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Production and Characterization of Duckweed Bio-Oil via Pyrolysis: A Renewable Alternative to Fossil Fuels

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Abstract **- Duckweed bio-oil has gained significant interest due to its exceptional benefits in raw material utilization and eco-friendliness. Research on microalgae cultivation and pyrolysis production lines is vital to enhancing the efficiency of duckweed biomass consumption for renewable energy. In this work, the pyrolysis process was applied to create bio-oil from duckweed. A fixed-bed reactor was connected to condensers, with heat delivered via a gas burner, and a thermocouple used to measure the reactor's temperature. A stopwatch was used to track the elapsed time until the last drop of product was visible from the system. The results show that both duckweed oils are heavy oils, with an API gravity of 8.73, densities of 1.079 g/cm³ and 1.006 g/cm³, high viscosities of 8.24 mm²/s and 9.32 mm²/s, respectively, a specific gravity of 1.01, a high flash point of 96 °C, and a pour point of 16 °C. The research confirms that duckweed biomass can be pyrolyzed to produce bio-oil. GC/MS analysis was conducted on the generated bio-oil, revealing the presence of multiple polyaromatic hydrocarbons. Consequently, carbon chain elements (C8-C28) are present in duckweed bio-oils. According to the findings, duckweed-derived bio-oil shows great promise as a fossil fuel alternative. This study suggests that, since microalgae have the potential to be a viable replacement for fossil fuels, efforts should be made to scale up microalgae production from the laboratory to industrial levels.**
Keywords: **Duckweed Bio-Oil, Pyrolysis, Renewable Energy, Microalgae, Fossil Fuel**

I. INTRODUCTION

Bio-oil has experienced significant growth and commercialization in recent years due to the increased demand for alternative liquid transportation fuels [1]-[5]. A variety of feedstocks can be utilized to produce bio-oil, such as plant oils, sugars, starches, lignocellulosic biomass obtained from energy crops or plant waste, animal oils, and biomass made from decomposed organic matter; cultured microorganisms can also be included. It has been noted that several feedstocks used in biofuels, including sugarcane, wheat grain, and maize starch, compete with food crops for nutrients, water, and agricultural land [6]-[11]. The creation of bio-oil from food crops, such as vegetables, may jeopardize food consumption since it converts raw materials used for food production into bio-oil [13]-[15]. Duckweed is one of the feedstocks that can be utilized to produce bio-oil and is an essential feed resource [19], [31], [32], as it does not directly compete with food production when used to generate liquid fuels [12], [17]. The primary goal of this research is to create and evaluate bio-oil from duckweed biomass.

II. MATERIALS AND METHOD

Duckweed was collected from stagnant water in the Diobu district of Port Harcourt, Rivers State. The materials used for the study included a single-shot pyrolyzer connected to a gas chromatography-mass spectrometry (GC-MS) system (Agilent 7890A/5975C, USA) [1], a pyrolytic system heater, a thermocouple, a condenser, water for cooling, a weighing balance, a retort stand, a beaker, a separating funnel, a round-bottom flask, and a gas burner, which served as the heat source for the reaction. The temperature of the cooling water was maintained at 26°C. A measuring cylinder containing condensed oil was utilized to track the rate of product production. A stopwatch was employed to measure the system's reaction time, and a thermocouple was connected to monitor the system's temperature. Figure 1 displays the biomass of the duckweed post-harvest, and Figure 2 depicts the pyrolysis setup with the harvested duckweed.

Fig. 1 Harvested duckweed sample

Fig. 2 Pyrolysis Setup

The duckweed plant was harvested and allowed to air dry for 14 days to eliminate any remaining moisture. Subsequently, 3.5 kg of dried duckweed was weighed and fed through the reactor's hopper. The hopper was then appropriately sealed using thread seal tape to prevent leaks. A glass condenser was closely attached to the reactor to cool the condensing vapor. Water at a temperature of 26°C was used for cooling in a counter-current configuration. No catalyst was applied. After that, the gas burner was turned on, and the pyrolysis proceeded until the last drop of oil was visible in the measuring cylinder. The amount of bio-oil produced was monitored based on temperature and duration. The produced bio-oil was immediately analyzed, and the results were recorded.

