Thermal Pyrolysis of Bicycle Waste Tyre Using Batch Reactor

Debalaxmi Pradhan and R. K. Singh

Abstract—**Recycling of used tyres has been valued by governments of all countries because the pollution caused by these waste tyres has become a rigorous subject in global environmental protection. In the present work, thermal pyrolysis of bicycle waste tyre samples was carried out in a semi batch reactor made up of stainless steel in a temperature range of 450°C to 650°C at a heating rate of 20^0C/min. The optimum liquid yield was obtained at 600°C for the pyrolysis of bicycle tyre at the feed size of 1cm. Effect of heating rate on the mass loss of tyre was examined using the thermo gravimetric analysis profiles (TGA) at a heating rates of 20°C/min. The tyre pyrolysis liquid product has been characterized including fuel properties, proximate analysis, and ultimate analysis, FT-IR, GC-MS. Fuel propertiesand chromatography studies show that it can be used as liquid fuels and chemical feed stocks, with obtained calorific value of 34.61MJ/Kg and empirical formula of $CH_{1.32}N_{0.01}S_{0.02}O_{0.42}$.**

Index Terms—**Pyrolysis, Bicycle Waste tyre, TGA, FT-IR, GC-MS**

I. INTRODUCTION

Now a day's wastes utilization is a major issue to get clean and healthy environment. The production of waste tyres throughout the world is estimated to be 1billion tons tyres per year [1]. The disposal of solid tyre wastes from human activity is a growing environmental problem for the modern society, especially in developing countries. This polymer solid waste is non-biodegradable because of their complex mixture of very different materials, which include several rubbers, carbon black, steel cord and other organic and inorganic components. One of the common ways of disposal is land filling, but land filling of used tyres needs a large space because the volume of tyres cannot be compacted [2]. Different recycling processes are being used such as reclaiming, incineration, retreading, grinding etc. but these different recycling processes have some drawbacks [3]. So there is necessary to find the alternative sources for recycling of these tyre wastes. Recycling of solid waste to a useful product is a sustainable approach for the future aspects. One process which has received considerable recent attention is pyrolysis of the tyre to produce oil, gas, and char which has high potential for the other applications.

Such as derived oil may be used directly as fuels or added to petroleum feed stocks and it may also be an important source for refined chemicals [3, 7, 15].The derived gases are useful as fuel; solid char may be used either as smoke less fuel, carbon black or activated carbon. Much interest is laid in the production of hydrocarbon liquids from waste tyres since the production of liquid product can be a substitute of fossil fuel. Pyrolysis has several advantages which allow the proper utilization of the obtained product. The calorific value of the oil is 42 MJ/Kg and sulphur content is between 0.5 and 1.5 wt% depending on process conditions and therefore the pyrolysis oils may be combusted directly [4]. Several technologies have been studied for tyre pyrolysis including thermogravimetric analysis, according toWilliams and Besler, thermogravimetric analysis of tyre showed two different areas of weight loss representing a lower and higher decomposition. From the study it has been found that Styrene butadiene rubber decomposed mainly at higher temperature of pyrolysis, while natural rubber decomposed at lower temperatures and poly butadiene rubber decomposed in two phases at both higher and lower temperatures [5]. Thus, the thermogravimetric analysis is usually the first approach in the research because of its reliability. Experimental work on Pyrolysis of tyre was carried out by M. Adrin using static-bed batch reactor at temperature between 450°C to 600°C and concluded that the increase in temperature increase the aromatic content of the oil with a consequent decrease in aliphatic content [6]. Paul T. Williams has pyrolyzed the scrap tyre using static batch reactor under N_2 atmospheres and obtained maximum 55% of liquid yield at 600°C [7]. Several studies on Thermal pyrolysis of waste tyre concluded that the pyrolytic oil of scarp tyre contains high concentrations of polycyclic aromatic hydrocarbons such as benzene, toluene and xylene etc. Similarly, the oil has been shown to contain limonene, a valuable product used in industrial applications including formulation of industrial solvents, resins and adhesives, as a dispersing agent for pigments [6, 9]. Extensive research has been carried out on Motor bike car, truck tyre pyrolysis and some of the works are concentrated on producing liquid fuels while others focused on investigating the properties of the activated carbon or carbon black produced.

The present study focus on the thermal pyrolysis of bicycle tyre in a semi-batch reactor at a temperature range of 450°C to 700°C and at a heating rate of 20°C/min. The effect of pyrolytic temperature on reaction time, liquid yield, char formation and volatiles were also studied. The obtained liquid was characterized for different physical and chemical analysis such as TGA, GC-MS, FT-IR.

