellulose Analysis ^b	29.04	----
Lignin Analysis	15.4575	----

a. EDX by Zeiss Evo Q800 plus.

b. By difference.

c. Heating Value (MJ/kg) = $[\{3.55 \times C^2\} - \{232 \times C\} - \{2230 \times H\} + \{51.2 \times (C \times H)\} + \{131 \times N\} + 20600] / 1000$ [15].

b. TGA of *achyranthes paludosa* biomass

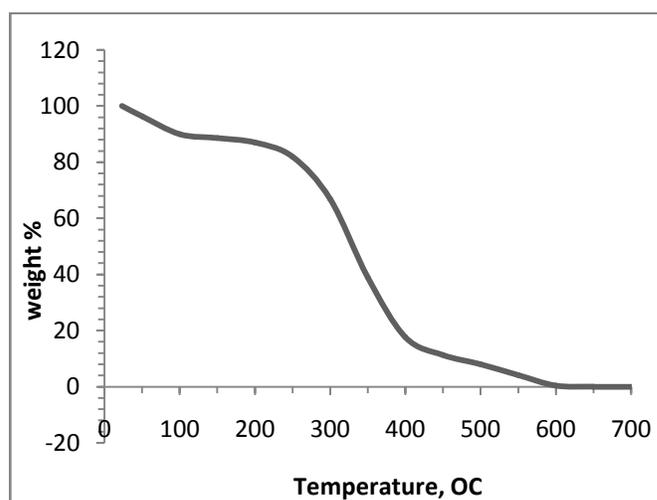


Fig.4. TGA of *achyranthes paludosa* biomass.

Thermo-gravimetric analysis of *achyranthes paludosa* was conducted in presence of air at a heating rate of 20^oC/min in Fig.4. The first region of thermal degradation occurred at the temperature range of 25 ^oC to 150 ^oC, which resulted in a weight loss of 10.57%, due to loss in moisture or water content. The second region of thermal degradation which occurred at the temperature range of 150 ^oC to 400 ^oC, which resulted in a weight loss of 73.17% due to decomposition of cellulose, hemi-cellulose and formation of volatiles (carbon dioxide and carbon mono-oxide) and degradation of weaker chemical bonds and side aliphatic chains. The third stage of thermal degradation occurred in the temperature range of 400 ^oC to 600 ^oC, with a loss in weight of 16.26% due to degradation of lignin as well as original structure also got destroyed. After this temperature no further decomposition takes place.

c. Energy dispersive x-ray

The energy dispersive x-ray of the biomass sample was conducted in ziesse Evo Q 800 plus in order to find the elemental composition of biomass, shown in fig 5.

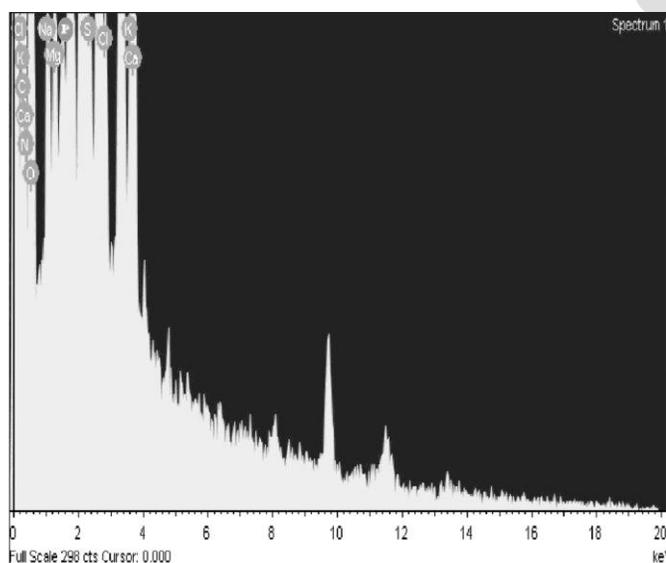


Fig 5: Energy dispersive x-ray of *achyranthes paludosa*

The biomass sample was placed over the carbon tape and was coated with Au. Hydrogen gas charged at 2 bar pressure for this process. EDX was done to see the percentage of impurities present in the sample. Some elements like CL-2.57. wt%, N-5.27 wt%, K-2.26 wt%, C- 40.41wt%, Ca-1.02 wt%, O-46.95 wt%, Na-0.54 wt%, Mg-0.24 wt%, and P-0.74wt % were found out from *achyranthes paludosa*.