The following analyses were carried out on the bio-oil: specific gravity, oil density, API gravity, pH, viscosity measurement, flash point, and pour point.

The chemical compositions of the produced bio-oil were examined using gas chromatography (GC) and mass spectrometry (MS). The carrier gas used in this experiment was helium, with the following parameters: 1 µL injection volume, 270°C injection port temperature, and a flow rate of 10.0 mL/min. The analysis was conducted at 40°C, with the temperature ramped to 46°C at a rate of 1.5°C per minute [13]. Once the temperature reached 209°C, the heating rate was increased to 4°C per minute. Real-time analysis of the pyrolysis sample's chemical composition was conducted using a single-shot pyrolyzer connected to a GC-MS system (Agilent 7890A/5975C, USA) equipped with an inert XL mass spectrum detector and a capillary column (30 m in length, 0.25 µm internal diameter, HP-5 MS) [1]. The total ion count (TIC) diagrams of the microalgal pyrolysis products were acquired at various temperature settings. The outcomes were evaluated using the Agilent MSD Productivity ChemStation for GC and GC/MS System Data Analysis program, achieved by comparing the retention times and peak area percentages of various compounds in the pyrolysis products with the NIST 2011 Database. Each chemical's concentration matched the peak area of that compound precisely.

III. RESULTS AND DISCUSSION

The experiment revealed that the volume of bio-oil generated increased with the reaction temperature as it rose from 50°C to 160°C. Since all of the bio-oil was extracted at this temperature, the bio-oil yield at temperatures between 400°C and 500°C was examined. Figure 3 illustrates how the pyrolytic system is affected by temperature. A total of 1.1 kg of duckweed char is produced when the plant is pyrolyzed. The physical characteristics of the bio-oil made from green algae were determined through analysis.

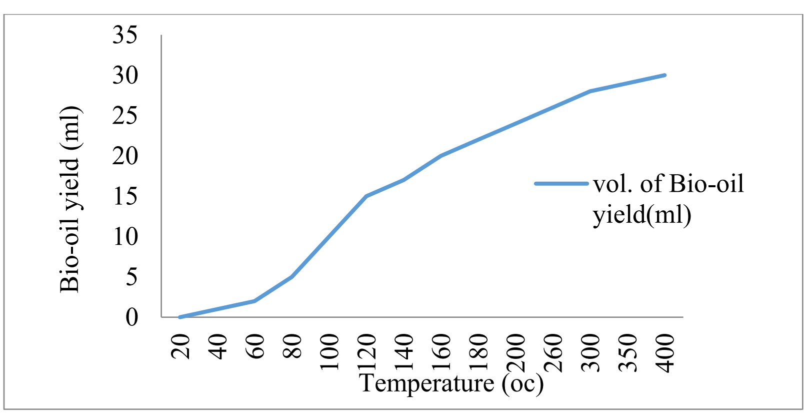

Fig. 3 Effect of Temperature and Time on Bio-Oil yield from Duckweed

The first product drop was observed at the 30-minute mark, and the volume of product formed from the pyrolysis process 46 minutes after the first drop was 2 mL, as illustrated in Fig. 4.