II. MATERIALS AND METHODS

The material obtained for pyrolysis was bicycle tyre (GRL, RALSON). It was cleaned and cut into approximate size of 1 cm^2. The proximate analysis was done by ASTM D3173-75 method and ultimate analysis was done using

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Elementor CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a method.

III. EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental setup for thermal pyrolysis. Pyrolysis experiments were carried out on bicycle waste tyres from 450-650°C at a heating rate of 20°C/min in a semi batch reactor made up of stainless steel having 16.5cm height, 4.7 cm ID and OD 5.0 cm in diameter. 20gm of waste tyres was taken in the reactor in each run and placed in an electrical heated furnace and the temperature was controlled by PID controller. The vapor from the reactor was condensed in a water cooled condenser and the non-condensable gas vented to atmosphere. The liquid was collected from the outlet of the condenser in a measuring cylinder, weighted and the remaining residue collected after cooling the reactor.

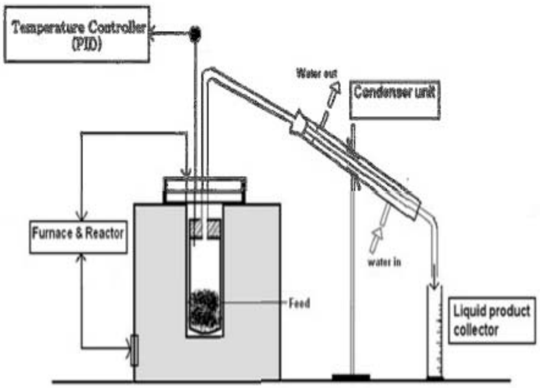

Fig. 1 Experimental Setup

A. *Thermo Gravimetric Analysis*

Thermo gravimetric analysis (TGA) of waste tyres was carried out using TGA/DTG-60 at a rate of 20°C/min in air atmosphere from room temperature up to 600°C to know the decomposition temperature or to find out the range of maximum degradation temperature.

B. *FTIR*

Functional group composition analysis of pyrolytic oil was carried out using Fourier Transform Infrared spectroscopy (FT-IR) analyzer (Perkin Elmer RX) in range 400-4000 $cm^{-1}$with 8 cm^{-1} resolution.

C. *GC/MS*

The composition of oil obtained from tyre pyrolysis was analyzed using gas chromatography/mass spectrometry (GC/MS- QP 2010 SHIMADZU), equipped with flame ionization and mass spectrometry detection (GC-FID-MS). A capillary column coated with a 0.25 µm film of DB-5 with length of 30 m and diameter 0.25 mm was used. The gas chromatography was equipped with a split injector at 200°C with a split ratio of 1:10. Helium gas of 99.95% purity was used as carrier gas at flow rate of 1.51 ml/min. The oven initial temperature was set to 70°C for 2 min and then increased to 300°C at a rate of 10°C/min for 7 min. All the compounds were identified by means of the NIST library. Mass spectrometer was operated at an interface temperature of 240°C with ion source temperature of 200°C of range 40-1000 m/z.

IV. RESULTS AND DISCUSSIONS

A. *Proximate and Ultimate Analysis*

The proximate and ultimate analyses of the bicycle tyre compare to other research work are presented in Table 1. There is a very small variation in case of proximate analysis;Y.M. Chang was found that carbon percentage of present work was more than that of bicycle tyre, which has been characterized in ultimate analysis. This may be due to the variation of rubber component.

TABLE 1 PROXIMATE AND ULTIMATE ANALYSIS OF TYRE

8	Present study	Y.M. Chang[15]
Proximate analysis		
Moisture content	0.55	1.31
volatile matter	62.00	62.32
Ash content	18.73	10.21
Fixed carbon	18.72	26.26
Ultimate analysis		
Carbon (C)	57.38	74.41
Hydrogen (H)	5.50	6.94
Nitrogen (N)	0.67	0.21
Sulphur (S)	3.24	1.60
Oxygen	33.22	5.02
H/C Molar ratio	0.10	---
C/N Molar ratio	86.26	---
Empherical formula	$CH_{1.15}N_{0.01}S_{0.02}O_{0.43}$	
GCV (Mj/Kg)	27.68	33.24

