

Characterization of Upgraded Pyrolytic Oil by Using ZSM-5 Catalyst in Thermal Pyrolysis of Scrap Tire

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Abstract

Relentlessness of energy predicament and environmental degradation are the two most vital problems across the globe; and, hence, are alarming issues. This is true for Bangladesh also. Nowadays recycling of scrap tire has emerged as a solution for minimizing energy crisis in one hand and eradication of environmental pollution on the other hand. In this backdrop, a catalytic pyrolysis experiment has been conducted taking scrap tires which were pyrolysed in a fixed bed reactor at 300-600°C in the presence of ZSM-5 Zeolite. The density, viscosity, calorific value, flash point and pour point of the characterized pyrolytic oil were 915.84 kg/m³, 6.35 cSt, 38.27 MJ/kg, 35°C and -11°C. Moreover, the effect of catalyst on the process of oil extraction and the composition of the pyrolysis oil was also investigated. It is found that, with escalating catalyst/tire ratio and pyrolysis temperature, there occurs decrease in yield of oil and char production and increase in yield of gas.

Keywords: Thermal pyrolysis, Scrap tire, ZSM-5 zeolite, Fixed bed reactor, Pyrolytic oil;

1. Introduction

Energy crisis along with environmental degradation is the main problem that mankind is facing now a days. The standard of living as well as the quality of life of a nation depends on its per capita energy consumption. As a developing country Bangladesh is surely facing scarcity of energy. Her per capita energy consumption as of 2014 stands at 222.22 kgoe (kilograms of oil equivalent), which is much below the world average of 1832 kgoe. Renewable energy sources may be an indigenous source of alternative energy for Bangladesh [1]. As the energy requirement is becoming severe day by day researchers are giving much effort on the potentials of utilizing suitable technologies to recuperate energy and useful by-products from industrial and domestic solid wastes. The disposal of solid tyre wastes from human activity is a growing environmental problem for developing countries. It is estimated that 20.5 million bicycle/rickshaw tires become scrap every year and wait for disposal [2]. Therefore, in recent years there has been an increased interest in production of oil fuel from waste tire by pyrolysis method [3]. This method for energy recovery from organic solid wastes basically involves the decomposition of the wastes at high temperatures (300–600) °C in an inert atmosphere. Pyrolysis of scrap tire can produce oils, chars, and gases. The oil from pyrolysis has the potential to be recycled as well as pyrolytic char can be used as a solid fuel or as a precursor for activated carbon. Roy et. al. [4-6] compared the derived oil from tire pyrolysis with petroleum naphtha; the conclusion was the naphtha from the derived oil had a higher octane number than petroleum naphtha but must be hydrofined and reformed in order to be used as a clean fuel. However, the high concentration of aromatic hydrocarbons [7-8] limited the derived oil from tire pyrolysis to be used as fuel. Since the derived oils contain concentrations of valuable chemicals such as benzene, toluene, xylenes, etc., so they can be extracted from the derived oils and used as chemical feedstocks in the chemical industry [9]. However, their concentrations are not sufficiently high so catalysts are introduced to produce more single ring aromatic compounds. Williams and Brindle [10-11] have conducted some important research in this field by using zeolite USY catalysts to study the influences of pyrolysis temperature and CT ratio on the yields of products and the composition of derived oils. After using catalysts they obtained pyrolytic oil with high concentration of certain single ring aromatic compounds such as benzene, toluene and xylenes. In the present study, the influences of pyrolysis temperature and CT ratio on the yield

and fraction of the derived oils were investigated. The physical properties of the pyrolytic oil viz. density, kinematic viscosity, flash point, pour point and Gross Calorific Value (GCV) are compared with the physical properties of conventional oils like diesel and furnace oil. The property of the derived oil had also been analyzed by Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy and Gas Chromatography (GC) - Mass Spectrometry (MS) for the purpose of potential use as chemical feedstock.