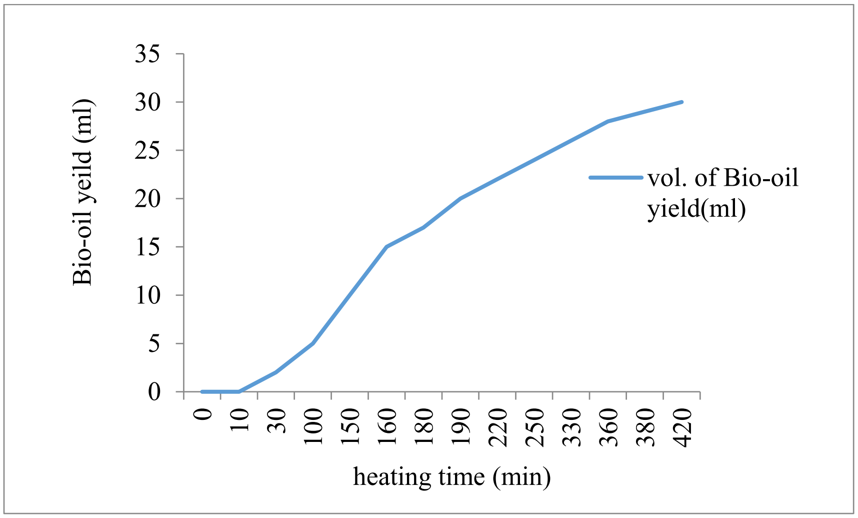

Fig. 4 Effect of Heating Time on Bio-Oil yield from Duckweed

Table I below depicts the physical properties of the produced bio-oil from duckweed and summarizes the primary byproducts of duckweed pyrolysis. The specific gravity of the bio-oil was 1.003. According to [17], the specific gravities of bio-oils derived from woody biomass typically range from 0.80 to 1.21, whereas other biomass, such as pine sap, has a specific gravity between 0.889 and 0.989.

The produced bio-oil has a specific gravity greater than that of gasoline, which ranges from 0.68 to 0.74. This indicates that, based on its specific gravity, bio-oil produced by pyrolyzing duckweed can be used as a mixture with biodiesel but not with gasoline.

TABLE I PHYSICAL PROPERTIES OF THE PRODUCED BIO-OIL FROM DUCKWEED

Physical Properties	Quantity	Unit
Density at 22℃	1.034	g/cm^3
Specific gravity	1.003	-
API gravity at 22℃	8.42	-
Viscosity	9.20	mm^2.S^{-1}
pH	5.2	-
Pour Point	15	^{0}C
Flash Point	96	^{0}C
Volatile matter	0.5	%
Fixed carbon	78.22	%

As shown in Table I above, the produced bio-oil from duckweed has an API gravity of 8.42 at 22°C, indicating that it is a very heavy oil. The viscosity of the bio-oil (mm²/s; at 22°C) is 9.32, indicating that it is a highly viscous fluid, comparatively greater than that of other biomass sources. Due to the intense heat used during the pyrolysis process, the viscosity of the bio-oils produced from the green algae increased as the temperature rose.

The duckweed bio-oil has a pH of 5.2. The pour point temperature of 15°C is within the range required for waxy crude oil. The temperature at which the bio-oil flashed was 96°C, which is the same as the temperature at which heavy crude oil and crude oil with a density greater than 0.900 can flash. The generated bio-oil has a volatile matter content of 0.5 and a fixed carbon content of 73.22, respectively.

As indicated in Table II, the reaction's heating time was monitored during the pyrolysis of microalgae to produce bio-oil. It was found that no product was generated from the pyrolysis process during the heating times of 0 to 10 minutes. When the system was heated for an extended period, more bio-oil product was generated, enhancing the bio-oil yield [16].

The experiment demonstrated that the volume of bio-oil generated rose along with the reaction's heating time, which increased from 30 to 180 minutes. Since all of the bio-oil had been recovered from the duckweed at this point, the bio-oil yield of the 420-minute heating duration was examined.