B. *Thermo Gravimetric Analysis*

TGA analysis shows the decomposition behaviors during heating or it is defined as a thermal analysis method which investigates the mass change of sample as a function of temperature and time. From the figure 2, it predicts that two stage weight losses were observed. At initial stage first stage decomposition occur from 250-380°C which may be due to the loss of oils, plasticizers and additives present in the tyre. This is followed by 2nd stage of decomposition treated as active pyrolytic zone from 380-550°C which includes the continuous cracking and rapid decomposition of the other tyre components such as NR, SBR and BR [10]. During the 2nd stage, the intermolecular associations andweaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produced. As a result, the larger molecule decomposes to smaller molecules in the form of gas phase. Then after 550°C the particle contains only fixed carbon and constant weight of ash content. In the same way P. T. Williams was found that the thermal decomposition starts at ~250°C, there follow two major losses of weight during the main devolatalization, and pyrolysis is essentially complete by 550°C above which there is essentially no further weight loss [5].

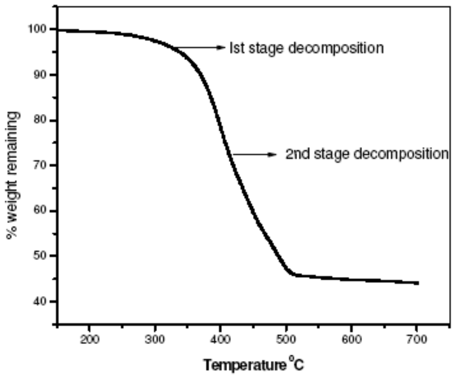

Fig. 2 TGA Curve

C. *Effect of Pyrolysis Temperature on Product Yield*

In general, pyrolysis temperature has a significant effect on product yield of tyre waste. The product distribution obtained from pyrolysis of prepared representative sample for temperature range of 450–700°C at every 50°C elevation in temperature for an average feed size as 1.5cm. The reaction temperature, weight fractions of liquid, char and volatile along with reaction time were plotted together in the Figure 3. Temperature for carrying out the pyrolysis of tyre oil was obtained based on thermogravimetric analysis between 450 to 700°C, in which the significant change in degradation of bicycle tyre sample was noticed. It is evident that the yield of pyrolytic oil increased from 19.65% to 49.6% by weight with increase in temperature at 450-600°C similarly the gas yield also increases with increase in temperature, but at the same time the char yield decreases with increasing temperature. The maximum yield of liquid (49.6%) was achieved at 600°C temperature; it's probably due to strong cracking of tyre rubber as proved by M. Rofiqul et al.[2] and also studied by Cunliffe et al., the increase of oil yield with increasing temperature was due to the secondary reaction [6]. In the temperature range of 550-700°C, the solid yields are almost equivalent to those of the values obtained by TGA of tyre rubber (44.53%) at 550°C presented in Fig. 2. It has also been proved by other researchers [2, 3, 6]. The char yield was more at lower temperature; it may be attributed to the non volatilization of fixed carbon on the other hand similar result has been obtained by M. Cunliffe et al. [6]. Fig. 3 shows that there is lack of influence of temperature in liquids and gas yield over 600°C, which is in accordance with what has been found by other authors [11]. Therefore 600°C seem to be the optimum temperature for recycling tyres by pyrolysis, since decomposition is complete and the same yields are obtained as at higher temperature. It was also observed that with increase in temperature reaction time decreases, because at low temperature the tyre compound takes more time to pyrolyse.

