Production and Analysis of Pyrolysis Oil (Bio-Oil) From Mahogany Wood

Abstract- This work presents the production and the analysis of pyrolysis oil (Bio-Oil). The pyrolysis oil was obtained from a hard wood chips (Mahogany). A pyrolysis batch type reactor was designed and constructed which was used to carry out the production process of the pyrolysis oil. During the production process, the temperatures at which the yields were obtained were recorded. This was done using a temperature regulator and a thermocouple mounted on the body of the furnace. The major findings of the study includes; the combustible organic compounds found in the pyrolysis oil which makes it an alternative source of fuel, the calorific values, the flashpoint as well as the pour point of the oil. The values of flash point, pour point, gross and net calorific values are 125°C, 4, 21.96MJ/kg and 20.65MJ/kg respectively. Based on these findings, it was observed and recommended that pyrolysis of biomass in the absence of oxygen can greatly contributes to a country's GDP, world's needs for alternate liquid fuels, source of renewable energy and cleaner environment by converting waste wood to pyrolysis oil production which can be used in an internal combustion engine.

Keywords: Alternative Energy, Biomass, Bio-Oil, Calorific Value, Flash point, Mahogany wood, Production process, Pyrolysis Oil, Renewable Energy, Temperature.

1. Introduction

The need for alternative fuels has recently come to the forefront of public interest, thanks to increased awareness in the global warming. The main contributor to global climate change has been carbon dioxide emissions created by burning fossil fuels (Cooper and Alley, 2002). One of the proposed solutions to mitigating global climate change is fuel shifting; supplementing fossil fuels with renewable, carbon-neutral biomass derived fuels (biofuels). Different forms of liquid biofuels are being developed; ethanol, bio-diesel and bio-oil.

This work seek to demonstrate how bio-oil is derived from plant material (biomass) via a thermal decomposition process called fast pyrolysis, and can be extracted from wood; and the chemical composition that makes it serve as a fuel . Despite the name bio-oil, it is not an oil like vegetable oil or petroleum oil because it contains up to 30% water. Bio-oil, unlike ethanol and bio-diesel, is considered a second generation biofuel because the fuel can be made from inedible lignocellulosic plant material using advanced thermochemical processes (UN- Energy, 2007).

Biomass is a vast renewable energy source that can be used to produce heat for home and industrial facilities, generate electricity and make transportation fuels. It is the earliest and now the third largest global source of energy, comprising up to 40% - 50% of energy usage in many developed countries (like USA etc.) and other developing countries that have large agriculture and forest area. As a result, it has the highest potential among other alternative energy options in terms of contributing to modern society's near term energy needs (Bridgwater, 2003). The use of biomass also offers an opportunity to produce carbon neutral energy, helping to mitigate greenhouse gas emissions and the adverse effects of global climate change. Furthermore, localized biomass resources can allow nations to achieve foreign energy independence and strive toward the emissions targets (Bridgwater 2003; Demirbas and Balat, 2006). Currently, it is estimated that 12% of the world's primary energy is supplied by biomass (Demirbas and Balat, 2006) and with the continual consumption of viable fossil fuel reservoirs, policies such as the emissions trading scheme around Europe and the possible future implementation of carbon taxes, the utilization of biomass energy is likely to increase and play a significant role in near term energy markets (Demirbas and Balat, 2006). In order to take advantage of the current infrastructure and energy conversion technologies available for liquid fuels, raw biomass must be converted into a liquid. One thermo-chemical process for doing so is termed fast pyrolysis (Bridgwater 2003) and other forms of conversion processes include biological and physical processes.

