Production by Pyrolysis and Analysis of Bio-oil from Mahogany Wood (*Genus species*)

Abstract- This work presents the production and the analysis of pyrolysis oil (bio-oil) obtained from a hard wood chips (Mahogany, *Genus species*). A pyrolysis batch type reactor was designed and constructed to carry out the production process of the pyrolysis oil. The yield of mahogany pyrolysis oil was optimized with reaction temperature to produce high quantity of gaseous outputs. Elemental analysis and Fourier transform infrared analysis were carried out. The FTIR analysis revealed the presence of aliphatic and aromatic compounds in the mahogany pyrolysis oil. The physio-chemical properties of mahogany pyrolysis oil were determined. 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 results showed that the flash point, pour point, gross and net calorific values are $125^{o}C$, 4, 21.96MJ/kg and 20.65MJ/kg respectively, at the end of pyrolysis. The maximum liquid yield is 60 wt % at $450^{o}C$. The combustible organic compounds of pyrolysis oil obtained at these optimum process conditions are analyzed for some of their properties as an alternative fuel.

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 (Cooper and Alley, 2002)

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) 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 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. The thermo-chemical process for doing so is termed fast pyrolysis and other forms of conversion processes include biological and physical processes (Bridgwater, 2003).

The pyrolysis the biomass 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, among others (Reference). Pyrolysis is a thermal decomposition process that occurs in the absence of air with short residence times at intermediate temperatures (400 – 500°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). This technology has the capability to produce bio-fuel with high fuel-to-feed ratios for competing 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 and Veziroglu, 2008).

Bio-oil is a liquid dark brown, fuel, derived from plant material (biomass) via a thermal decomposition process called fast pyrolysis. It constituted for a multicomponent mixture composed of various molecules that are produced by the pyrolysis of cellulose, hemicellulose and lignin. Bio-oil is most suitable as a "drop-in" replacement for heat and power applications. Its production is done by treating the biomass in reactor. The biomass from wood residues is fed into a reactor where it is rapidly converted into a vapour. The resulting 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 turning 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) (Ozcimen and Karaosmanoglu, 2014). 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 (Samy and Boateng, 2010). 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).

The reactor is the heart of the pyrolysis process and thermal apparatus or vessel use for controlling the reaction process. This is where the reaction takes place, where biomass is pyrolyzed to pyrolysis gas and char. In the reactor there are high temperatures, up to 1000 °C. The temperature must not fluctuate more than 20% of the intended reactor temperature because it can have effects on the quality of the char. One of the primary functions is to ensure a low oxygen supply at 2%. (Schmidt et al., 2012). There are number of reactor designs that can be employed and are capable of achieving the heat transfer requirements. Fluidized beds; 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 (Hariram and Mohammed, 2014).

A new approach in the heating system was developed to recover the hydrocarbons from waste tire in a fixed bed reactor under inert atmosphere. It was noticed that at 475°C, the pyrolysis reaction yielded optimum liquid/gas at a vapor residence of 5 sec. The physio-chemical analysis includes elemental analysis, gas chromatography mass spectrometry,

Fourier transform infrared analysis and distillation showed the presence of hydrocarbon limonene, short and long chain alkyl, aromatic hydrocarbons in various quantities (Suhanya et al, 2013).

Further development of pyrolysis technology is ongoing and many research articles have been published on the theme in bio-oil applications in recent times. 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. For the purpose of this work, pyrolysis method was employed to extract bio-oil from wood (Mahogany). The resulting bio-oil was characterized for some physical-chemical parameters using Elemental analysis and Fourier transform infrared analysis.

2. MATERIALS AND METHODS

2.1 Reactor Design and Operation

The essential components of pyrolysis process are show in Fig. 1. The pyrolytic reactor (Fig. 2) was designed for waste materials of biomass, agricultural wastes, and scrap tyres, among others. It consists of a batch reactor made of mild steel sealed at one end and constructed for batch operation. The top of reactor can be open for feeding the raw material and solid residue (char) can be removed at the end of the operation. The temperature inside the reactor is measured by using thermocouple. 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. During the reaction, the top is kept closed by a cover plate tightly secured to the system, prevented ingression of atmospheric air into the reactor, thereby achieving pyrolysis conditions. The pyrolyser it has a coating 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. The load used was of 1kg of wood chips sample 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.

