RECOVERY OF VALUE ADDED CHEMICALS FROM WASTE TYRE PYROLYSIS

Debalaxmi Pradhan[1], R.K. Singh[2*]

[1,2]*Department of Chemical Engineering, National Institute of Technology, Rourkela*

** Corresponding author. Tel: +91 6612462251, E-mail: rksingh@nitrkl.ac.in*

Abstract:

Thermal pyrolysis of waste bicycle tyre samples was carried out in a tubular semi batch reactor made up of stainless steel at temperature range from 450 ºC to 700 ºC. This paper studied the effect of temperature on pyrolysis of waste bicycle tyres to find the optimum temperature of maximum liquid yield. The maximum liquid yield of 49.6% was obtained at a temperature of 600 ºC and a heating rate of 20 ºCmin^{-1}.The thermal degradation temperature of tyre samples was studied using TGA at different rate of heating in air atmosphere. The oil samples obtained at different temperature are analysed according to their fuel properties, elemental analysis and functional group presents.

Keywords:*Thermal pyrolysis, Waste tyre, pyrolytic oil, TGA, FTIR*

Introduction:

Now a day's wastes utilization is a major issue to get clean and healthy environment. Due to increase in population a vast quantity of waste generated from different sources. Plenty of waste generates like bicycle tyre, tubes and from different vehicles but their utilization is zero. Though these wastes are non-biodegradable, becomes a source of pollution to environment. One billion tons of tyres are generated in the world per year, due the vast increase of transportation vehicles like bicycle, motorcycle, cars and buses in the world [1].Different recycling processes are being used such as reclaiming, incineration, retreading, grinding etc. but these recycling processes have some draw backs [2, 10]. Several literatures have given conclusion on production of hydrocarbon liquids from waste tyres by thermal pyrolysis. Pyrolysis experiments on tyre was carried out by Adrin M. et al using static-bed batch reactor at temperature between 450 and 600^{0}C and given conclusion on the effect of temperature have a negative effect on liquid yield. [3]. M. Rofiqul Islam et al have pyrolyzed the motorcycle tyre waste at different feed size (2 cm^3, 4 cm^3, 8 cm^3 and12 cm^3) using fixed-bed fire tube heating reactor and obtained 49% of liquid yield at a temperature of 475^{0}C at feed size of 4 cm^3[4]. Paul T. Williams has pyrolyzed the scarp tyre using static batch reactor under N_2 atmospheres and obtained maximum 55% of liquid yield at 600^{0}C [5]. P. T. Williams has concluded that the pyrolytic oil of scarp tyre contains high concentrations of polycyclic aromatic hydrocarbons. [6] This conclusion is also given by [7]. Waste tyre was pyrolyzed in horizontal oven from 550 to 900^{0}C by [8] and observed that after 550^{o}C there was no effect of temperature on product yield. Hooshang Pakdel has developed the vacuum pyrolysis process for used tyres and got 45% of oil from which 27% of waste naphtha. And the author showed that the mass spectrometry provides superiorquantitative capabilities, while infrared spectroscopy is anexcellent complementary technique for simultaneous qualitative analysis of pyrolytic oil [9].The present work is focused on pyrolysis of bicycle waste tyres using semi batch reactor to know the effect of temperature on oil yield and the oil is characterized according to their fuel properties.

Materials and Methods:

Raw materials:

The raw materials, Indian made (RALSON, GRL) waste tyres were used in experiments with an approximate size of 1-1.5 cm.

Methods:

Thermogravimetric analysis:

Thermogravimetric analysis (TGA) of waste tyres was carried out using TGA/DTG-60 at a rate of heating 5, 10, 15, and 20 ^{0}C/min in air atmosphere from room temperature up to 600^{o}C to know the decomposition temperature or to find out the range of maximum degradation temperature.The liquid was collected from the outlet of the condenser in a measuring cylinder, weighted and the remaining residue collected after cooling the reactor.