Pyrolysis among the biomass energy conversion process has attracted more interest in producing liquid fuel product because of its advantages in storage, transport and versatility in application such as combustion engines, boilers, turbines etc. For the purpose of this work, pyrolysis method was employed to extract bio-oil from wood (Mahogany). Pyrolysis is a thermal decomposition process that occurs in the absence of air with short residence times at intermediate temperatures (400 – 500^{o}C) and with rapid quenching of vapours into a liquid ‘bio-oil’ (Shaddix and Hardesty, 1999). It should be noted that the bio-oil feedstock (biomass) is the main variable affecting the quality (Bridgwater, 2005). Pyrolysis technology has the capability to produce bio-fuel with high fuel-to-feed ratios. The ultimate goal of this technology is to produce high-value bio-oil for competing with and eventually replacing non-renewable fossil fuels. However, the development of advanced technologies is the next challenge for pyrolysis researchers to achieve this target. It is necessary to convert biomass into liquid fuels for direct use in vehicles, trains, ships and aeroplanes to replace petrol and diesel (Demirbas, 2002; Muradov et al., 2008). Further development of pyrolysis technology is ongoing and many research articles have been published on the pyrolysis concept in bio-oil applications in recent times.

Bio-oil is a dark brown, free owing liquid fuel that is derived from plant material (biomass) via a thermal decomposition process called fast pyrolysis. It is a multicomponent mixture composed of various molecules that are created by the pyrolysis of cellulose, hemicellulose, and lignin. Bio-oil is most suitable as a “drop-in” replacement for heat and power applications. Biomass from wood residues is fed into a reactor where it is rapidly heated into a vapour. The resulting biomass vapour passes into a cyclone where solid particles (char) are removed. The vapour then enters a quench tower or condenser where it is quickly cooled into bio-oil.

Non-condensable gases are either returned to the reactor to maintain process heating or exported for other uses. This process produces three products: bio-oil (60 - 75 %wt), char (15 - 20 %wt) and non-condensable gases (10 - 20 %wt). Reactor is a thermal apparatus or vessel use for controlling the reaction process. There are number of reactor designs that can be employed and are capable of achieving the heat transfer requirements noted above. They include: Fluidized beds, both bubbling and circulating; Ablative (biomass particle moves across hot surface like butter on a hot skillet); Vacuum; Transported beds without a carrier gas. Of these designs, the fluidized and transported beds appear to have gained acceptance as the designs of choice for being reliable thermal reaction devices capable of producing bio-oil in high yields.

The presence of water in bio-oil which lowers the heating value, viscosity, flame temperature, combustion rate makes its application in power generation and engine use low demanding in many countries. In general, bio-oil will separate into two distinct phases (aqueous and non-aqueous) if the bio-oil contains more than 30 %wt water (Oasmaa and Czernik, 1999). Research is currently being performed to reduce water content of bio-oil by drying the feedstock prior to pyrolysis (Wang, et al, 2008). Furthermore, availability of raw material through which the bio-oil would be obtained is another major concern in the production of bio-oil when this raw material (wood) is not readily available due to deforestation which has been a big challenge threatening global warming.

Pollutant emissions are a direct consequence of combustion and have been receiving increased public attention due to their impact on health and environment. Consequently, combustion devices must be optimized to reduce these pollutant emissions. The primary pollutant emissions that are typically exhausted from combustion devices using low sulphur content fuels like bio-oil include CO, NO_x etc.

The aim of this project is to produce and analyze the chemical components of bio-oil from mahogany wood; to design and construct a simple pyrolysis reactor; to produce bio-oil by pyrolysis, and to analyse the pyrolysis oil (bio-oil) to determine its chemical composition that enables it to serve as a fuel. The impact of bio-oil production and potential benefits to the environment and local economy add to its attractiveness. By providing a market for local forestry products and by locating in proximity to the state’s timber base, a bio-oil plant could be a significant contributor to rural economic development. Furthermore, because bio-oil is produced from a renewable feedstock, it is considered by many to be carbon-neutral, and does not contribute to greenhouse gas emissions. This may make it possible for a bio-oil production facility, or a facility using bio-oil to generate electricity, to participate in certain programs designed to encourage renewable energy generation, or to receive financial incentives for reducing atmospheric emissions of carbon.

