

Production, Characterization and Evaluation of Pyrolysis Oil from Tyre Wastes Available in Bangladesh

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Abstract

Globally, scrap tyres are increasing due to the increased number of vehicles. In contrast, in the recent years, alternatives to fossil fuels are exploring to overcome the fossil fuel crisis. In this study, pyrolysis of bicycle and rickshaw tyres wastes was conducted and parametric effects (e.g., the effect of temperature, feed size and apparent vapor residence time etc.) on the pyrolysis product yields were determined. A fixed bed electric heating reactor was used for pyrolysis at 400 - 550 °C, maintaining various particles sizes and a constant heating rate of 20°C/min. The optimum Tyre Pyrolysis Oil (TPO) yield of 42 wt.% was obtained at 500 °C for a sample size of 4.0 cm³. The fuel properties (e.g., density, viscosity, calorific value, flash point, pour point, sulphur content, ash content etc.), functional group studies of the TPO were determined and was compared with the conventional fuel and with international standards. The physico-chemical properties of TPO confirm the use of TPO as furnace oil in various industrial processes. The fractionation of bio-oil gives various value added products including bio-gasoline, bio-kerosene and others chemicals. The commercial implementation of the pyrolysis and follow-up technologies for waste tires processing will allow energetic valorization of waste tyres in Bangladesh.

Key words: Waste Tyre, Pyrolysis Oil, Physico-chemical characteristics, FTIR, Optimum condition

I. Introduction

Every year, over 1.5 billion tons of tyres are manufactured by more than 450 Tyres and Tube Industries around the world¹ and Bangladesh alone produces 120,000 tons annually². Approximately, 20.5 million automobile tyres are scrapped each year in Bangladesh, accounting for approximately 37% of the country's total tyre garbage production³. Waste tyre disposal is a common environmental problem posing potential fire hazards, toxic pollutants like CO₂, CO, SO_x and NO_x emissions during combustion, soil and water pollutions as well as health hazards including upbringing place for disease carrying mosquitoes and other pests³. To overcome the associated problems with waste tyres in an environmentally friendly and cost-effective manner, different approaches including retreating, reclaiming, burning, grinding and so on applied⁴. Tyres are typically made from natural rubber (NR), synthetic rubber (SBR) or butadiene rubber (BR). To produce tyres, various additives e.g., oil, plasticizer etc. are mixed collectively with rubber. Decomposition temperatures ranges at 150 - 350 °C for processing oils, plasticizers and other organic additions, 330 - 400 °C for NR, and 400 - 480 °C for SBR and BR⁵. Previous studies reported that the volatile portion of the tyres entirely disintegrates under 500°C of reactor temperature and the rate of decomposition is highest around 400 °C⁶. Fast pyrolysis, a thermal breakdown process marked by rapid

method for the generation of liquid fuels with a greater yield. Although, fixed bed pyrolysis reactors are not appropriate for large volumes of tyre pyrolysis due to inefficient heat transfer, however, for laboratory scale, it is very commonly used. In lab scale fixed bed pyrolysis, the highest amount of oil yield (60.0 wt.%) was achieved at 425°C which reduced to 54.12 wt.% 500 °C with an escalate in gas yield and a decrease in char yield⁷. Three phases of pyrolysis for tyre waste were defined: i) First stage (150–350 °C), connected to the breakdown of volatile content (e.g., oil, additives, and plasticizer) in rubbers; ii) Second stage (300 – 450 °C), the mass decrement owing to the degradation of NR constituent and iii) Third stage (about 400–500 °C), the deterioration of SBR and/or BR constituents in the tyre⁸. Additionally, tyre pyrolysis is a first-order irreversible and independent reaction, with an activation energy of 147.95 kJ/mol⁹. Ablative pyrolysis, uncommon compared to the other forms, is a technique that may be used to rapidly pyrolyze materials like tyres¹⁰. Lower temperatures partly pyrolyzed the tyre, producing less oil and allowing the maximum amount of solid material to remain as char. On the other hand, higher temperatures promote the gas formation as a result of vapour decomposition towards permanent gases and subsequent re-polymerization as well as carbonization processes converts oil hydrocarbons to char¹². So, the common temperature for high liquid (pyrolytic oil) yield is in between 250 - 450 °C¹¹.