Experimental procedure:

Figure 1 show the experimental setup for thermal pyrolysis. Pyrolysis experiments were carried out on bicycle waste tyres from 450-700^{o}C at a rate of heating of 20^{o}C min^{-1} in a semi batch reactor made up of stainless steel having 16.5cm height, 4.7cm 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 vapour from the reactor was condensed in a water cooled condenser andthe non-condensable gas vented to atmosphere.

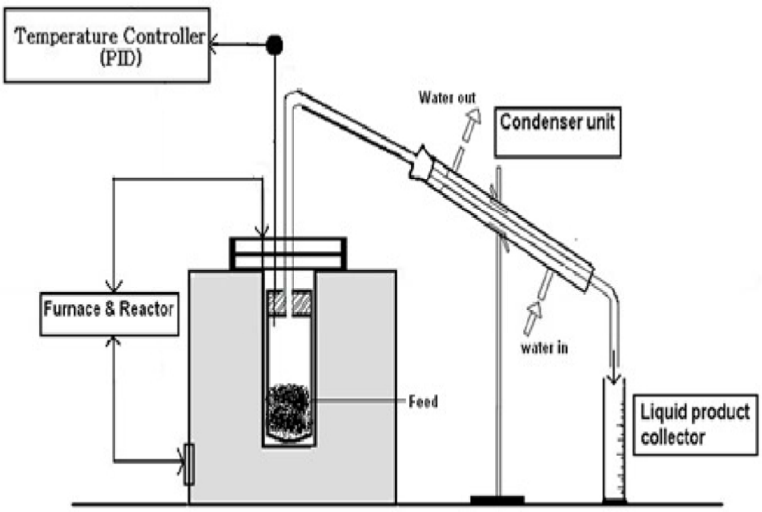

Fig.1: Pyrolysis setup

FTIR analysis of pyrolytic oil:

Fourier Transform Infrared spectroscopy is an important analysis technique which detects various characteristic functional groups present in oil an interaction of an infrared light with oil, chemical bond will stretch, contract, and bend, and as result each functional group tends to absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. Based on this principle functional group present in the pyrolytic oil were identified. The FTIR spectra were collected in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution. The FTIR imaging is carried out using Perkin Elmer RX. By the help of FTIR analysis it is observed that the functional groups present in pyrolytic oil are aromatics and hydrocarbons which have been explained detail in table-3.

Elemental analysis:

The elemental analysis was done by using Elemental CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a.

Results and Discussions:

Characterization of material

Raw materials were characterized according to their proximate analysis and thermal properties. The proximate analysis of waste tyres is given in table 1, which shows that the maximum 62 % volatile material presents in waste tyres with 18.72 % of fixed carbon and remaining ash and moisture.

Table 1 Proximate analysis of tyre

Components	Weight %
Moisture	0.55
Volatility	62
Ash	18.73
Fixed carbon	18.72

Thermogravimetric analysis:

Thermogravimetric analysis of waste tyre was carried out with a thermogravimetric analyzer at heating rates of 5, 10, 15 and 20^{o}C/min in air atmosphere. Three stage weight losses were observed at 10, 15 and 20^{o}C/min rate of heating conditions. But two stage decomposition curves observed at 5^{o}C/min rate of heating. For example, the initial decomposition at 5^{o}C occurred between 34.69 to 221.50^{o}C, that represents a 1.09% weight loss and in rapid decomposition, the 2nd decomposition of the sample occurred between 221.50^{o}C to 600^{o}C representing a 69.12% weight loss with 29.79% of final residue. In this case, 2nd stage decomposition continued till final temperature, may be due to the very slow rate of heating.