2. Materials and Methods

2.1. Reactor Design

System Components: The essential components of pyrolysis system have been identified. The pyrolysis reactor is designed for pyrolysis of waste materials like biomass, agricultural wastes, scrap tyres etc. The reactor employed here is a cylindrical, batch type. The top side of reactor can be open for feeding the raw material and solid residue (char) can be removed at the end of the experiment. The temperature inside the reactor is measured by using thermocouple. During the reaction, the top side is kept closed by a cover plate tightly secured to the system. This prevents ingression of atmospheric air into the reactor, thereby achieving pyrolysis conditions. The pyrolyser is provided with a clay mixed with bentonite insulation in between the thickness of the wall to prevent the heat loss to the surrounding. An exit pipe at the side carries away the evolved gases during pyrolysis.

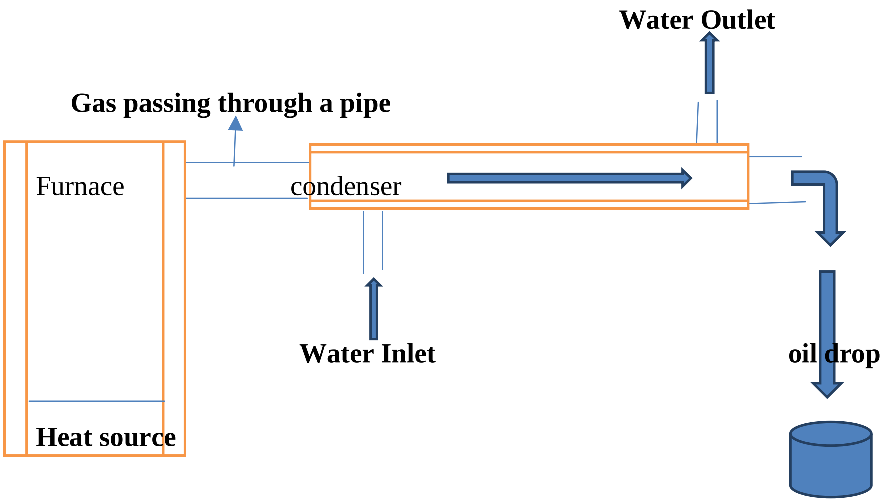


Figure 1: Schematic diagram of a pyrolysis plant

2.2. Condenser

A condenser is provided for condensation of volatile gases which is then known as bio-oil or Pyrolytic oil. Hot gases passed through the inside tube of condenser and condensed with the help circulation of cold water surrounding the tube.