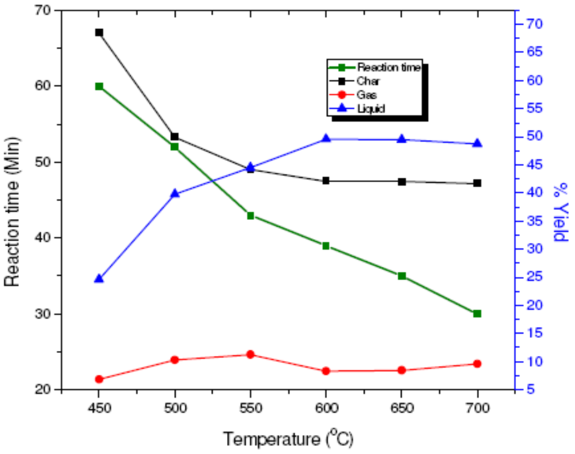

Fig. 3 Effect of temperature on product yield

D. *Characterization of the Liquid Product*

i. *Physical Properties of the oil*

The suitability of the liquid derived from thermal pyrolysis of waste bicycle tyre can be analyzed according to their fuel properties. The following properties were determined by using IS: 1448 methods and summarized in Table 4. It shows that density of the tyre oil was found more than that of diesel and less than that of Motorcycle tyre oil. According to M. Rofiqul et al., low viscosity shows the positive quality in the handling and transporting of the liquid. The obtained flash point was low as compared to diesel and motorcycle tyre. But it was more than that of gasoline.The low flash points of the tire-derived liquids are not surprising since the product liquids represent un-refined liquids with a mixture of components having a wide distillation range [2, 6]. The sulphur content was slightly higher than that of diesel and it is quite similar to light fuel oil. Which is typically about 1.4-1.5 wt% explained by Cunliffe et al. The oil produced consisting of various fraction in the boiling range of 72-362°C which is somewhat similar to diesel. The important requirements for diesel fuel are its ignition quality, viscosity, and water, sediment, and sulfur contents. Therefore, the pyrolytic liquids require preliminary treatments such as decanting, centrifugation, filtration, desulphurization, and hydro treating to be used as fuels. The treated pyrolysis oil could be used directly as fuel oils or blended with diesel fuels, which will reduce the viscosity and, increase the pH value and flash point of the resulting blends. Consequently, the atomization will be improved, ensuring a complete burnout of the fuel [18]. Based on its fuel properties, tire-derived pyrolytic liquids may be considered as a valuable component for use with automotive diesel fuels. Moreover, the liquids may be directly used as fuels for industrial furnaces, power plants, and boilers [2].

ii. *FT-IR analysis of the oil*

The tyre pyrolysis oils were analyzed for their broad chemical properties in the form of their functional group. The functional group was analyzed using Fourier transform infrared spectroscopy analyzer and the chemical composition was characterized by using gas chromatography/mass spectrometry analyzer. The FT-IR is the most appropriate analytical tool to determine saturated, aromatic, and polar components [2]. The Table 2 shows the FT-IR analysis of tyre pyrolytic oil.

TABLE 2 FT-IR ANALYSIS OF OIL

Functional groups	Wavelength range
C-H $_{\text{Stretch}}$	2955.67
C-H $_{\text{Stretch (ALDEHYDE)}}$	2727.11
C=O $_{\text{Stretch}}$	1670.23
C=C$_{\text{Stretch}}$ (ALKANE)+N-H BEND	1644.81
C-H(Phenylring Substitution)	1605.88
C-H BEND (Alkane)	1453.64
C-H BEND (Alkane)	1376.15
C-N$_{\text{Stretch}}$ (Amines)	1310.93
C=O $_{\text{Stretch}}$	1155.10
C-H BEND (Alkene)	964.70
C-H BEND (Alkene) + Phenyl Ring Substitution	814.18

The FT-IR analysis of the oil indicates that the functional group present mainly aromatics groups alkanes, alkenes, ketones and aldehydes, all of which have been identified in the oil derived from pyrolysis of tyres by other researchers [2, 3, 6, 12]. The observation of weak absorption peaks at 964.70 cm-1 and 814-18 cm-1revealed a strong C=H bends and strong C=H bends with phenyl ring substitution. A strong absorption peak in the region of 2955.67 cm-1 and 2727.11reveled that C-H stretching vibration and C-H stretching with aldehyde. So far amines, carboxyl group and C-H bend was also observed with their corresponding wave length.