D. Characterization of *achyranthes paludosa* bio-oil

a. Physical characterization of *achyranthes paludosa* bio-oil

The average chemical composition of *achyranthes paludosa* bio-oil is CH_{3.93}N_{0.11}O_{1.42}P_{0.0036}. The oil was characterized by higher oxygen content than that of the original biomass feedstock. The notable rise in the oxygen content in bio-oil is not commendatory since high oxygen content is not encouraged for the manufacturing of transportation fuel. This can only be enhanced by upgrading the bio-oil. From the result of the elemental analyses, the carbon, hydrogen and nitrogen content of *achyranthes paludosa* bio-oils are 27.61, 9.05 and 3.51, respectively at 500 ^oC. These values are higher than that of the raw materials which in turn indicate that the bio-oil has a higher energy density. The H/C ratio (3.93) of bio-oil was higher than that of the original material and a comparison of this value with conventional fuels indicates that the bio-oil obtained in this study lies between those of light and heavy petroleum products. The low ash content (0.0043) suggests that the bio-oil has obvious advantages as a clean fuel oil. It can be observed that *achyranthes paludosa* pyrolytic oil is denser and the value was found to be 0.9238 kg/m³. The flash point of the oil was found to be 48 ^oC, which means it can be stored safely. Calorific value of the oil is 9.97 MJ/kg which determined by modified Dulong formula [15] which is quite lower than gasoline (42-46 MJ/kg) and diesel (42-45 MJ/kg) [16]. The initial boiling point of the pyrolytic oil was 92^oC which means that the liquid contain considerable amount of volatile matter. The final boiling point of the pyrolysed oil was 365 ^oC.

Table 3
Physical properties of *achyranthes paludosa* pyrolysis oil

Properties	Achyranthes paludosa bio-oil	Methods
Density at 15 ^o C (kg/m ³)	0.9238	ASTM D 1298 – 99
Specific gravity at 15 ^o C/15 ^o C	0.9246	ASTM D 1298 – 99
Kinematic viscosity at 40 ^o C (centistoke)	24.51	ASTM D 445-04
Kinematic viscosity at 100 ^o C (centistoke)	4.03	ASTM D 445-04
pH	4.15	-
Flash point by Pensky-Martens Closed Cup Tester (^o C)	48	ASTM D 93 – 02a
Fire Points by Cleveland Open Cup Tester (^o C)	69	ASTM D 92 – 02b
IBP (^o C)	92	ASTM D 2887-08
FBP(^o C)	365	ASTM D2887-08
Ash content	0.0043	ASTM D482-80
Appearance	Dark brown	-
C	27.61	Perkin Elmer (2400 Series II CHN/0)
H	9.05	Perkin Elmer (2400 Series II CHN/0)
N	3.51	Perkin Elmer (2400 Series II CHN/0)

P ^a	0.26	Ziess Evo Q800 plus
O ^b	59.57	-
H/C	3.93	-
O/C	1.42	-
Empirical Formula	CH _{3.93} N _{0.11} O _{1.42}	-
	P _{0.0036}	
GCV (MJ/kg)	9.97	Dulong formula (15)

b. FT-IR of *achyranthes paludosa* bio-oil

The pyrolytic oil FT-IR was done in order to determine the functional group present in complex bio-oil shown in fig.6. The O-H stretching vibration at 3220.76 cm⁻¹ indicated the presence of alcohols and phenols, such as toluene and methanol fractions. The low frequency values for these bands suggested that hydroxyl groups were involved in hydrogen bonds [17]. The C-H stretching vibration at 2923.33cm⁻¹; 2853.06 cm⁻¹; 1455.17 cm⁻¹; and 1379.01 cm⁻¹ indicated the presence of alkanes.