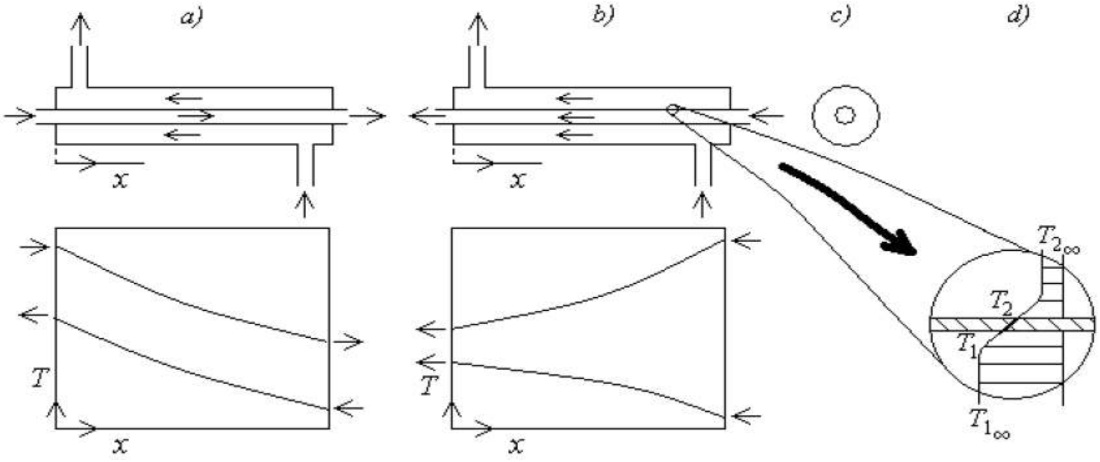


Fig. 2: Schematic diagram of a Condenser

2.3. Instrumentation

The instrumentation panel consists of a fuse unit, on-off switch, and thermometer. The temperature of the pyrolysis is measured by a thermocouple connected to a temperature indicator of 1°C accuracy. The time is measured by a digital timer of 0.01 second accuracy. The weight of input feedstock and residue after pyrolysis are measured by a weighing balance of 1g accuracy.

Table 1: Design Specifications

S/N	Components	Specifications
1.	Furnace outer dimensions	240mm x 400mm
2.	Furnace inner dimensions	230mm x 400mm
3.	Pipe size through which the hot gas passes	20mm x 250mm
4.	Condenser	20mm x 26mm
5.	Length of condenser exit to oil collector	50mm
6.	Height of the heater from furnace	9mm
7.	Length of condenser	500mm
8.	Electrical heater capacity	1.8kW
9.	Feedstock	1kg
10.	Required time for 1kg	120minutes
11.	Temperature	350 – 460^{o}C

2.3. Experimental Setup

The pyrolysis setup used in this experiment is shown in Fig.3. It consists of a batch reactor made of mild steel sealed at one end. The reactor is heated internally by an electric heater, with the temperature being measured by a Cr-Al: K type thermocouple fixed inside the reactor, and temperature is controlled by an external PID controller. 1kg of wood sample were loaded in each pyrolysis reaction. The condensable liquid products were collected through the condenser and weighed. After pyrolysis, the solid residue left inside the reactor was removed. Reactions were carried out at different temperatures ranging from 350 – 460ºC.