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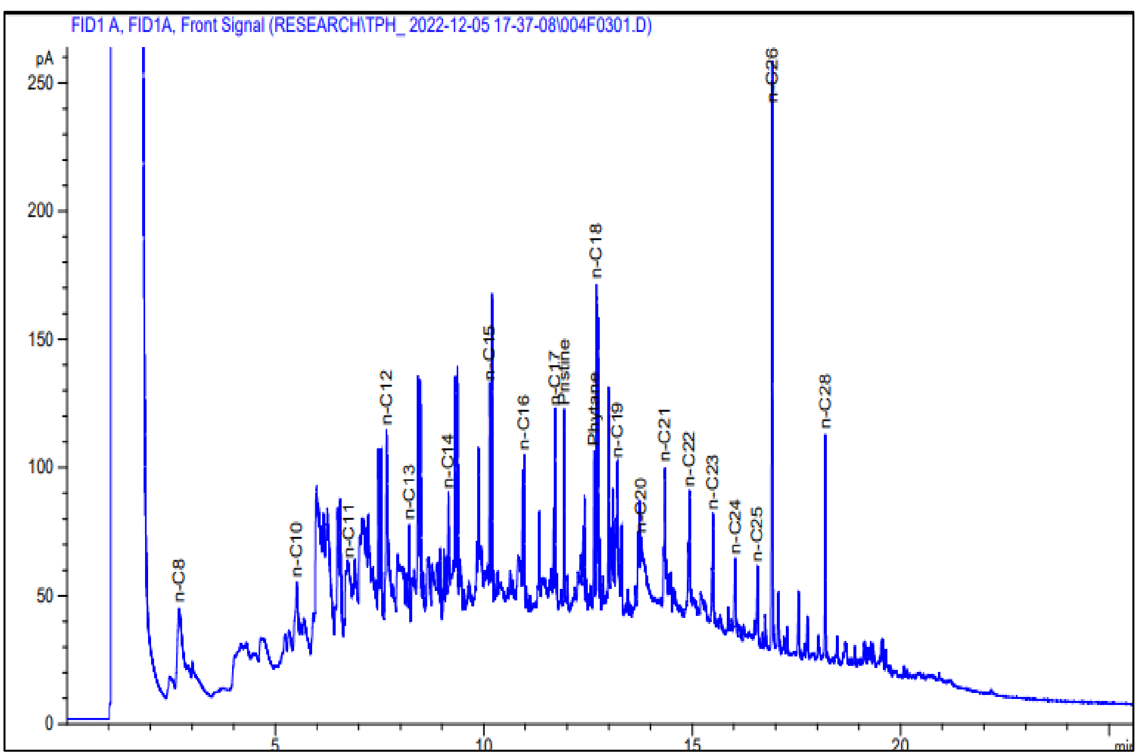

Fig. 5 TIC Diagrams of for Bio-Oil Produced from Pyrolysis of Duckweed

Fig. 5 shows the TIC diagrams of bio-oil generated from duckweed pyrolysis. The pyrolyzed products predominantly comprised 22 types of chemicals, including hydrocarbons, alcohols, acids, and others.

TABLE III MS RESULTS FOR RETENTION TIME AND COMPONENT OF BIO-OIL PRODUCED FROM MICROALGAE

Compound		R.T.	QIon	Response	Conc.	Units	Dev(Min)
Target Compounds							**Q value**
1	Naphthalene	3.158	138	721	1.21	ppm	100
2	Acenaphthylene	4.557	162	833	1.82	ppm	100
3	Acenaphthene	4.754	163	364	1.60	ppm	100
4	Fluorene	5.367	176	267	1.33	ppm	96
5	Phenanthrene	6.437	188	784	4.89	ppm	100
6	Anthracene	6.534	188	295	1.88	ppm	100
System Monitoring Compounds							
7	o-Terphynyl	7.080	220	1063	0.17	ppm	0.23
8	Fluoranthene	7.870	212	989	9.50	ppm	100
9	Pyrene	8.082	212	566	4.89	ppm	100
10	Benzo(a)anthracene	9.599	238	1038	8.70	ppm	100
11	Chrysene	9.652	238	408	3.51	ppm	100
12	Benzo(b)fluoranthene	10.780	262	1276	13.27	ppm	100
13	Benzo(k)fluoranthene	10.825	262	870	8.64	ppm	100
14	Benz(a)pyrene	11.134	262	649	10.45	ppm	#38
15	Dibenz(a,h)anthracene	12.337	286	246	7.19	ppm	#50
16	Indeno(1,2,3-cd)pyrene	12.282	286	237	7.77	ppm	100
17	Benzo(g,h,i)pyrene	12.656	286	278	8.29	ppm	100

The pyrolyzed products of duckweed at a temperature of 350°C predominantly consisted of 17 distinct types of chemicals, including acids, hydrocarbons, alcohols, and several other organic compounds, according to further analysis. The compounds identified in the analysis were used for system monitoring, specifically [22], [23], [24], [25], [26], [27], [28], [29], and [30].