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heating rates, is well known as an efficient transformation

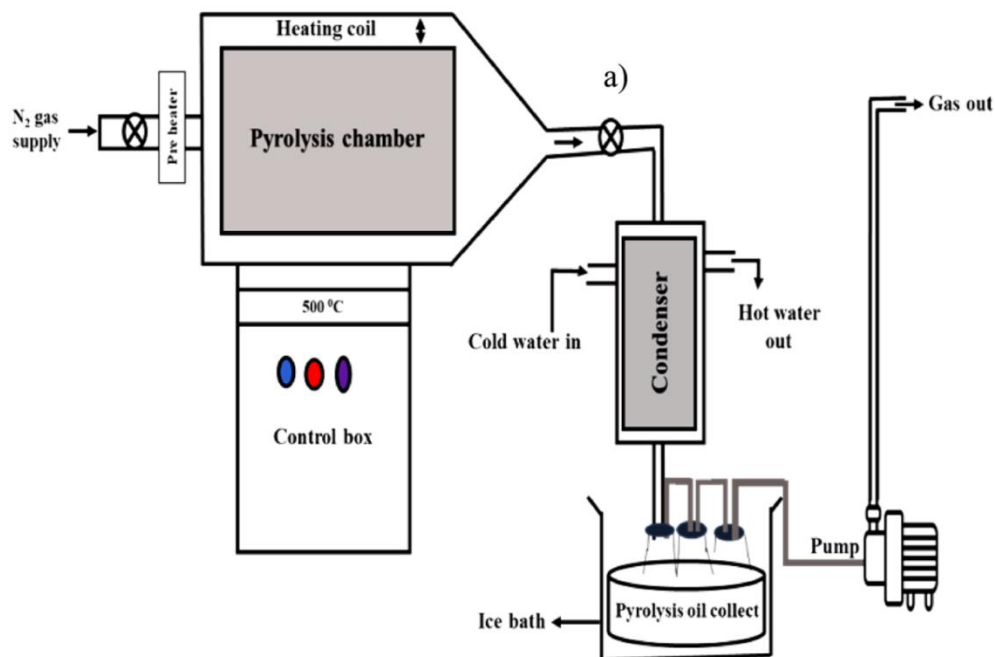


Fig. 1. A schematic view of the experimental setup.

The particles size of crushed waste rubber size/ raw materials plays a vital role in achieving the desired products. The smaller the sample size, the more the reaction surfaces, resulting in a higher heating rate and a rapid disintegration of the waste tyres sample. In addition, the gas phase is benefited from smaller particle size. At 450 °C, the highest liquid yield was reported for a sample size of 0.75 cm³.¹¹ Furthermore, a sample size of 4 cm³ at 500 °C and the vapor holding time of 5 seconds, has a lower chance of subsequent cracking when the temperature of reactor is optimized¹³. Excess pyrolysis time for accomplishing the conversion, resulting in an incomplete depolymerization of the sample, leading to more char and less oil production whereas shorter operating time resulted in higher quantity of oil and lower measure of char¹¹.

This paper aims to pyrolyze the locally available waste tyres from bicycles and rickshaws with a focus to liquid pyrolysis oil / Tyre Pyrolysis Oil (TPO) yield. The optimization of process parameters (operating temperature, reaction time, feed size, heating rate etc.) were explored in this study. The physico-chemical characteristics of the produced TPO were studied and compared with commercial diesels and international standards. The FTIR study of the oil was carried out to identify the functional groups present in the TPO.

II. Materials and Methodology

Collection of waste tyre

Tyre wastes from bicycles and rickshaws was gathered from different disposal sites in Dhaka City Corporation and chopped into three different sizes of 2×1×0.5cm³; 4×2×0.5cm³ and 4×3×0.5cm³. Before placing the samples into the reactor, these were thoroughly cleansed to eliminate any soil or extraneous elements.