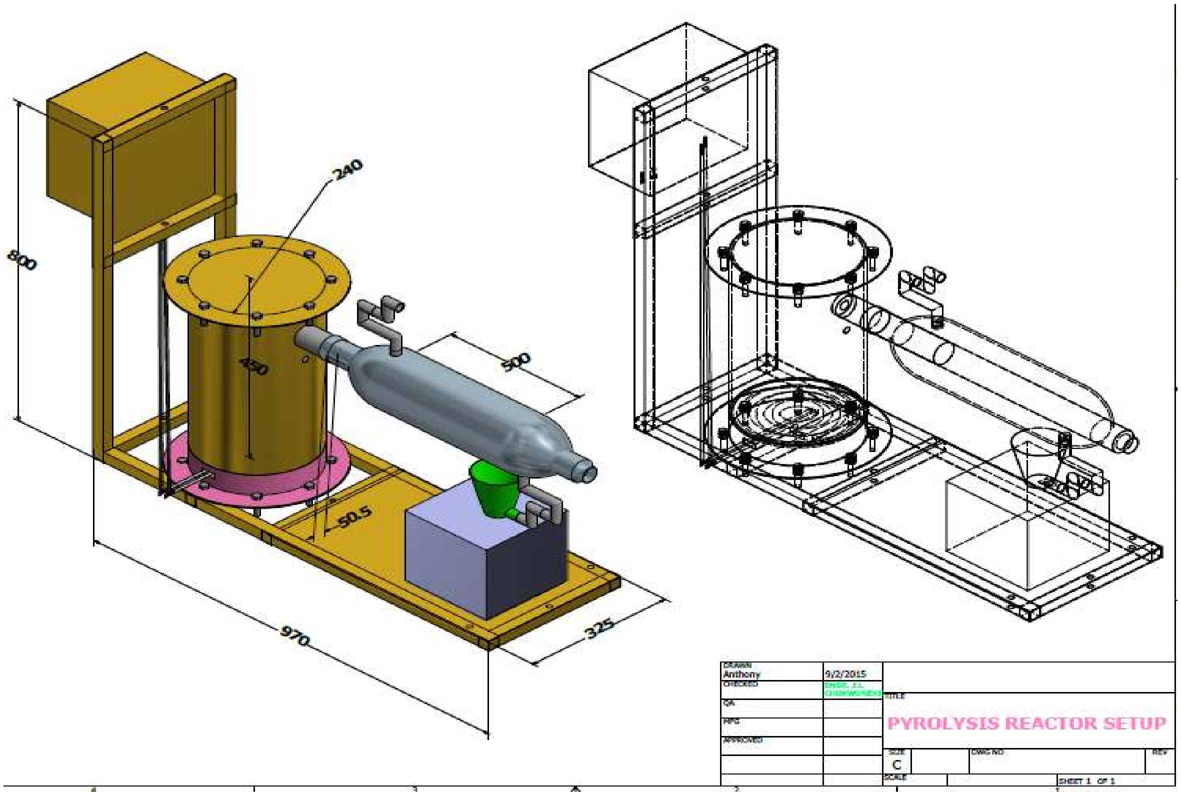


Fig 3: Designed pyrolysis setup.

The experiments were conducted by maintaining the pyrolysis reactor under various conditions. Different temperature conditions and heating rate are required for different feed and types of pyrolysis. For slow pyrolysis temperature requirement is 250 to 500^{o}C and heating rate is about 10 – 20^{o}C/min. The reactor designed in this work is essentially batch operated. Generally, the most important controlled process variables to be considered during start-up include: pressure and temperature. Start-up burner will be supplied to heat the reactor walls initially. The reactor vessel during start-up will not be pressurized. However, during the course of heat distribution the reactor walls via the start-up burner, gradual pressure will be added into the vacuum. The reactor process vessel will be inserted before supplying heat via the start-up burner. This will be necessary to provide conditions adequate and necessary for the pyrolysis reaction to occur efficiently without disturbances.

2.4. Design Calculations

The volume flow rate of the product gas from a desired net heating value is found by:

$$V = Q \div LHV \qquad 1$$

For the reason that the volume of gases change with temperature or pressure, it is necessary to specify the temperature and pressure the flow rate was measured at. However, Eq. 1 assumes standard conditions of temperature and pressure (i.e. 1 atmosphere and 0 – 20^{o}C).

Most pyrolytic reactions are predominantly endothermic. This Implies heat must be supplied to the reactor for these reactions to take place at the designed temperature. The amount of external heat supplied to the reactor depends on the heat requirements of the endothermic reactions as well as the pyrolysis temperature. The general energy balance equation is given by:

$$Q = m \times C_p \times \Delta T \qquad 2$$

The first step of this mass balance involves resolving the heat energy content of wood supplied to the reactor. For the constant-pressure reaction, the enthalpy of the product is equal to the sum of the reactant enthalpies and any heat transfer to the system. That is;

$$H_p = H_r + Q \tag{3}$$

This is basically the measure of time that wood particles will remain in the reactor until they are converted into products and ejected. Anticipated residence time for 1kg of feedstock is between 110-150minutes.

3. Results and Analysis

Table 2: Results of the Characteristics Pyrolysis Oil from Mahogany.