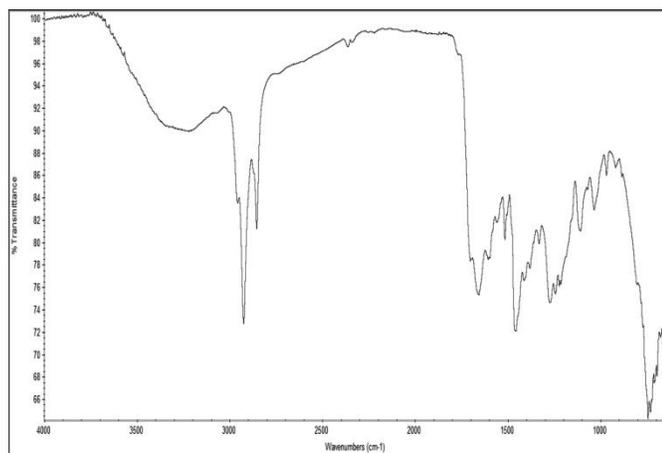


Fig 6: FT-IR of *achyranthes paludosa* bio-oil

The P-H sharp vibration at 2361.60 cm⁻¹ and 2341.12 cm⁻¹ indicated the presence of phosphine. The C=O stretching vibration at 1654.22 cm⁻¹ and 1604.86 cm⁻¹ indicated the presence of alkenes/aromatics. The N=O asymmetric stretch vibration at 1559.34 cm⁻¹ and 1514.31 cm⁻¹ indicated the presence of nitro groups. The Ar C-C stretching vibration at 1411.73 cm⁻¹ indicated the presence of aromatics. The Ar-N stretching vibration at 1329.29 cm⁻¹ indicated the presence of amines. The C-O Stretching vibration at 1272.29 cm⁻¹, 1242.21 cm⁻¹, 1221.03 cm⁻¹, 1106.08 cm⁻¹, and 1032.24 cm⁻¹ indicated the presence of esters. The =C-H out of plane vibration at 966.72 cm⁻¹ and 915.61 cm⁻¹ indicated the presence of alkenes. The C-H out of plane, vibration at 742.33 cm⁻¹, 728.52 cm⁻¹, 709.09 cm⁻¹, and 693.20 cm⁻¹, indicated the presence of mono, poly and substituted aromatics ring.

c. Gas Chromatography-Mass Spectroscopy

Gas chromatography/Mass spectroscopy has become a quick, convenient and powerful tool for characterizing complex and heterogeneous bio-oil samples [18]. The GC-MS of the *achyranthes paludosa* bio-oil was done and the main identified compounds are listed in the table 4. Bio-oil was a complex mixture and contained a wide variety of oxygenated organic compounds, such as carboxylic acids, phenols and ketones. To characterize the pyrolytic oil, the oils were separated into four fractions: phenolic compounds, oxygenated compounds, nitrogenous compounds, and hydrocarbon compounds. The results of the gas chromatography of the oil showed that the compounds identified in the bio-oils were divided into three groups: (1) Phenolic compounds, including phenol and its derivatives, were 14.8%, in the bio-oil derived from Alligator weed, respectively; (2) other Oxygenated compounds, in the bio-oil was 14.66 % for Alligator weed, (3) Nitrogenous compounds, were 37.97 % which are the largest, (4) Hydrocarbons in the bio-oil were 9.35 %. The identification of chemical compounds present in the bio-oil was determined by the data provided by NIST library. The liquid product contained 35 types of chemical compounds having chain length in the range of C₆ – C₂₄ similar to a mixture of transportation fuels. The highest peak areas of the chemical compound analyzed by GC-MS were 2, 4-Dimethoxytoluene, Hexadecanenitrile, Octadecanenitrile, 2, 4-Di-tert-butylphenol, 1,1H-Benzo[a] carbazole, 2-methylPyridine, 4-acetoxy-acetophenone, 3-Aminopyridine. 2,4-Di-tert-butylphenol is a raw material for phosphite anti-oxidants. The antioxidants are primarily used in the manufacture of polyolefins; 2, 4 DTBP and 1, 1H-Benzo[a] carbazole normally used for the manufacturing of pharmaceuticals/drugs/medicines and fragrances. 2-methylpyridine is used as an adhesive for textile tire cord. 2-methylpyridine is also a precursor to the agrichemical, nitrapyrin, which prevents loss of ammonia from fertilizers. 4-acetoxy-acetophenone or 4'-Hydroxyacetophenone has been used as ketone component in the preparation of 1-aryl-3-phenethylamino-1-propanone hydrochlorides, potential cytotoxic agents, via Mannich reactions [19]. 3-Aminopyridine can be used in the synthesis of organic ligand 3-pyridylnicotinamide.

