



Catalytic Pyrolysis of Waste Tires: The Influence of ZSM-Catalyst/Tire Ratio on Product

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In this research, the effect of ZSM-5 zeolite catalyst was investigated in the thermal pyrolysis of catalysis of waste tires in Bangladesh. The tires of bus and trucks were pyrolysed in a fixed bed reactor and the derived pyrolysis gases were passed through a condenser. The main objective of this study was to investigate the effect of ZSM-5 on the composition of pyrolytic waste tires oil. The influences of pyrolysis temperature, catalyst-tires (CT) ratio on the production of the derived products were also investigated. While the catalyst-tire (CT) ratio and the pyrolysis temperature were increased the production of char and oil increased but the production of gas was in decreasing trend. Moreover, the CHNS analysis revealed that the percentage of carbon increased from 86.81% to 88.60% and the percentage of sulfur decreased from 1.325% to 1.064% while the catalyst-tire ratio was increased from 0.1 to 0.15. It was noticed from the GC-MS data that the certain aromatic compounds were a high amount as the catalyst-tire ratio was increased gradually. The presence of toluene and O-xylene in pyrolytic oil of waste tires increased significantly with a 0.15 CT ratio and this pyrolytic oil would be potentially used as chemical feedstock in different industries.

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INTRODUCTION

The large amounts of waste tire are increasing annually in all over the world and their dumping are creating environmental as well as economical problems [1]. Energy crisis and environmental degradation are the most treacherous problems for human being. The energy crisis problem has become a burning question in Bangladesh. Renewable energy resources of Bangladesh can minimize the energy crisis as an alternative energy source [2]. About 20.5 million bicycle/rickshaw tires are disposed every year as scrap in Bangladesh [3]. Therefore, the research in oil production by pyrolysis of waste tires has become a great interest in recent years. The decomposition of waste tires at high temperature ranging from 300 to 600 °C in an inert atmosphere and energy recovery is the basic principle of waste tire pyrolysis. Pyrolysis of waste tires for producing oil fuel is an attractive method to recycle the scrap tires and became a promising research area in the renewable energy research field. The pyrolysis of tires produces oils, chars, gases, and steel cords and all of these products are potential to be recycled. The liquids of tire pyrolysis (a mixture of paraffins, olefins and aromatic compounds) have a high gross calorific value (GCV) around 41–44

MJ/kg; therefore, it would be used as an alternative source of conventional liquid fuels [4-6]. In addition to, the oil contains highly concentrated aromatic compounds such as, benzene, toluene, xylenes and limonene which are being used in different chemical industries [7]. Therefore, catalysts are being used to produce the low concentrated single ring aromatic compounds.

In this study, the effects of CT ratio on the composition of the pyrolytic waste tire oil were investigated. The physical properties of the pyrolytic oil such as density, kinematic viscosity and Gross Calorific Value (GCV) were measured and also compared with the physical properties of conventional oils like diesel and furnace oil. The property of the pyrolytic tire oil was also analyzed by CHNS elemental analysis. In addition, Fourier Transform Infra-Red (FTIR) Spectroscopy and Gas Chromatography (GC) - Mass Spectrometry (MS) were studied to investigate possibility of potential oil exist in waste tires as a chemical feedstock.

MATERIAL AND METHODS

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Raw materials

The scrap tires of buses and trucks were used as feedstock raw materials for the pyrolysis process. These tires were collected from the car garage of bus and trucks. (Ferighat, Khulna, Bangladesh). the scrap tires were cut into small pieces ($1 \times 1 \times 0.75$ cm) or 0.75cm^3 for each feedstock of the pyrolysis process.

