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Pyrolysis of *Alternanthera philoxeroides* (alligator weed): Effect of pyrolysis parameter on product yield and characterization of liquid product and bio char

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ABSTRACT

In the present work, fast pyrolysis of *Alternanthera philoxeroides* was evaluated with a focus to study the chemical and physical characteristics of bio-oil produced and to determine its practicability as a transportation fuel. Pyrolysis of *A. philoxeroides* was conducted inside a semi batch quartz glass reactor to determine the effect of different operating conditions on the pyrolysis product yield. The thermal pyrolysis of *A. philoxeroides* were performed at a temperature range from 350 to 550 °C at a constant heating rate of 25 °C/min & under nitrogen atmosphere at a flow rate of 0.1 L/min, which yielded a total 40.10 wt.% of bio-oil at 450 °C. Later, some more sets of experiments were also performed to see the effect on pyrolysis product yield with change in operating conditions like varying heating rates (50 °C/min, 75 °C/min & 100 °C/min) and different flow rates of nitrogen (0.2, 0.3, 0.4 & 0.5 L/min). The yield of bio-oil during different heating rate (25, 50, 75 and 100 °C/min) was found to be more (43.15 wt.%) at a constant heating rate of 50 °C/min with 0.2 L/min N₂ gas flow rate and at a fixed pyrolysis temperature of 450 °C. The High Heating Value (HHV) value of bio-oil (8.88 MJ/kg) was very less due to presence of oxygen in the biomass. However, the high heating value of bio-char (20.41 MJ/kg) was more, and has the potential to be used as a solid fuel. The thermal degradation of *A. philoxeroides* was studied in TGA under inert atmosphere. The characterization of bio-oil was done by elemental analyser (CHNS/O analyser), FT-IR, & GC/MS. The char was characterized by elemental analyser (CHNS/O analysis), SEM, BET and FT-IR techniques. The chemical characterization showed that the bio-oil could be used as a transportation fuel if upgraded or blended with other fuels. The bio-oil can also be used as feedstock for different chemicals. The bio-char obtained from *A. philoxeroides* can be used for adsorption purposes because of its high surface area.

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1. Introduction

Our present world relies on energy, obtained from different sources of fossil fuels. Due to vast expanding urbanization in cities throughout the world, reliability on fossils fuels has also plummeted. Hunger for energy needs is depleting fossil fuel sources day by day. With increase in energy demands, rise in petroleum prices and environmental related problems alternative way needs to be implemented. This crisis can only be overcome by the use of biomass, which is the third largest energy source present in today's world. For the production of conventional hydrocarbon transportation fuels, the only renewable source of fixed carbon is biomass [1]. Biomass generally consists of cellulose, hemicellulose, & lignin, which are good source of fuels and chemicals. Biomass can be converted into transportation fuels by two major processes viz. (a) thermo-chemical (combustion, gasification, pyrolysis, liquefaction, hydrogenation, carbonization and torrefaction) and (b) biochemical (anaerobic and aerobic fermentation to produce ethanol, butanol, methanol, etc.). Different structures of biomass decomposed at various temperature ranges. Lignin decomposes at higher temperature range compare to cellulose and hemicellulose, which decomposes at lower temperature range. Hence, lignin gains thermal stability during thermal degradation [2]. Out of these processes

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pyrolysis is more efficient to convert biomass into three different states of matter (solid: char, liquid: bio-oil, gas: Syn-gas). The bio-oil obtained from different biomass via thermo-chemical conversion, consists more than 300 organic compounds. Bio-oil thus obtained from thermo-chemical conversion is a good source of feedstock for different chemical manufacturing, and also has higher energy content compare to biomass, and can be transported easily. Another advantage of bio-oil is that it is cleaner than biomass, since many impurities (minerals and metals) are left in the bio-char after pyrolysis [3]. The bio-oil can be upgraded to refined fuels, which can be use directly or blended with different petroleum products or use as chemical feedstock [4]. Due to their high viscosity, poor heating value, corrosiveness and instability, their direct use as conventional fuels may present some difficulties [5,6]. The bio-char can also be used as solid fuel or used for other applications such as soil modification, manufacturing of activated carbon and bio-carbon electrodes or used in metallurgical and leisure industries [7–9]. The Syn-gas which is composed of methane, carbon dioxide, hydrogen, carbon monoxide, trace amount of propane and other compounds, can be used to fire boilers for electricity generation or can be used as an alternative to Liquid petroleum gas.

Invasive aquatic weeds possess problem to native flora and fauna. They have capability to absorb all nutrients from wetlands within two weeks and destroy all native plants, causing huge problems [10]. They pose problems by blocking waterways, jamming turbines in hydel power plants, reducing native fish population, inflecting water, providing shelter to disease causing insects, etc. Therefore, they should be destroyed or converted into organic manure and transportation fuels.