Proximate analysis	**Value**
Flash point ^{0}C	125
Pour point ^{0}C	4
Gross calorific value (HHV) (MJ/Kg)	21.96
Net calorific value (LHV) (MJ/Kg)	20.65
Ultimate analysis (w %)	**Value**
Carbon	52
Hydrogen	6
Ash	0.03
Oxygen	38
Nitrogen	0.3

The flash point of the pyrolysis oil indicates the lowest temperature at which the pyrolysis oil can form an ignitable mixture in air near the surface of the oil. To determine this, 10ml volume of the pyrolysis oil was poured into an evaporating dish and a thermometer was suspended at the centre of the dish ensuring that the bulb just dips inside the oil without touching the bottom of the dish. The temperature of the oil gradually rises using an electric stove at a temperature of 95^{0}C. The temperature at which the oil sample gives off a bluish smoke continuously is noted as the smoke point and the temperature at which flame was observed is known as the flash point.

Pour point is the temperature at which the pyrolysis oil becomes semi solid and loses its flow characteristics. To determine this 10ml of the oil sample was put in a refrigerator and allow for some time, when flow ability of the oil reduces, the temperature of the oil was taken.

Calorific value: the combustion heat of fuel is the amount of heat produced when the fuel is burned completely. The two heating (gross or high heating value and net or low heating value) are defined. The HHV of the sample was determined by means of the following Institute of Gas Technology (IGT) formula shown in Eq.4.

The amounts of elements (C, H, O, N and Ash) are expressed in mass percentages.

$$HHV\ \left(\frac{kJ}{kg}\right) = 354.68C + 1376.29H - 15.92Ash - 124.69(O + N) + 71.26 \tag{4}$$

The LHV is calculated from the HHV and hydrogen content of the pyrolysis oil by the equation;

$$LHV\left(\frac{J}{g}\right) = HHV\left(\frac{J}{g}\right) - 218.13H\ (w\%) \qquad 5$$

No subtraction of free water has to be made because the water in bio-oil cannot be removed by physical methods as is the case for heavy petroleum fuel oils.

Table 3. Pyrolysis Temperature and Yield.

Pyrolysis temperature (^{0}C)	Yield (w %)
350	42
365	48
380	51
400	56
450	60
460	55

The yield was collected with a beaker at different temperatures and placed on a weighing balance. The weight of yield was taken and its percentage then was determined.