Experimental set-up and procedure

The batch type fixed-bed fire tube reactor was used for waste tires pyrolysis process. The length of the reactor feeder was 55 cm, the outer and the inner diameter of the feeder were 17.0 cm and 16.3 cm, respectively. Fig. 1 shows the experimental set-up of the reactor. There were two major components of reactor such as reactor feeder and condenser. The reactor feeder was used for maintaining constant temperature inside the reactor where as the condenser was used for condensing the pyrolytic vapor to liquid [8]. The N_2 gas cylinder was connected to the reactor feeder for ensuring an inert atmosphere in the feeder. About 1.5 kW capacity was maintained by three tube heaters having a 10 mm diameter. A distributor plate was fitted to support the feedstock, which was placed on a 30 mm distance from the bottom of the reactor. Glass wool and asbestos rope were used for the thermal insulation of the reactor chamber.

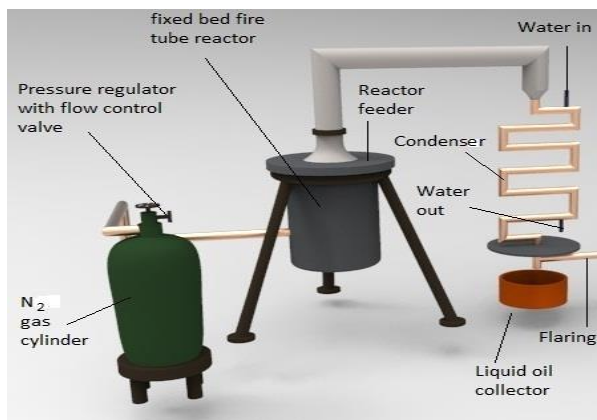


Figure 1. Schematic representation of experimental set-up of reactor

The experiments were performed for waste tires of bus and trucks. The inside temperature of the reactor chamber was recorded by the thermocouple sensors. One kilogram of scrap tire as raw material was fed into the reactor for each experiment and the powder form of ZSM-5 zeolite catalyst was added to the raw material inside the reactor. Before the start up of the experiment, the N_2 gas flow was supplied in the reactor for a few minutes before the experiment. The temperature of the reactor was maintained at 300°C and the temperature was recorded by a temperature recorder. The colorless gas was emitted

from the reactor after the decomposition of raw materials (waste tires). The pyrolytic gaseous product was passed through condenser and the gas was condensed into liquid pyrolytic oil. The experiments were performed with two different CT ratios of 0.1 and 0.15 sequentially. The oil samples were stored in the beakers.

RESULTS AND DISCUSSION

Effect of pyrolysis temperature on product yield

The catalytic pyrolysis of scrap tire was conducted at different temperature ranging from 300°C to 600°C . The authors' previous study of catalytic pyrolysis of waste tire revealed that the liquid production rate increased till to the liquid maximum yield and then the liquid production rate decreased while the pyrolysis temperature was gradually increased [9]. The effect of temperature and catalyst on pyrolysis products of waste tire is shown in Figs. 2 to 4.

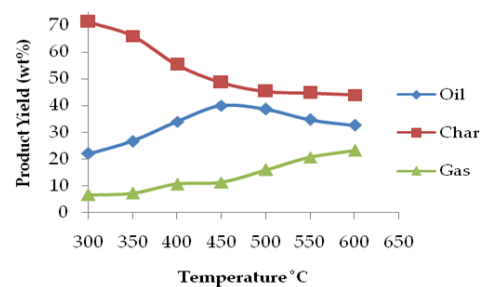


Figure 2. Effect of temperature on product yields for tire pyrolysis (without catalyst)

For waste tire pyrolysis associated without catalyst, the maximum yield of liquid 42.0% (wt) was found at 450°C without catalyst. But the liquid yield has decreased to 32.67 % (wt) at a temperature of 600°C [8].

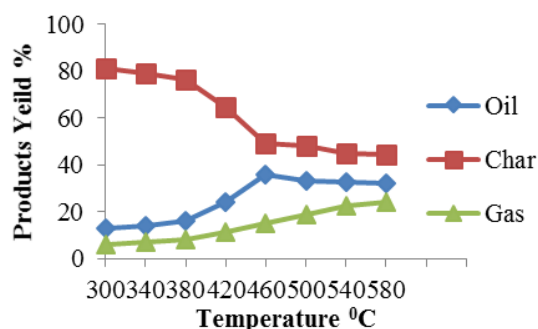


Figure 3. Effect of Catalyst on product yields of tire pyrolysis (CT ratio 0.1)

The maximum oil yield was about 35.83% (wt) at 460°C and the yield decreased to 31.95% (wt) while the temperature was at 580°C with a 0.1 CT ratio.