There have been many studies on the pyrolysis of different weeds to produce bio-oil and other products. Kittiphop Promdee et al. [11], carried pyrolysis experiments of Manila Grass and water hyacinth in tube furnace reactor in N₂ atmosphere in temperature range of 450–600 °C to study the effect of feeding rate, the control gas flow, the temperatures in reactor and reactor operate on pyrolysis product yields. Nazim Muradov et al., carried the pyrolysis of fast-growing aquatic biomass – Lemna minor (commonly known as duckweed) in a quartz tube reactor purged with argon gas (36–150 ml/min) at temperature range from 400 to 700 °C with the emphasis on the characterization of main products of pyrolysis. During the experiment, it was observed that even at relatively low rates of pyrolysis (at 500 °C) it is possible to obtain in excess of 40 wt.% of bio-oil from dry duckweed. Faster pyrolysis rates would significantly increase the bio-oil yield [12]. Seung-Soo Kim et al.; carried the pyrolysis of Milkweed in a thermo-gravimetric analyser and a bubbling fluidized bed reactor in nitrogen atmosphere at a gas flow rate of 40 ml/min, in a pyrolysis temperature maintained between 425 °C and 550 °C to see the effect of temperature on pyrolysis yield. From the experiment Seung Kim et al. concluded that unlike other lignocellulosic biomass, milkweed has a higher HHV (>30 MJ/kg) and higher density and pH compared to other biomass, and can be easily converted to hydrocarbon fuel [13]. P. Manara et al. carried the pyrolysis of red seaweed residues by means of a thermo-gravimetric analyser and a fast pyrolysis captive sample reactor at a range of 450–650 °C in helium atmosphere. P. Manara found that product yield distribution is a function of the feedstock and the temperature & at medium temperature (550 °C), pyrolysis gives higher oil (reaching values of 70 wt.%) yields and lower char yields.

Alternanthera philoxeroides, (Martius) Grisebach, a South American weed of the family amaranthaceae has also been discovered in Madhya Pradesh, Maharashtra, Assam, Meghalaya, Arunachal Pradesh, Bihar, Haryana, Himachal Pradesh, Karnataka, Kerala, Orissa, Tamil Nadu, Uttarakhand, Uttar Pradesh and West Bengal. Like several other American weeds, these invasive weeds might have reached India along with some packing material during the Second World War. The species was collected for the first time in India near an aerodrome at Calcutta [14]. Alligator weeds have a negative impact on waterways; it reduces oxygen content, light penetration in water also reduces water flow. It also has a negative impact on zoological and botanical habitat such as fish and birds, death of other water plants. It is rather difficult to control and helps in the breeding of mosquitoes. In this study, *A. philoxeroides* was selected as feedstock for bio-fuel production and objectives of the study are as follows:

1. Determine the effect of pyrolysis temperature, sweeping gas flow rates, & heating rates on product yield.
2. Characterization of the liquid product obtained at ideal pyrolysis condition and to investigate whether it can be used as an alternative of fossil fuels or as feedstocks for different chemical manufacturing.
3. Characterization of the bio-char obtained as a result of pyrolysis and find its applicability as a solid fuel.

2. Experimental setup and procedure

2.1. Raw material preparation

The biomass sample (feedstock) used in the study was obtained from Howrah district, West Bengal, India. Prior to use, the biomass was thoroughly washed to remove any foreign materials that came with the plant. The cleaned sample was then sun dried for 7 long days and later dried in a hot air oven at 100 ± 5 °C for 4 h to remove all unbound moisture. The dried sample was then grinded and passed through a screen of 72 B.S. The screened samples were used for the fast pyrolysis process.

2.2. Pyrolysis system

The pyrolysis was carried out in the experimental setup given in Fig. 1. The glass reactor was 12.7 cm in height and has 3 cm of internal diameter. The glass reactor was connected to a fractionating column, having dimension of 30 cm in height and internal diameter of 3 cm. The fractionating column was insulated up to condenser opening to avoid heat loss and pre-condensation. The reactor was heated externally by 800 Watts electric muffle furnace. Temperature within the reactor was measured by a k-type thermocouple attached to an external PID controller. Another PID controller controlled the heating rate and temperature of furnace. The outlet of the reactor was connected to a series of condensers to condense the vapours coming out of the reactor. The condensate was collected in measuring cylinder after the experiment. The yields of the liquid product and chars were determined by weighing. The Syn-gas volume was measured by downwards displacement of water. The compositional analysis of Syn-gas by GC–MS gave out the exact mol %, of the different gases present.

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