2. Materials and Methods

2.1 Raw Material

The raw materials used as feedstock for the pyrolysis were the waste tire of buses/trucks. The tires were collected from the nearby bus repairing garage at Ferighat, Khulna, Bangladesh. In order to maintain uniformity of the samples of tires, they were chopped cross-section wise as $1.00 \times 1.00 \times 0.75\text{cm} = 0.75\text{cm}^3$.

2.2 Experimental Set-up and Procedure

In present study Batch type fixed-bed pyrolysis reactor was used. The length of main reactor chamber was 56 cm; outer and inner diameter of the chamber was 16.7cm and 16.0 cm respectively. Fig. 1 shows the (3-D) schematic view of the experimental unit which consists of reactor furnace system for maintaining constant temperature inside and condenser for condensing the pyrolytic vapor to liquid [12]. The N_2 gas inlet was connected below of the reactor. Three 10 mm diameter tube heater of a total capacity of 1.5 kW were fixed in equal spacing inside the reactor. The reactor was thermally insulated with glass wool and asbestos rope.

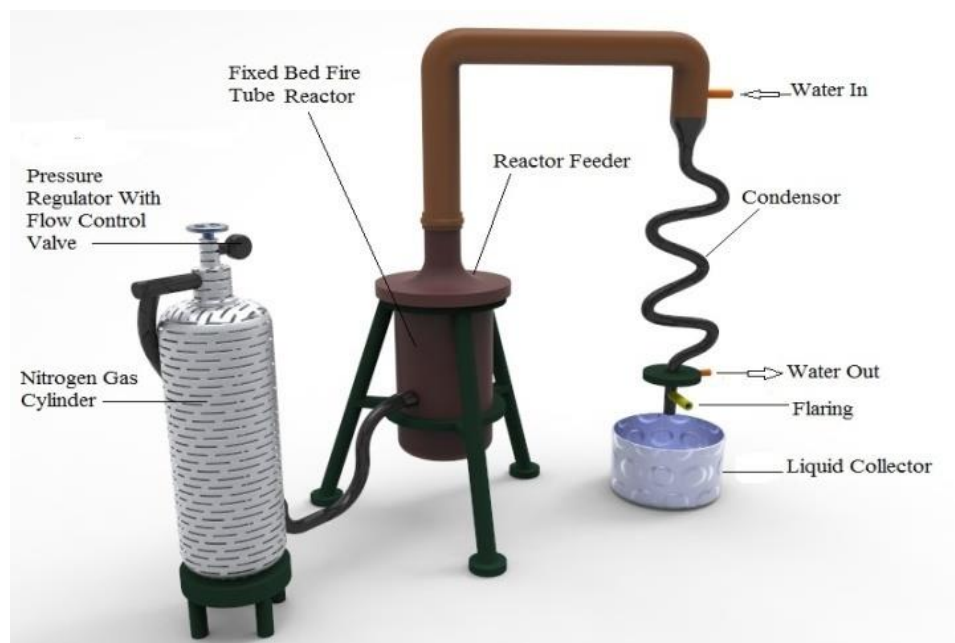


Fig. 1: Schematic diagram (3-D) of Experimental set-up.

The experiments were performed for bus and truck tires. The temperature inside the chamber was recorded by thermocouple sensors and 1 kg raw material was taken in the reactor for each experiment. The catalyst (ZSM-5 zeolite) was taken into reactor after loading feed materials. Before the start of the operation, the reactor was purged by flowing N_2 for 2 minutes to remove the inside air. The reactor heater was switched on and the temperature of the reactor was allowed to rise to a desired value of 300°C indicated by the temperature recorder. After the decomposition of feed materials, colorless gas came out from the reactor. Pyrolytic vapor product was passed through the condenser pipes to condense them into liquid and then collected in the beakers. After cooling down the reactor, the char product was brought out from the chamber. Char was collected and weighed. The liquid was then weighed and gas weight was determined by subtracting the sum of the liquid and char weight from the total weight of feedstock. Initially, the experiments were performed by varying the temperature within the range of $300\text{--}600^\circ\text{C}$ at every 40°C interval for a particular feed size of tire.