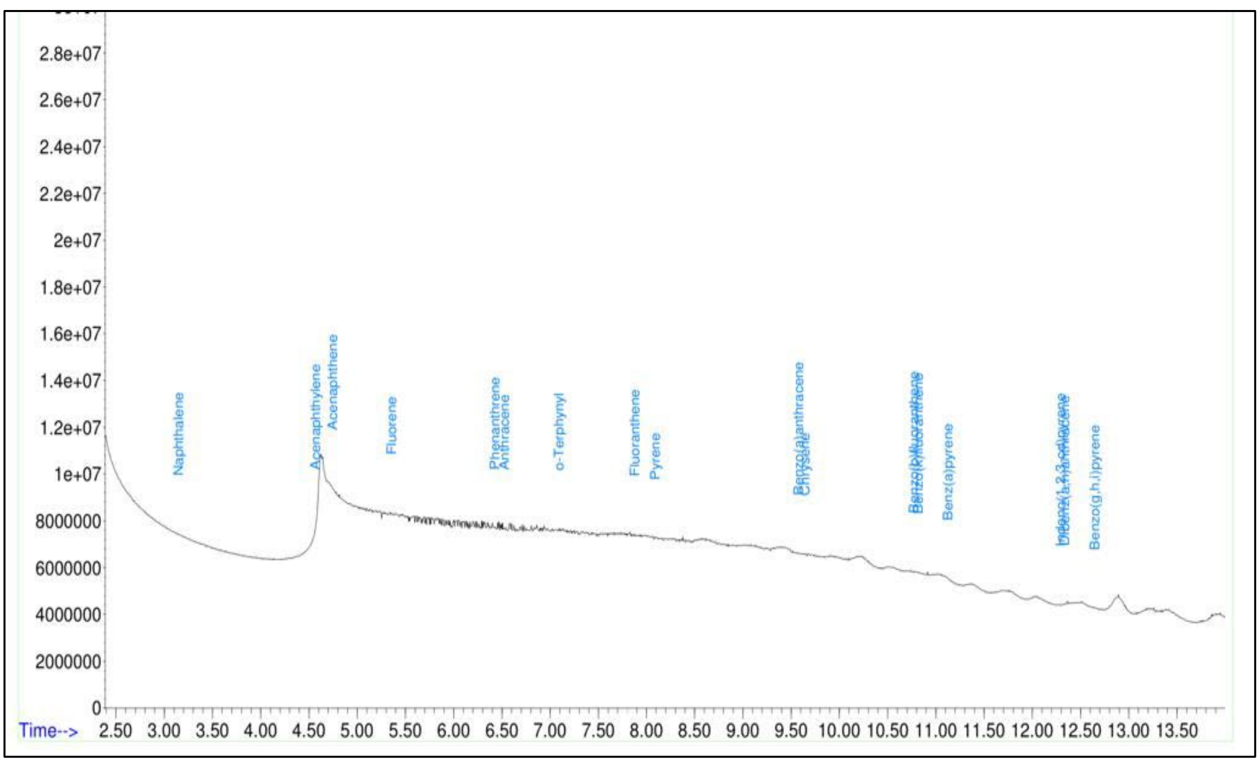

Fig. 7 TIC Diagram for MS Analysis of Bio-Oil Produced from Duckweed

IV. CONCLUSION

The study concludes that the pyrolysis of duckweed biomass produced bio-oil. GC/MS analysis conducted on the produced bio-oil sample showed that the bio-oil from duckweed contains several polyaromatic hydrocarbons, consisting of 38 different compounds, including hydrocarbons, alcohols, and acids. The bio-oil produced from duckweed is a potential alternative to fossil fuel and is classified as a biodegradable and environmentally friendly biomaterial. Furthermore, it was demonstrated that duckweed is a potentially useful biomass for large-scale bio-oil production, as 3.5 g of duckweed produced 30 mL of bio-oil, indicating that an increased quantity of duckweed results in increased bio-oil production. It is imperative to convert the laboratory-scale production of bio-oil from duckweed biomass to an industrial scale to realize its essential benefits as an alternative to fossil fuel.

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