Water Outlet

Gas passing through a pipe

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Water Inlet   oil drop
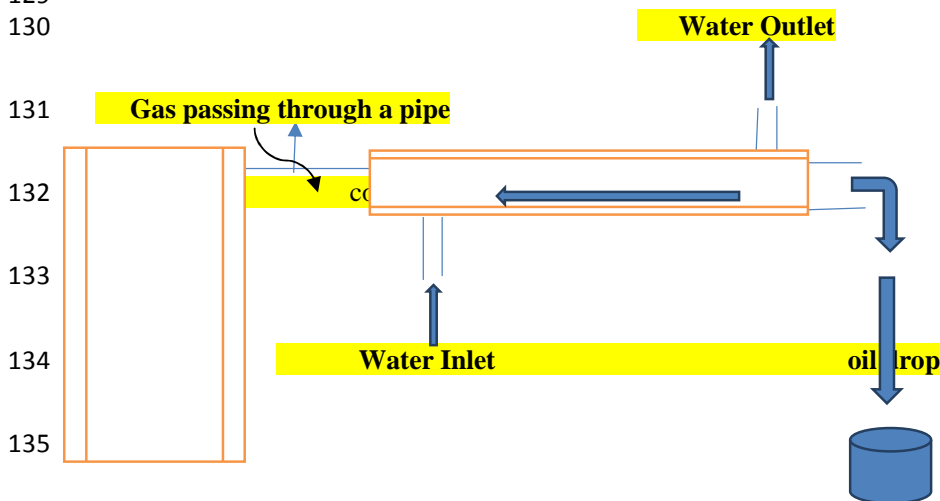
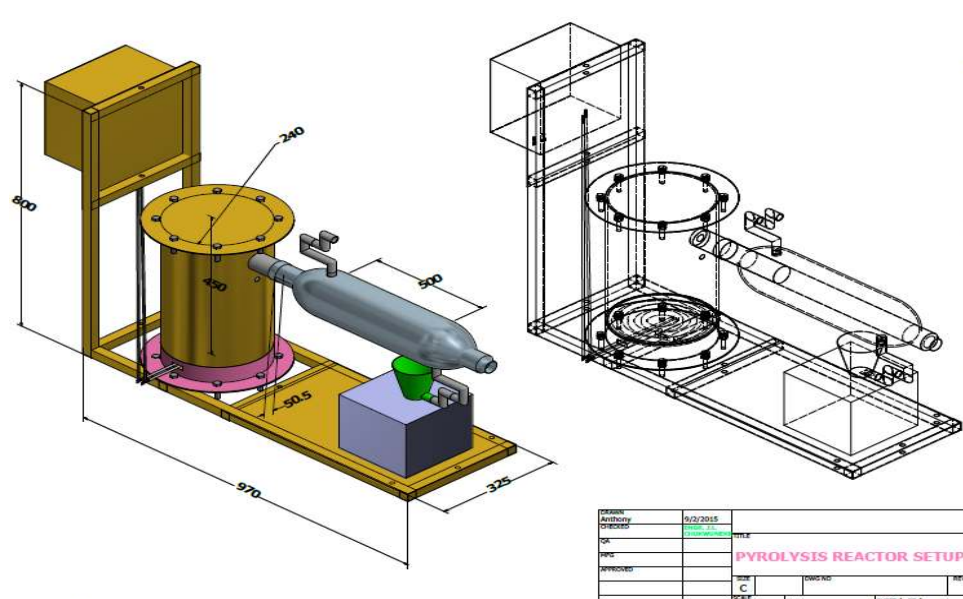**Fig. 1. Schematic diagram of pyrolysis reactor**

138
139 **Fig. 2. Designed pyrolytic reactor setup (dimensions "mm")**

140 The experiments were conducted by maintaining the pyrolysis reactor under various
141 conditions. Different temperature conditions and heating rate are required for different feed
142 and types of pyrolysis. For slow pyrolysis temperature requirement is 250 to 500°C and
143 heating rate is about 10 – 20 ^{o}C/min. Generally, the most important controlled process
144 variables to be considered during start-up include: pressure and temperature. Start-up burner
145 will be supplied to heat the reactor walls initially. The reactor vessel during start-up will not
146 be pressurized. However, during the course of heat distribution the reactor walls via the start-
147 up burner, gradual pressure will be added into the vacuum. The reactor process vessel will be
148 inserted before supplying heat via the start-up burner. This will be necessary to provide
149 conditions adequate and necessary for the pyrolysis reaction to occur efficiently without
150 disturbances. The pyrolytic reactor design specifications are shown in Table 1.