3. Result and Discussion

The result and discussion of the present study are described in the subsequent section. Effect of temperature on product yield, comparison of pyrolysis liquid properties with other commercial fuels, FTIR analysis and GC-MS results are analyzed one by one below.

3.1 Effect of temperature on product yield

Under this study of catalytic pyrolysis of waste tire, the experiments were conducted in the temperature range of 300°C to 600°C. In this temperature range thermal cracking of certain hydrocarbons take place. The effect of temperature and catalyst on pyrolysis products of waste tire is shown in fig. 2.

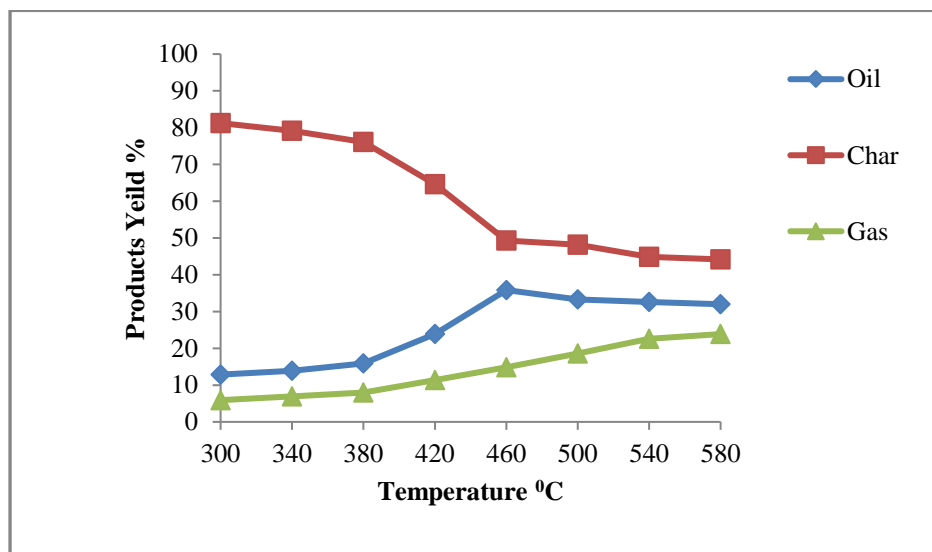


Fig. 2: Effect of Catalyst on product yields for tire pyrolysis (CT ratio 0.1) with feed size 0.75 cm³

Experimental data were collected at every 40°C interval. From fig. 2, it is observed that with the increase in temperature the liquid production rate increases until it reaches a maximum value and then decreases. The maximum oil yield of about 35.83% (by weight) can be obtained from the pyrolysis of waste tire with catalyst. The yield then decreases to 31.95% (by weight) at a temperature of 580°C. At higher temperature maximum yield of liquid was achieved probably due to strong cracking at this temperature. It can be assumed that the decreasing of liquid yield at higher temperatures was due to the rapid increase of gas yield; the char yields at these temperatures were also decreased. Such a result suggests that higher temperature volatilizes some of the solid hydrocarbon content of char and decomposes some oil vapors to permanent gases. S. Hossain et al [13], the pyrolytic oil obtained from pyrolysis of waste tire without catalyst was a maximum value of 42.0% (wt) for sample size of 0.75cm³ and then decreases for larger sample while the char yield increases and gas yield decreases through all the sample sizes from 1.31 to 2.25cm³. The gas yield increases over the whole temperature range to a maximum value of 23.87% at 580°C, while char yield decreases up to 460°C and then remains almost constant. This is probably due to improved cracking of the tire at this temperature and rubber of the tire is not fully decomposed at a temperature less than 460°C. It was also observed that solid yield decreases, liquid and gas yields increases. It is also envisaged that the liquid product yield in catalytic pyrolysis is always lower than of non- catalytic pyrolysis when the catalyst was used in the pyrolysis of waste tires.