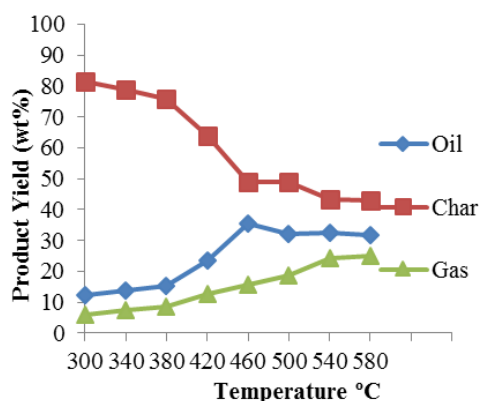


Figure 4. Effect of Catalyst on product yields of tire pyrolysis (CT ratio 0.15)

Fig. 4 shows the similar temperature effect on oil yield at a 0.15 CT ratio. The oil yield was increasing while the pyrolysis temperature was increased. The maximum oil yield was obtained about 35.63% (wt) at 460°C and then the yield decreases to 31.86% (wt) at a temperature of 580°C.

Comparison of pyrolytic liquid properties with other commercial fuels

The properties of pyrolytic oil of waste tire was measured at two different catalyst and tire ratio such as 0.1 and 0.15. The different properties of pyrolytic oil can such as density, kinematic viscosity and Gross calorific value (GCV). Were measured and compared with the properties of conventional diesel and furnace oil (see Table. 1).

Elementary analysis

The elemental analysis of the pyrolytic liquid was carried out at two different CT ratio such as 0.1 and 0.15, respectively. The elemental analysis data are shown in Figs. 5 and 6. The elemental analysis data for two CT ratio of pyrolytic oil samples are summarized in Table 2.

TABLE 1. Properties of Raw Pyrolytic Oil, Catalytic Oil with Conventional Diesel and Furnace Oil.

Physical Properties	Without Catalyst	Present Study Pyrolytic oil with CT ratio 0.1	Present Study Pyrolytic oil with CT ratio 0.15	Literature values [8]	
				Diesel	Furnace oil
Density (kg/m ³), 30°C	935.1	915.84	903.92	820 to 860	890 to 960
Kinematic Viscosity in @40°CSt (centistokes)	6.59	6.35	6.12	3 to 5	45
Gross Calorific Value (MJ/Kg)	37.98	38.27	38.96	42 to 44	42 to 43

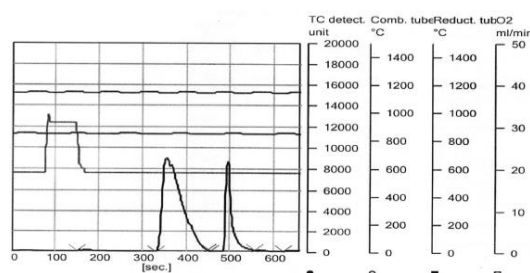


Figure 5. Elemental analysis of the sample with catalyst (CT ratio 0.1)

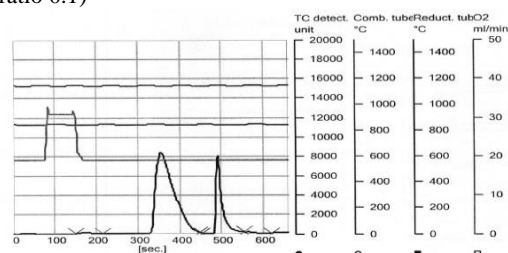


Figure 6. Elemental analysis of the sample with catalyst (CT ratio 0.15)

TABLE 2. Elemental analysis data of pyrolytic oil samples of different CT ratio

Elemental Analysis (wt %)	Catalytic Pyrolysis of Waste Tires with CT ratio 0.1	Catalytic Pyrolysis of Waste Tires with CT ratio 0.15
Carbon	86.81	88.60
Hydrogen	8.258	8.486
Nitrogen	0.00	0.00
Sulphur	1.325	1.064

FTIR spectroscopy data analysis

It was noticed from the results of FTIR analysis that the pyrolytic oil contained the hydrocarbon compounds are quite similar for different CT ratio. While the CT ratio changed from 0.1 to 0.15 the rate of catalytic cracking increased and the aromatic content in the liquid fuel was significantly increased. The presence of aromatic compounds improves the octane number in liquid fuels. FTIR results are given in Table 3.