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152

Table 1. Design specifications of pyrolytic reactor

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.	Amount of feedstock by batch	1kg
10.	Required time for 1kg of sample	120minutes
11.	Operating temperature	350 – 460°C

153
154 **2.3 Instrumentation**
155 The instrumentation panel consists of a fuse unit, on-off switch, and thermometer. The
156 temperature of the pyrolysis is measured by a thermocouple connected to a temperature
157 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.

2.4. Design Calculations

The volume flow rate of the product gas from a desired net heating value is found by (Bridgwater, 2005):

$$V = Q \div LHV \qquad\qquad \text{Eq. 1}$$

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) (Bridgwater, 2005).

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 (Bridgwater, 2005).

$$Q = m \times C_p \times \Delta T \qquad\qquad \text{Eq. 2}$$

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 (Bridgwater et al, 2001).

$$H_p = H_r + Q \qquad\qquad \text{Eq. 3}$$

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 (Bridgwater, 2003).

2.5 Analyzes in the bio-oil

Physio-chemical analysis, Elemental analysis and Fourier transform infrared spectrometry analyses were carried out on the mahogany pyrolysis oil to understand its properties and characteristics for its usage in internal combustion engine. Fourier transform infrared spectrometry was used to study the FTIR pattern (Hariram and Mohammed, 2014).

2.5.1 Experimental procedure for flash point

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 (Sipila et al, 1998).

2.5.2 Experimental procedure for pour 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 (Sipila et al, 1998).

2.5.3 Experimental procedure for calorific value

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 (Oasmaa and Kuoppala, 2003). 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.

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

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

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

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 (Oasmaa and Kuoppala, 2003). The bio-oil 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.

3. RESULTS AND DISCUSSION

3.1 Results of physico-chemical parameters for pyrolitic bio-oil

Table 2 shows thermal parameters and chemical composition of the pyrolytic bio-oil obtained from mahogany wood.

Table 2. Results of physico-chemical parameters for pyrolitic bio-oil

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

The elemental analysis was carried out on the mahogany pyrolysis oil to identify the presence of various elements, organic and in-organic materials. It was noticed the mahogany pyrolysis oil contained 52%, 6%, 0.3%, 38% and 0.03% by weight of Carbon, Hydrogen, Nitrogen, Oxygen and in-organic ashes respectively as shown in table 2.

3.2 Results of yield for pyrolitic bio-oil

Table 3 shows pyrolysis temperature and yield of the bio-oil obtained from mahogany wood.