Table 4
GC-MS compounds in *achyranthes paludosa* bio-oil

SL. No	Compound	Area (%)
1	Pyrocatechol	2.18
2	2,4-Ditert-butylphenol	4.54
3	2,6-Dimethylphenol	2.17
4	2-methoxy-4-(1-propenyl)	1.17
5	Benzene,1,3-dihydroxy-	2.19
6	2-ethoxyphenol	1.29
7	2-methoxy-phenol	1.26
8	Hexadecanenitrile	6.44
9	4,5-Dimethyl-ortho-phenylenediamine	1.10

10	3-Aminopyridine	2.72
11	2-methyl Pyridine	3.35
12	Ethan amine, N,N-dimethyl	2.83
13	Aniline, N-methyl	2.37
14	1,1H-Benzo[a] carbazole	4.21
15	Propanenitrile	2.31
16	Propanedinitrile	0.68
17	3-(1H-Imidazol-1-yl)-1-propanamine	1.25
18	Acetic Acid	0.58
19	Propanoic acid,2-hydroxy-,methyl ester	0.43
20	2 propanone, 1,3-dihydroxy	0.47
21	n-heptadecanol	1.38
22	1,3-Benzene dicarboxylic acid	2.31
23	4-acetoxy-acetophenone	2.86
24	2,4-Dimethoxytoluene	6.63
25	Benzene,1methyl-3nitro	1.53
26	1,4-Benzenediamine,N,N'-diethyl	1.79
27	1-1-(m-Hydroxyphenyl)-2-methylaminoethanol	1.86
28	Eicosane	2.59
29	1-Hexane	1.34
30	Tridecane	2.82
31	1,4-cyclohexadiene,1-methyl-4-(1-methylethyl)	0.42
32	Tetracosane	0.19
33	Benzene,(1-methylethyl)	0.39
34	Octadecane	1.60
35	Octadecanenitrile	5.53

E. Characterization of *achyranthes paludosa* biochar

a. SEM analysis of *achyranthes paludosa* biochar

The two SEM images show the surface morphology of biomass before and after pyrolysis. The effect of pyrolysis on biomass had drastically affected the complex structure of hemi-cellulose, cellulose and lignin. The degradation of these complex structure happened at different stages of pyrolysis. Fig 7(a) & (b) are the images of *achyranthes paludosa* biomass and biochar taken at 5KX magnification at an acceleration voltage of 20 KV by Ziess Evo Q800 Plus. The second image of biochar showed heterogeneous distribution of pores and rough texture. The average pore sizes present on the char surface was found to be 4.83 μm . The pyrolysis temperature led to the change in size and shape of particle. High heating rate of pyrolysis led to the release of volatile matter and increased in the size and portion of voids and a decreased in cell wall thickness. Therefore SEM porosity increased with a pyrolysis temperature [13]. Fast volatile matter release during pyrolysis produces considerable interim above compression and bunch of the smaller pores. This process results into to larger internal cavities and additional open structure. The porosity of char increases with increase in temperature.