TABLE 3. FTIR Functional groups data of pyrolytic compounds

Absorbance Range (cm ⁻¹)	Functional Group	Class of Compound	Present Study CT ratio 0.1	Present Study CT ratio 0.15
4400-4670	C-H	Aliphatic	4385-4667	4377-4475
4000-4350	C-H	Aromatic	4007-4065	4065-4329
3670-4000	O-H	Hydroxyl group	3681-3938	3677-3943
2000-2700	C=C, C=N	Alkynes, Aliphatic Nitrites	2047-2246	2046-2358
1750-2000	C=O	Carboxylic Acid	1802-1939	1795-1991

Gas Chromatography-Mass Spectrometry (GC-MS) analysis

The main products of solid heavy automotives are condensable liquids. It is difficult to quantify the various diversified and numerous components of the pyrolytic oil samples. GC/MS analysis is a very efficient quantification process and this process was carried out with the pyrolysis liquids of 0.15 CT ratio. The GC-MS analysis is carried out to investigate the nature and the presence of different compounds of the pyrolytic liquid [10]. The results of GC-MS analysis of pyrolytic oil of scrap tire was summarized in Table 4. The GC-MS analysis revealed the presence of chemical compounds, retention time and the percentage area of different compounds were compared to the total area of the chromatogram. This comparison gave the estimation of relative concentration of the pyrolytic liquid compounds. The GC-MS results of tire pyrolysis liquids 0.15 CT ratio showed that the concentrations of toluene, o-xylene, D-limonene, naphthalene was high comparing with other compounds.

TABLE 4. The GC-MS analysis data of 0.15 CT ratio catalytic pyrolysis of waste tire

Peak	Retention Time	Area %	Name of the Compounds
1	3.05	1.69	Pentane, 2,4-dimethyl-2-nitro-
2	3.092	1.08	Oxetane, 2,2,4-trimethyl-
3	3.567	7.55	Toluene
4	3.783	0.70	3-Hexanone
5	5.267	1.46	Ethylbenzene
6	5.442	8.11	o-Xylene
7	5.925	1.46	1,3,5,7-Cyclooctatetraene
8	5.983	1.57	Benzene, 1,3-dimethyl-
9	7.3	1.00	Hydroperoxide, 1-ethylbutyl
10	7.55	0.66	1,2,6-Hexanetriol
11	7.742	2.07	Benzene, 1-ethyl-3-methyl-
12	7.783	1.46	Benzene, 1-ethyl-2-methyl-
13	7.933	0.66	Mesitylene
14	8.308	0.87	.alpha.-Methylstyrene
15	8.642	2.47	Mesitylene
16	8.75	1.00	Benzene, 1-ethenyl-2-methyl-
17	9.475	1.61	Mesitylene
18	9.533	2.05	o-Cymene
19	9.675	4.49	D-Limonene
20	9.875	0.49	Indane
21	10.133	1.06	Benzene, 1-propynyl-
22	11.483	1.10	Benzene, 1-methyl-3-(1-methylethenyl)-
23	12.425	0.50	Benzene, 1,2,3,4-tetramethyl-
24	13.3	1.93	Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
25	13.483	1.73	2-Methylindene
26	14.358	4.80	Naphthalene
27	16.083	0.97	Caprolactam
28	16.333	0.73	1H-Indene, 1,3-dimethyl-
29	16.492	1.07	1H-Indene, 1,3-dimethyl-
30	16.6	0.78	Naphthalene, 1,2-dihydro-3-methyl-
31	17.3	3.86	Naphthalene, 2-methyl-
32	17.683	1.97	Naphthalene, 2-methyl-
33	17.925	0.61	Cyclohexasiloxane, dodecamethyl-
34	18.958	0.76	1H-Indene, 1,1,3-trimethyl-