Table 3. Pyrolysis Temperature and Yield

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

In Fig. 3, it can be observed that from the origin, at 0 $^{\circ}$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 has been completed.
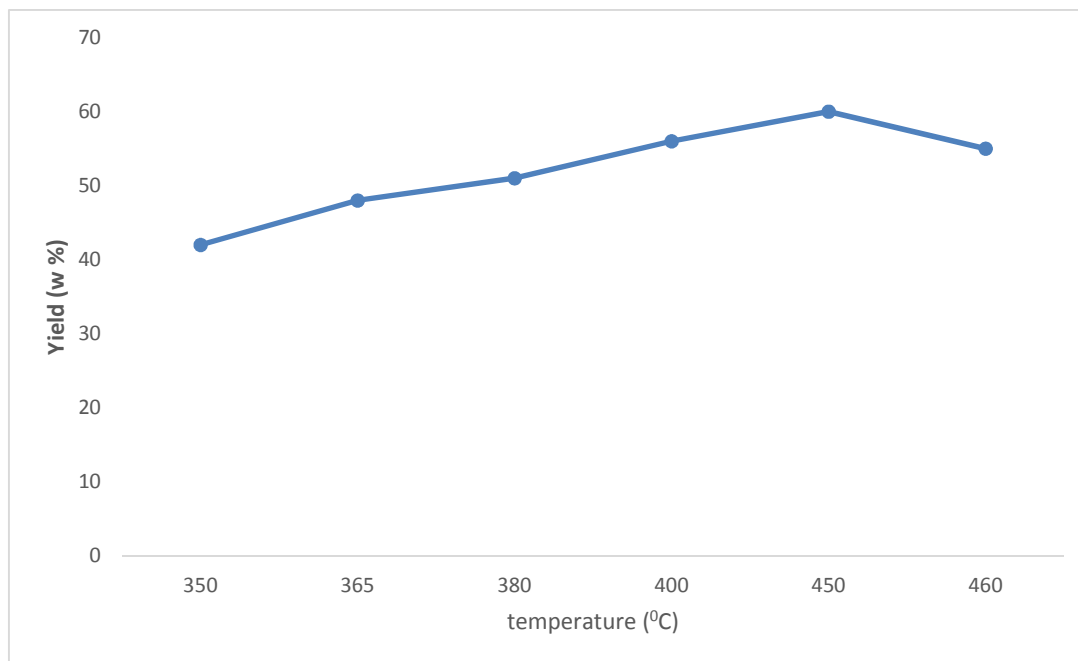
Fig. 3. Variation of pyrolytic bio-oil yield with temperature

3.3 Results of analysis for infrared spectroscopic

Fourier Transformed Infra-Red (FTIR) Spectroscopy is an excellent tool for functional group analysis and identification of organic compounds. The spectrum (FTIR) of bio-oil from Mahogany wood is shown in Fig. 4 and its interpretation in Table 4. The spectrum shows the possibility of five hydrocarbons in chemical composition of bio-oil. 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. Increase the discussion on the outcome of the bio-oil spectrum.
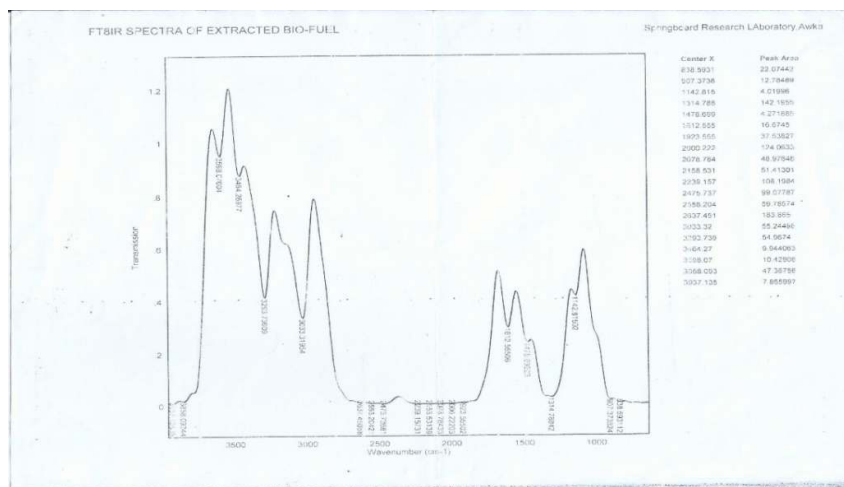
Fig. 4. FTIR spectrum pyrolytic bio-oil of mahogany

Table 4. Interpretation of spectrum (FTIR) 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	$R-S-C\equiv N$	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	$R-C\equiv N$	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

4. CONCLUSION

From the experimental investigation and analysis, the following conclusions were derived: A pyrolysis batch reactor was successfully designed and constructed with the overall yield of mahogany pyrolysis oil was found to be 52%; The maximum yield of bio-oil (above 55%) was obtained under the conditions of pyrolysis at temperature of 450°C; the elemental analysis revealed the presence of Carbon, Hydrogen, Nitrogen and Oxygen, at 52%, 6%, 0.3% and 38% respectively; the FTIR analysis showed evidence of many aliphatic and aromatic compounds; the oil possessed favourable flash point; the heating value of the oil is moderate and has HHV of 21.96MJ/kg. The conclusion of this work is that pyrolysis is a

good alternative source of fuel. Heat production from pyrolysis produce lower emissions including CO, NO_X and smog particles

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