So no third stage decomposition has taken place. In case of 10, 15 and 20^{o}C/min rate of heating a three stage weight loss curve was obtained which was observed from figure 2.The detailed % of decomposition in each stage is described in table 2. From table 2; it is clearly visible that at a rate of 20^{o}C/min heating, weight loss was more at 2nd stage in comparison of 10 and 15^{o}C/min rate of heating. So the pyrolysis experiment of waste tyre has done at 20^{o}C/min heating rate. Due to high decomposition rate per unit time, the rapid decomposition zone or 2nd stage of decomposition is treated as active pyrolytic zone. During the 2nd stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produces because the lower temperature. During the 3rd stage with higher temperature chemical bonds are broken and the parent molecular skeletons are destroyed. As a result, the larger molecule decomposes to smaller molecules in the form of gas phase. The TGA of tyre sample at different rate of heating from 5^{o}C to 20^{o}C in air atmosphere shows that the there is a small change in variation of weight loss and it is explained that if the rate of heating increased the pyrolysis process is increased. In all these cases the 1st stage decomposition represents the evaporation of moisture contents or more volatile compounds, 2nd decomposition indicates the formation of volatiles mainly CO and $CO_{2.}$ During the 3rd stage, the pyrolysis residue slowly decomposed, with the weight-loss velocity becoming smaller and smaller and the residue ratio tends to be constant at the end the decomposition of hydrocarbon.

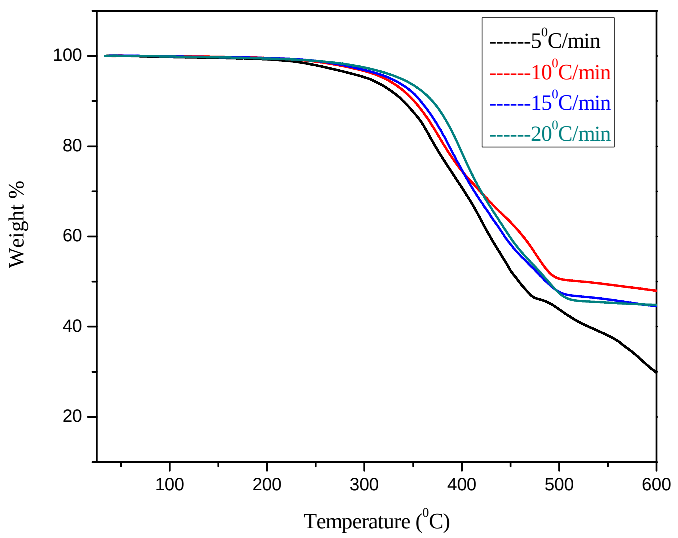

Fig. 2: TGA Thermograph of Tyre

Table 2

Rate of heating °C/min		5	10	15	20
Temperature range (°C)	1st stage	34.69 to 221.50	39.5 to 238	35.82 to 268.61	33.50 to 228.62
	2nd stage	221.50to 600	238to481	268.61to482.82	228.62 to492.07
	3rd stage		481 to600	482 .82to 600	492.07 to600
Weight loss,(%)	1st stage	1.09	1	1.65	0.8
	2nd stage	69.12	44.61	47.56	50
	3rd stage		6.45	6.25	4.37
	Residue	29.78	47.94	44.54	44.83

Effect of temperature on product yield of tyre pyrolysis:

Figure 3 show the influence of temperature on pyrolysis yield. Temperature has a significant effect on pyrolysis product yield means the yield of pyrolytic oil increased with temperature but up to a certain temperature. In this case, the yield of pyrolytic oil increased from 24.64% to 49.6% by weight at 450-600°C and after that it was not in appreciable range. This happens due the formation of more non-condensable gas. At the same time the formation of residue was decreased to 68.5% from 41.65% by weight from 450 to 700°C. At higher temperature pyrolysis the secondary cracking taking place inside the reactor, causes the formation of more gases. So 600°C is the optimum temperature to get pyrolytic oil from waste tyres with a minimum completion time and oil yield. The results are summarised in Table 3.