35	19.05	0.77	Biphenyl
36	19.183	0.60	Trichloroacetic acid, undecyl ester
37	19.333	0.77	Naphthalene, 2-ethyl-
38	19.542	2.48	Naphthalene, 2,6-dimethyl-
39	19.808	1.11	Naphthalene, 1,2-dimethyl-
40	19.867	1.54	Naphthalene, 2,6-dimethyl-
41	20.192	1.67	Quinoline, 2,4-dimethyl-
42	20.767	1.01	Cycloheptasiloxane, tetradecamethyl-
43	20.875	0.83	Acetamide, 2,2-diphenyl-N-(3,3,5-trimethylcyclohexyl)-
44	20.942	1.52	Oxalic acid, monoamide, N-(4-chlorophenyl)-, nonyl ester
45	21.217	0.73	Phenol, 2,5-bis(1,1-dimethylethyl)-
46	21.625	1.69	Naphthalene, 2,3,6-trimethyl-
47	21.908	0.75	Naphthalene, 2,3,6-trimethyl-
48	22.425	0.74	Fluorene
49	22.725	0.50	9H-Fluorene, 9-methyl-
50	23.292	0.57	Cyclooctasiloxane, hexadecamethyl-
51	23.9	0.56	Octadecane, 2,6,10,14-tetramethyl-
52	24.225	0.69	Chamazulene
53	25.058	0.95	Phenanthrene
54	25.208	0.65	Cyclononasiloxane, octadecamethyl-
55	26.375	0.50	Dotriacontane
56	26.442	0.63	Phenanthrene, 4-methyl-
57	26.675	0.53	Phenanthrene, 4-methyl-
58	26.883	0.51	Cyclodecasiloxane, eicosamethyl-
59	28.242	0.72	Heptadecanenitrile
60	30.825	8.20	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)
61	32.358	4.45	Bis(2-ethylhexyl) phthalate

CONCLUSION

The pyrolysis of waste tires with different catalyst-tire ratio such as 0.1 and 0.15 was successfully carried out. The pyrolytic liquid yield was the maximum (35.63%, wt) at 460°C temperature and then decreased gradually while the temperature was increased. While the catalyst-tire ratio was increased from 0.1 to 0.15 the sulfur content has decreased as well as the percentage of carbon content has increased from 86.81% to 88.60%. It was observed that the gross calorific value (GCV) was better with a 0.15 CT ratio than 0.1 CT ratio. Moreover, The FTIR and GC-MS analysis showed that the amount of aliphatic and aromatic compounds was high at a 0.15 CT ratio. The pyrolytic oil of waste tires with a high catalyst-tire (CT) ratio could be recommended as a environment friendly and a potential fuel for its high calorific value, low content of sulfur and the presence of high content of aromatic compounds.

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Persian Abstract

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چکیده

در این مطالعه، تاثیر کاتالیست ZSM-5 بر فرآیند پیرولیز حرارتی ضایعات تایر در بنگلادش مورد مطالعه قرار گرفت. تایرهای اتوبوس و کامیون در یک راکتور بستر ثابت پیرولیز شد و گاز حاصل از یک کندانسور عبور داده شد. هدف اصلی این مطالعه بررسی تاثیر ZSM-5 بر روی ترکیب درصد لاستیک پیرولیز شده است. تاثیر دمای پیرولیز، نسبت کاتالیست به تایر بر روی تولید محصول مشتق شده مورد بررسی قرار گرفت. در حالی که نسبت کاتالیست به تایر و دمای پیرولیز افزایش می یافت، تولید قطران و روغن تولید شده افزایش می یافت. در ادامه آنالیز عنصری انجام شد و در نهایت آنالیز GC-MS انجام شد.