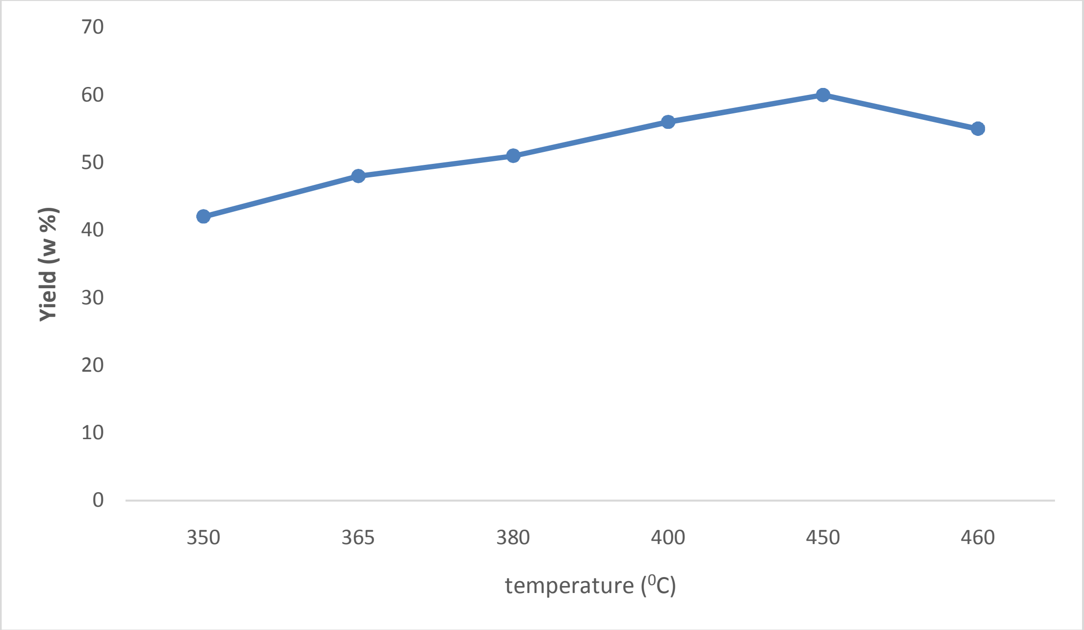
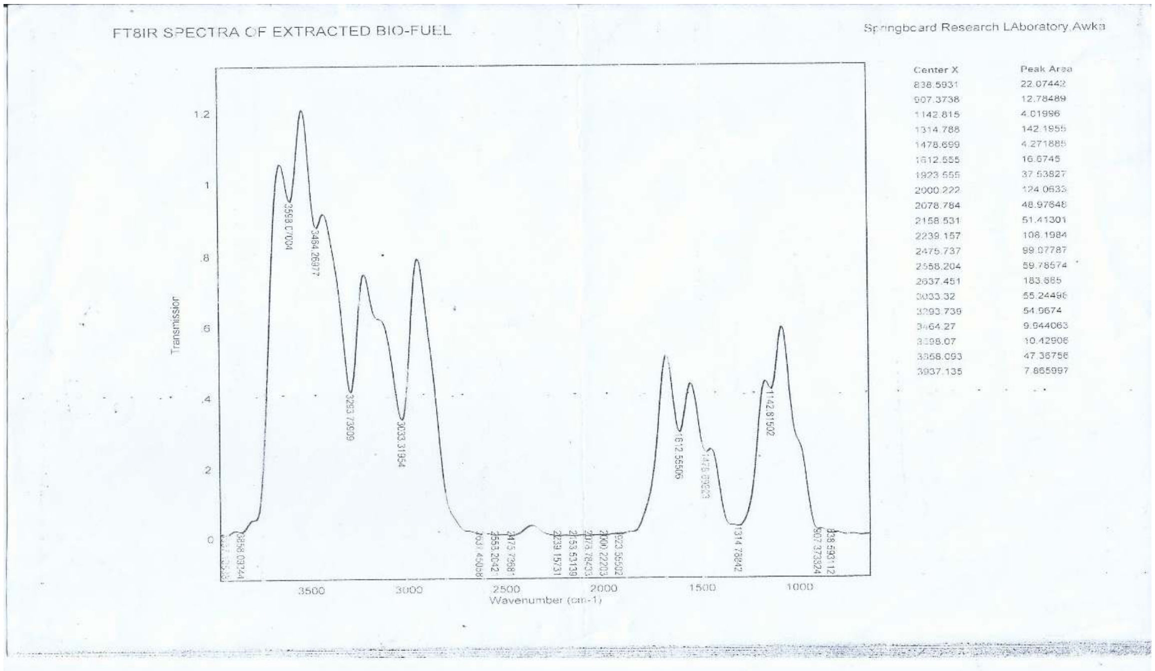


Fig 4: Variation of Pyrolysis Oil Yield and Temperature

From fig. 4, it can be observed that from the origin, at 0^{o}c that no bio-oil was produced, the heat input to the wood was only used for the thermal transformation of the components of the wood namely; cellulose, hemicellulose and lignin. As the temperature approaches 350^{0}c, the first trace of bio-oil was observed. With further increase in the pyrolysis temperature, the percentage of bio-oil yield increased rapidly with its maximum occurring at 450^{0}C. Above 450^{0}c, it was observed that despite the further increase in the pyrolysis temperature, that the bio-oil yield did not improve as expected, rather it started diminishing. The explanation to this is that above 450^{0}c, most of the wood particles must have pyrolysed. The system will eventually get to a temperature at which no bio-oil production will be observed, showing that the pyrolysis process have been completed.