3.2 Comparison of Pyrolysis Liquid properties with other commercial fuels

The properties of pyrolytic oil obtained from waste tire pyrolysis using catalyst or without catalyst are very important for judging the quality of the pyrolytic liquid. The properties of pyrolytic oil can be determined by the following tests such as Gross calorific value (GCV), GC-MS, FTIR Spectroscopy. These are briefly described below:

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	Reference with [12]	
			Diesel	Furnace oil
Density (kg/m ³), 30°C	935.1	915.84	820 to 860	890 to 960
Kinematic Viscosity at 40°C (centistokes)	6.59	6.35	3 to 5	45
Flash Point °C	37	35	≥ 55	70
Pour Point °C	-7	-11	-40 to -1	10 to 33
Gross Calorific Value (MJ/Kg)	37.98	38.27	42 to 44	42 to 43

The density of the pyrolytic oil with catalyst has decreased a little when catalyst is used. Which is more favourable compared with diesel and furnace oil. Kinematic viscosity, flash point and pour point have also decreased for pyrolytic oil produced with catalyst. Gross calorific value of the produced pyrolytic oil has increased when catalyst is used.

3.3 Compositional Group Fourier Transform Infra-Red (FTIR) Spectroscopy

From the FTIR analysis it is revealed that the oil obtained from wastes tire mostly the hydrocarbon compounds but in catalytic cracking the aromatic content in the liquid fuel is increased. The effect of aromatic compound in liquid fuel which is increased the cyclic group as well as octane number is also increased. The strong absorbance peaks between 4350-4000 cm⁻¹ represent the aromatic C-H stretching vibration; indicate the presence aromatic compounds. The absorbance peaks between 1800-2000 cm⁻¹ and 2000-2250 cm⁻¹ symbolize the C=O and C≡C vibration respectively which specifies the aldehydes, ketones and alkynes. The FTIR results are shown in Table 2.

Table 2: The FTIR Functional Groups and the Indicated Compound of Pyrolysis

Absorbance Range (cm ⁻¹)	Functional Group	Class of Compound	Without catalyst	Present Study CT ratio 0.1
4670-4400	C-H	Aliphatic	4410-4590	4385-4667
4000-4350	C-H	Aromatic	4000-4250	4007-4328
3680-4000	O-H	Hydroxyl group	3685-3960	3681-3938
2000-2250	C≡C	Alkynes	2030-2237	2047-2246
1800-2000	C=O	Aldehyde, Ketone	1810-1990	1802-1939

3.4 Gas Chromatography-mass spectrometry:

The major products of solid heavy automobiles are condensable liquids. Since the liquids are consists of various diversified and numerous components, it is difficult to quantify them. GC/MS analysis is a very efficient quantification process for this. GC/MS analysis was carried out with the pyrolysis liquids obtained for feed size of 0.75 cm³ with CT ratio of 0.1. The objective of the experiment was to get an idea of the nature and types of compound of such liquids, in order to establish the possible ways of treating and reusing them [14].

Table 3 shows the tentative compounds assigned and their percentage area compared to the total area of the chromatogram, which gives an estimate of their relative concentration in the pyrolytic liquids with catalyst (CT ratio 0.1). It can be seen that tire pyrolysis liquids with catalyst have a higher concentrations of Benzeneacetamide, Cyclopentene, 1-ethenyl-3-methylene, D-Limonene, Naphthalene etc.