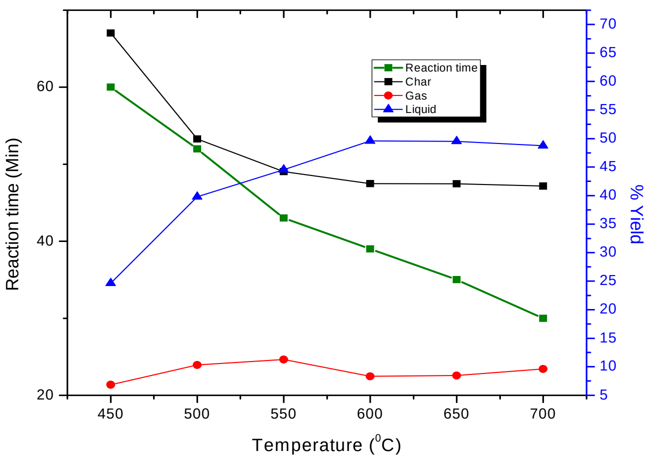

Fig3: Effect of temperature on pyrolysis

Table 3 Product yields of tyre pyrolysis

Temperature (°C)	% Oil	% Char	% Gas	Reaction time (min)
450	24.64	68.5	6.85	60
500	39.8	49.9	10.3	52
550	44.55	44.2	11.25	43
600	49.6	42.1	8.3	39
650	49.5	42.05	8.45	35
700	48.75	41.65	9.6	30

FTIR analysis of Tyre pyrolytic oil:

Figure 4 show the FTIR spectra of tyre pyrolytic oil. FTIR is a fast, cheap, reliable, accurate, and non-destructive method for pyrolytic oil analysis. The FTIR analysis of tyre pyrolytic oil revels that, the functional group present are almost aromatics and hydrocarbons. Table 4 shows the functional groups present in pyrolytic oil analysis with the corresponding wave lengths.

Table 4 Functional present in the tyre pyrolytic 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

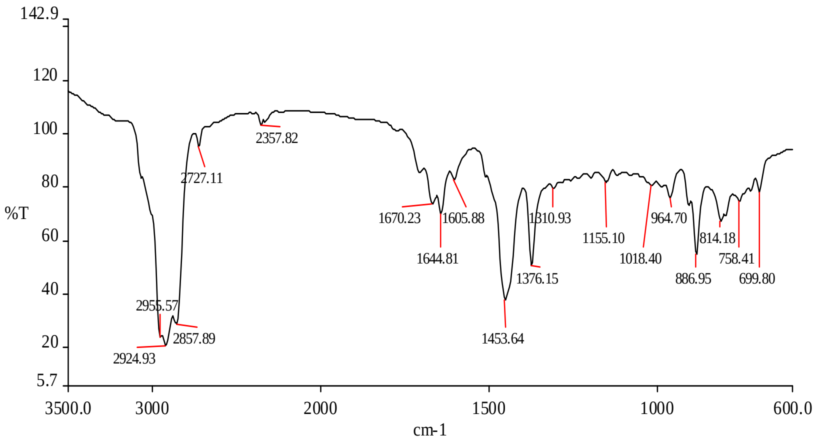

Fig 4: FTIR spectra of tyre pyrolytic oil

Characterisation of tyre pyrolytic oil:

The tyre pyrolytic oil was characterized according to fuel properties and elements present in that. The fuel properties of waste tyre pyrolytic oil like flash point, fire point, pour point, cloud point and density given in table 5 and the elemental analysis (CHNS) of tyre pyrolytic oil is given in table 6.

Table 5: Fuel property of tyre pyrolytic oil

S.No	Characteristic	Value
1	Specific Gravity	0.9181
2	Density @15^{0}C in kg/cc	0.9179
3	Kinematic Viscosity @100^{0}C in Cst	5.31
4	Conradson carbon Residue	0.56
5	Flash Point by Abel method(^{0}C)	-9
6	Fire point(^{0}C)	-4
7	Cloud Point(^{0}C)	-12
8	Pour point(^{0}C)	-87
9	Gross Calorific value in MJ/Kg	34.6
10	Sulphur Content	1.38%
11	Calculated Cetane Index	28
12	Initial boiling point(^{0}C)	72
13	Final boiling boiling point(^{0}C)	362