Center X	Peak Area
838.5931	22.07442
907.3738	12.78489
1142.815	4.01996
1314.788	142.1955
1478.699	4.271885
1612.555	16.6745
1923.555	37.53827
2000.222	124.0633
2078.784	48.97648
2158.531	51.41301
2239.157	108.1984
2475.737	99.07787
2558.204	59.78574
2637.451	183.565
3033.32	55.24496
3293.739	54.9674
3464.27	9.944063
3598.07	10.42906
3858.093	47.36756
3937.135	7.865997

Fig 5: FTIR Spectra of Pyrolysis Oil Graph

Table 4: Interpretation of FTIR Spectra of Pyrolysis oil from Mahogany Wood

S/N	Wavelength (cm^{-1})	Functional group	Compounds
1	836.5931	C-CI	Aliphatic chloro compound
2	907.3738	R-0-R	Ether C-0 stretch
3	1142.815	$H_2C=CH$	Vinylidene C=C vibration
4	13214.788	CH_3	Methyl CH stretch
5	1612.555	RNH_3	1^0 amine NH stretch
6	1923.555	R-S-C≡N	Thiocyanate SCN anti-symmetric Stretch
7	2000.222	RC00H	Carboxylic acid C0 stretch
8	2078.784	RC00H	Carboxylic acid C0 stretch
9	2158.531	$H_2C=CH_2$	Ethene CH antisymmetric stretch
10	2239.157	$R_2C=0$	Carbonyl compound C0 stretch
11	2475.737	R-C≡N	Nitriles CN antisymmetric stretch
12	2558.204	CH_2SH	Thiol SH stretch
13	2637.451	CH_2	Methylene CH stretch
14	3033.32	RCH0H	1^0 alcohol 0H stretch
15	3293.739	R_2NH	2^0 amine NH stretch
16	3464.27	R_2CH0H	2^0 alcohol OH stretch
17	3598.07	R_2CH0H	2^0 alcohol OH stretch
18	3858.07	R_3CH0H	3^0 alcohol OH stretch
19	3937.135	R_3CH0H	3^0 alcohol OH stretch

Fourier Transformed Infra-Red (FTIR) Spectroscopy is an excellent tool for functional group analysis and identification of organic compounds. Fourier Transformed Infra-Red (FTIR) spectra of bio-oil extract from Mahogany wood are shown in fig. 5 and table 4. FTIR analysis was employed in the study of the inherent combustible compounds present in the produced pyrolysis oil extracted from Mahogany wood. Combustible hydrocarbons is defined as a compound that will burn or support combustion when mixed with oxygen and ignited to glow. The study reveals that the pyrolysis oil extracted from Mahogany wood were observed to possess 5 combustible hydrocarbons. The medium band at 1612.555cm^{-1}and 3293.739cm^{-1} were thus assigned to NH stretch of amine compounds. The strong band around 3033.32-3937.135cm^{-1} were found to correspond to OH stretching vibration of alcoholic compounds of methanol, ethanol and phenol. The spectra wavelength at 2239.157cm^{-1} were assigned to C=0 stretching vibration of carbonyl combustible hydrocarbon, whereas the peak value at 2158.531cm^{-1} and 2475.737cm^{-1} were assigned to C=C and C≡N anti-symmetric stretching vibration of ethene and nitrile compounds capable of burning.

4. Conclusion

From the analysis of the work, it shows that pyrolysis oil has some combustible compounds which make it an alternate source of fuel. The pyrolysis of biomass in the absence of oxygen can improve a country's GDP if a country ventures into it. The pyrolysis oil discussed herein base on the findings are suitable for an internal combustion engines if fractional distillations are carried out or blended with a fossil fuel like diesel and it is suitable for use in equipment that combusts fuel to generate energy or heat such as boilers, furnace, power generating plant etc..During the production it was observed that the residence time for 1kg of the wood to be converted to pyrolysis oil was measured as 120minutes. To this regard it follows that in an industrial production, a lesser time would be achieved and a high yield can be obtained. Hence, optimization of the reactor and more effort is recommended to improve yield.

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