Table 3: Tentative GC/MS characterization of catalytic pyrolysis of waste tire (CT Ratio 0.10)

Peak	Ret. Time	Area %	Compounds Name
1	3.042	0.78	Pentane, 2,4-dimethyl-2-nitro-

2	3.558	4.65	Benzeneacetamide
3	5.258	1.83	Ethylbenzene
4	5.442	6.49	Cyclopentene, 1-ethenyl-3-methylene-
5	5.575	0.71	Z-1,6-Undecadiene
6	5.925	1.78	Styrene
7	5.983	1.97	o-Xylene
8	7.75	2.33	Benzene, 1-ethyl-3-methyl-
9	7.792	2.02	Benzene, 1-ethyl-4-methyl-
10	7.933	0.83	Mesitylene
11	8.308	1.28	.alpha.-Methylstyrene
12	8.642	3.05	Mesitylene
13	8.75	1.42	Benzene, 1,1'-(1-ethenyl-1,3-propanediyl)bis-
14	9.475	1.99	Mesitylene
15	9.542	2.33	o-Cymene
16	9.675	4.92	D-Limonene
17	9.875	0.75	Indane
18	10.133	1.72	1H-Indene, 1-chloro-2,3-dihydro-
19	11.483	1.49	Benzene, 1-methyl-3-(1-methylethenyl)-
20	13.3	2.80	Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
21	13.483	2.66	Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
22	14.358	5.55	Naphthalene
23	16.133	2.50	Caprolactam
24	16.333	1.26	1H-Indene, 1,3-dimethyl-
25	16.483	1.48	1H-Indene, 1,3-dimethyl-
26	16.6	1.24	Naphthalene, 1,2-dihydro-3-methyl-
27	17.3	4.96	Naphthalene, 1-methyl-
28	17.683	2.79	Naphthalene, 2-methyl-
29	18.958	0.85	1H-Indene, 1,1,3-trimethyl-
30	19.05	1.32	Biphenyl
31	19.333	1.16	Naphthalene, 1-ethyl-
32	19.533	3.47	Naphthalene, 1,6-dimethyl-
33	19.8	1.42	Naphthalene, 1,3-dimethyl-
34	19.867	1.59	Naphthalene, 2,6-dimethyl-
35	20.192	1.71	Quinoline, 2,4-dimethyl-
36	20.342	0.86	Acenaphthylene
37	20.875	0.70	1,1'-Biphenyl, 4-methyl-
38	20.942	1.28	Heneicosane, 10-methyl-
39	21.217	0.90	Phenol, 2,5-bis(1,1-dimethylethyl)-
40	21.617	1.60	Naphthalene, 2,3,6-trimethyl-
41	21.908	0.84	Naphthalene, 2,3,6-trimethyl-
42	22.325	0.74	1-Hexadecanol
43	22.425	1.26	Fluorene
44	22.617	0.79	1,1'-Biphenyl, 2,4'-dimethyl-
45	22.725	0.98	9H-Fluorene, 9-methyl-
46	22.883	1.56	Diphenylamine
47	24.225	0.77	(2-Methyl-3-biphenyl)yl)methanol
48	25.05	2.09	Phenanthrene
49	25.167	0.68	Phenanthrene
50	26.375	0.65	Phenanthrene, 4-methyl-
51	26.442	1.05	Phenanthrene, 4-methyl-
52	26.675	0.69	Phenanthrene, 4-methyl-
53	28.225	0.80	Fluoranthene
54	28.775	0.78	Fluoranthene
55	30.817	1.89	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)

4. Conclusion

In this study, pyrolysis of waste tire without catalyst and with catalyst was experimented. For with catalyst the catalyst/tire ratio was 0.1. The maximum oil yield of about 35.83.0% (by weight) can be obtained from the pyrolysis

of waste tire with catalyst. The yield then decreases to 31.95% (by weight) at a temperature 580°C. It was also observed that by using catalyst the GCV has slightly decreases. FTIR results shows higher absorbance range as it indicates the presence of aliphatic and aromatic class compounds by the effect of catalyst. From the analysis of the GC-MS the yield of product were containing significant amount of cyclic and aromatic groups. The pyrolytic oil can be suggested as a probable unconventional fuel such as alcohol to commercial diesel as well as rubber based tire waste management toward the safe and healthy environment.

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