Table 6: Elemental analysis of tyre pyrolytic oil

Element present in tyre oil	Weight (%)
Carbon	57.79
Hydrogen	6.35
Nitrogen	0.86
Sulphur	3.01
Oxygen (O) (By differences)	32.16
H/C Molar ratio	0.11
Empherical formula	$CH_{1.32}\ N_{0.01}\ S_{0.02}\ O_{0.42}$

Conclusion:

Pyrolysis of bicycle tyre was carried out in a semi batch reactor made up of stainless steel. A maximum of 49.6% oil yield was obtained at a heating rate of 20 ^{0}C min^{-1} at 600 ^{0}C. FTIR study on the pyrolytic oil shows that the oil obtained from pyrolysis of tyres have the same functional group in other tyre fuels which has already discussed by other researchers. From the physical property analysis of the tyre pyrolytic oil it has concluded that the calorific value of the tyre pyrolytic oil is in comparable range with refined liquid fuels and thus can be used as an alternative to fossil fuel after proper treatment.

Comparison of tyre pyrolytic oil properties with refined liquid fuels:

Properties	Specific Gravity	Kinematic Viscosity	Flash Point	Pour Point	GCV (MJ/Kg)	IBP (°C)	FBP (°C)	Chemical Formula
Fuels	15°C/15°C	@40°C (cst)	(°C)	(°C)				
Tyre Pyrolytic Oil	0.9181	5.31	-9	-87	34.68	72	362	-
Gasoline	0.72-0.78	-	-43	-40	42-46	27	225	C_4-C_{12}
Diesel	0.82-0.85	2-5.5	53-80	-40 to -1	42-45	172	350	C_8-C_{25}
Bio-Diesel	0.88	4-6	100-170	-3 to 19	37-40	315	350	C_{12}-C_{22}
Heavy Fuel Oil	0.94-0.98	>200	90-180	-	40	-	-	-

References:

1. Bangladesh Bureau of Statistics. Statistical year book of Bangladesh 2004.24th ed. Dhaka:(2005)Government of Peoples Republic of Bangladesh.
2. Rodriguez IM, Laresgoiti MF, Cabrero MA, Torres A, Chomón MJ, Caballero B,(2001). Pyrolysis of scrap tyres. Fuel Processin Technology (72): 9-22.
3. Adrian M.cunliffe, Paul T.Williams,(1998).Composition of oils derived from the batch pyrolysis of tyres. Journal of Analytical and applied Pyrolysis (44): 131-152.
4. Islam M.R, Haniu H, Beg Alam M.R,(2008).Liquid fuels and chemicals from pyrolysis of motorcycle tyre waste Product yields, compositions and related properties. Fuel,(87): 3112–3122.
5. Williams P.T, Besler S, Taylor D.T,(1990).The pyrolysis of scrap automotive tyres,The influence of temperature and heating rate on product composition. Fuel (69): 1474–1482.
6. Williums P.T, Cunliffe A.M,(1998).Composition of oil derived from the batch pyrolysis of tyres. Journal of Analytical And applied Pyrolysis (44): 131-152.
7. Cao Q, Jin L.E, Bao W.R, Lu Y. K,(2008). Factors Influencing the Quality of Pyrolytic Oil from Used Tyres. Energy Sources Part A, (30):833–841.
8. A.M. Fernández, (November 2009) Pyrolysis of Tyre Wastes, 1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy,Madrid, (S01-2):12- 13.
9. Hooshang Pakdel,(1994). Simultaneous gas chromatographic-Fourier transform infrared spectroscopic-mass spectrometric analysis of synthetic fuel derived from used tire vacuum pyrolysis oil, naphtha fraction, Journal ofChromatography A, (683): 203-214.
10. Sharma, V. K., Fortuna, F., Mincarini, M., Berillo, M. and Cornacchia, G., (2000). Disposal of waste tyres for energy recovery and safe environment. Applied Energy (65):381-394.