TABLE 3 GC-MS ANALYSIS OF OIL

S. No.	Area %	Compound	Chemical Formula
1	7.30	1,2-Dimethylbenzene	C_8H_{10}
2	2.40	D-Limonene	$C_{10}H_{16}$
3	4.03	m-Ethylmethyl benzene	C_9H_{12}
4	3.50	(4E,6Z)-2,6-Dimethyl-2,4,6 Octatriene	$C_{10}H_{16}$
5	1.22	(6Z)-2,6-Dimethyl-1,6 Octadiene	$C_{10}H_{18}$
6	2.25	1,2,3 Trimethyl benzene	C_9H_{12}
7	1.75	2,6 Octadiene -2,6-Dimethyl(E)	$C_{10}H_{18}$
8	1.44	Trycyclo[5.2.1.0 1,5] Decane	$C_{10}H17$
9	8.17	1,4- Diethyl benzene	$C_{10}H_{14}$
10	39.54	4-Isoproponyl-1-Metyl-1-cyclohexene	$C_{10}H_{16}$
11	3.46	Benzene,Methyl(1 -Methylene)	$C_{10}H_{12}$
12	0.97	Benzene,(1 -Methylene-2-cyclopropen-1-yl)	$C_{10}H_{10}$
13	0.61	3-Methyllindene	$C_{10}H_{10}$
14	0.65	1-Methyl-3-(1-,ethyl-2-propenyl)benzene	$C_{11}H_{14}$
15	0.88	1-Methyl-4-(1-,methyl-2-propenyl)benzene	$C_{13}H_{18}$
16	0.85	2-Butene, 3-methyl-1-phenyl	$C_{11}H_{14}$
17	2.03	2H-Azepine-2-one, hexahydro	$C_6H_{11}NO$
18	1.53	1,3 Dimethyl-1H-indene	$C_{11}H_{14}$
19	2.10	1,2,3-Trimethyllindene	$C_{12}H_{14}$
20	2.32	Pentobarbital	$C_{11}H_{18}N_2O_3$
21	4.07	1-methyl-4-(1,5 dimethyl-4-hexenylidene)-1-cyclohexene	$C_{15}H_{24}$
22	1.18	(+)-(Z) Longipinane	$C_{15}H_{26}$
23	1.74	Napthalene, 2,3,5 Trimethyl	$C_{13}H_{14}$
24	0.92	Heptadecane	$C_{17}H_{36}$
25	0.63	1,4 dimethyl-7-ethylazulene	$C_{14}H_{16}$
26	1.06	Hexadecanitrile	$C_{16}H_{31}N$
28	1.21	Heptadeanenitrile	$C_{17}H_{33}N$

iii. GC-MS analysis of oil

The objective of studied GC-MS analysis to get an idea of nature and type of compound present in pyrolytic oil.Table 3 summarizes main components with their percentage area were compared to the total area of the chromatogram, which gives an estimate of their relative concentration of the oil. And which shows that the liquid contains mainly complex mixture of many aliphatic and aromatic compounds. Such as alkylated benzenes, alkanes, alkenes, tetra methylbenzene, methyl indene, butene and limonene. Rodriguez et al. reported that tyre pyrolysis oil produced in a fixed-bed reactor at 5000C consisted of 62.4 wt % aromatic compounds, 31.6 wt % aliphatic compounds, 4.2 wt % nitrogen-containing compounds, and 1.8 wt % sulfur-containing compounds [3].The tyre pyrolysis liquids are a very complex mixture, containing many aliphatic and aromatic compounds with their total concentration of 49.54% and 16.65%, respectively [2]. Limonene, one of the major products has wide industrial applications including formulation of industrial solvents, resins and adhesives, as a dispersing agent for pigments, as a fragrance in cleaning products and as an environmentally acceptable solvent [6, 9, 13, 14]. As a summary of the results, it can be mentioned that tyre oils are a very complex mixture of organic compounds of C6-C17 carbons and with a very great proportion of aromatics. The high proportion of aromatics in tyre oils is attributed to recombination reactions that take place among aliphatic and aromatic free radicals and also to cyclation of aliphatic chains [6, 18, 19].

TABLE 4 PHYSICAL PROPERTIES OF THE OI

Fuel Properties	Present work	Diesel	Islam MR[2]
Density (Kg/m^3) at 15^0C	917.9	820-860	957
Kinematic Viscosity at 40^0C in cSt	5.31	2- 4.5	4.75
Flash point	-9^0C	≥55	≤32
Pour point	-87^0C	-40 to -30	-6
Gross Calorific Value (MJ/Kg)	34.61	43.8	42.00
Sulphur content	1.38%	1.2%	…..
Conradson Carbon Residue	0.56%	0.30	…..
Distillation Range	$72-362^0C$	$180- 340^0C$	

V. CONCLUSION

Thermal pyrolysis of bicycle tyre has been pyrolyzed in the batch reactor to determine the tyre source on the yield and composition of pyrolysis products. The maximumliquid yield was obtained (49%) at 600°C temperature with a heating rate of 20°C/min. The effect of temperature on the product distribution shows that at lower temperature, decomposition was incomplete, with increase char yields and decrease in liquid and gas yield and at higher the temperature, secondary cracking reaction takes place thereby an increase in gaseous product is observed. FT-IR study on the pyrolytic oil shows that the oil obtained from pyrolysis of bicycle tyre has same functional groups as compared with oil obtained from tyre fuels as reported in literature. GC-MS analysis revealed pyrolytic oil contains benzene, aromatic and aliphatic compound as major component. The pyrolytic oil obtained has significantly higher calorific value and thus can be used as an alternative to fossil fuel after proper treatment.

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