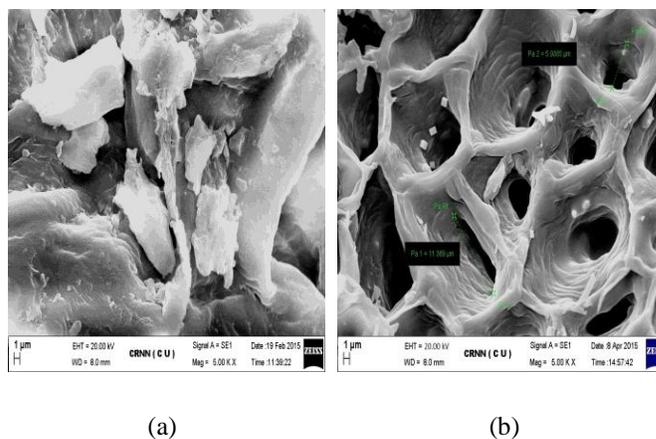


Fig 7: SEM of alligator biomass (a) and biochar; (b) After pyrolysis

b. FT-IR of *achyranthes paludosa* bio-char

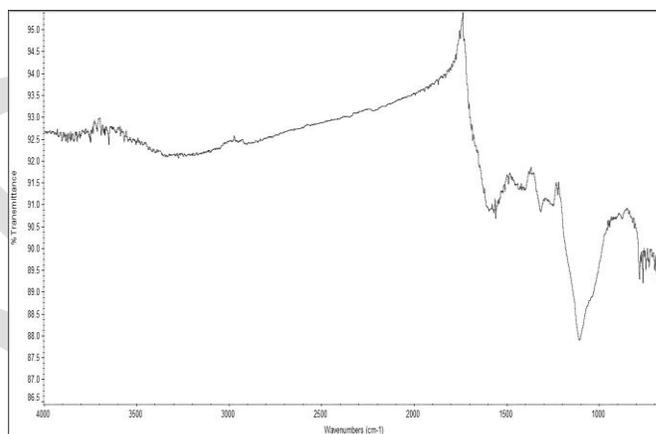


Fig 8: FT-IR of *achyranthes paludosa* bio-char

The *achyranthes paludosa* bio-char obtained at 500^oC, was analyzed to determine the functional groups present in the bio-char sample by thermo fisher scientific Nicolet i35 (iD3 ATR) FT-IR with a resolution of 4cm⁻¹ at a range of 4000 to 600 cm⁻¹. Since pyrolysis was organized at an elevated temperature of 500^oC, there was no presence of OH group and aldehydes and ketones group in the bio-char sample. The C=C stretching vibration at 1568.32 cm⁻¹ indicated the presence of alkenes. The C-O stretching vibration at 1557.85 cm⁻¹ indicated the presence of carboxylic acid. The Ar C-C stretching vibration at 1416.56 cm⁻¹ indicated the presence of aromatics. The Ar-N stretching vibration at 1313.42 cm⁻¹ indicates the presence of amines. The C-N stretching vibration at 1221.46 cm⁻¹ indicates the presence of amines. The C-O stretching vibration at 1105.45 cm⁻¹ indicates the presence of alcohols. The C-H out of plane, stretching vibration at 779.41 cm⁻¹ and 762.10 cm⁻¹ indicates the presence of 1,2,3-tri substituted aromatics. The C-H out of plane, stretching vibration at 728.38 cm⁻¹ and 698.06 cm⁻¹ indicates the presence of 1,2,5-tri substituted aromatics.

VI. CONCLUSION

Achyranthes paludosa as biomass was taken for the pyrolysis experiments which were accomplished in a semi-batch reactor made up of Pyrex glass at temperature range from 400°C to 600°C at a rate of 25 °C/min to produce pyrolytic bio-oil. The maximum yield of bio-oil was found to be 38.52% at 500°C. The pyrolysis was carried out at a constant temperature and heating rate 500°C and 25°C/min at a various sweeping gas flow rate and it was observed that the liquid yield percentage increased when the flow rate of gas was increased from 0.1 to 0.2 L/min. However, the liquid yield decreased when the flow rate was increased from 0.2 to 0.5 L/min. The calorific value of the bio-oil was found to 24.72MJ/kg using modified Dulong formula. The major compounds present in bio-oil were found out using GC-MS. The compounds are 2, 4-Dimethoxytoluene, Hexadecanenitrile, Octadecanenitrile, 2, 4-Di-tert-butylphenol, 1,1H-Benzo[a] carbazole, 2-methylPyridine, 4-acetoxy-acetophenone, 3-Aminopyridine. The obtained liquid product can be used as a replacement for fossil fuel. The pyrolysed bio-oil can be used directly or blended with diesel or can be used as a precious feedstock for chemical industries. The wide ranging pores in the bio-chars enable its use as an absorbent or fuel for charcoal stove. In future, the pyrolysis will be conducted in inert atmosphere and in the presence of catalysts and the bio-oil will be upgraded so that it can be blended with diesel or used as a fuel.

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