Pyrolysis plant and process of pyrolysis

A batch reactor, made of stainless-steel, with a length and inner diameter of 30.0 cm and 3.0 cm, respectively was used for the pyrolysis process. The major components are fixed-bed reactor chamber, the electrical heating elements for maintaining the temperature inside, the water-cooled condensing coil to convert the condensable vapor to pyrolytic liquid, sensor, insulator, a thermal coil, storage tank, valve and gas exit line. Figure-1 illustrates the schematic of tyre pyrolysis process experimental setup.

A 300-500 g sample was loaded manually in each run. Nitrogen gas (N₂) was passed into the reactor for 2 minutes to purge the reactor in order to take away the inside air before pyrolysis started. A steady supply of N₂ gas was maintained to keep the reactor inert and to move the pyrolyzed product from within the reactor to the condenser

and then the condensed liquid was collected in the bottles. Upon completion of pyrolysis, the vapor outlet was shut down and the reactor heater and the N₂ gas supply were turned off. The char product was extracted from the reactor chamber once the system cooled down and weighed.

Physiochemical and Elemental Analysis

The physical (Viscosity index, Density, Flash point, Pour point, Fire point etc.), chemical (Carbon Residue, Ash content) and elemental analysis (Sulphur content) of TPO were carried out using various apparatus according to Petroleum (IP) and American Society for Testing and Materials (ASTM) test methods.

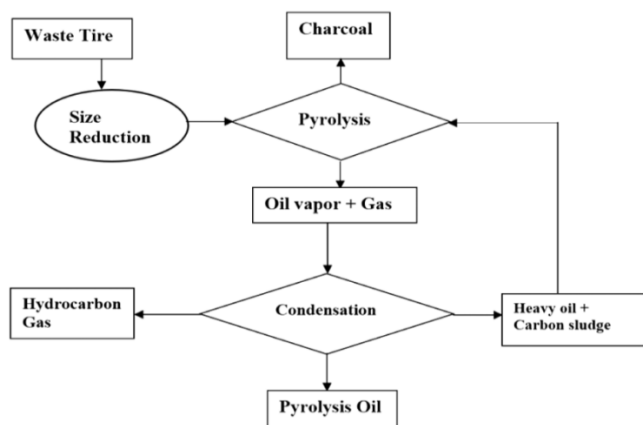


Fig. 2. A schematic diagram of the pyrolysis process

Product formation during pyrolysis

During pyrolysis process, TPO was the primary expected product, whereas char and gas came out as byproducts. Multiple experimental runs were performed with the collected tyre wastes. The possible reaction pathways and yield of products, their chemical constituents during waste tyre pyrolysis process are listed below:

- Tyre rubber → Gas + Oil (Tar) + Char (i)
- Oil (Tar) → hydrocarbons (HCs) + CO + CO₂ + H₂ (ii)
- Heavy HCs → Light HCs + H₂ (iii)
- Gas → H₂ + Light HCs (iv)
- Light HCs → HCs + CO + H₂ (v)
- Char → CO + CO₂ + H₂ + Solid residual material (vi)

III. Results and Discussions

Effect of Temperature on Pyrolysis Product Yield

Table 1 and Figure 3 shows that with the increase of temperature from 400 °C to 550 °C, the yield of gas increased with a subsequent decrease in the yield of liquid. This may be happened owing to vapor decomposition into permanent gases and subsequent repolymerization and carbonization processes of oil hydrocarbons into char¹².

The experiments were conducted by changing the temperature between the span of 400– 600°C for different feed sizes of the raw materials. A simplified flow diagram of the pyrolysis process of waste tyres is shown in Figure-2.

Table 1. Pyrolysis product mass balance with different temperature

Temperature (°C)	Pyrolysis Gas (wt.%)	Pyrolysis Oil (wt.%)	Char (wt.%)
400	7	34	59
450	11	41	48
500	14	42	44
550	20	38	43

Figure 3 also indicates that pyrolysis of waste tyre was not completed at a temperature below 450 °C. With the increase of pyrolysis temperature, liquid and gas yields increased, whereas solid yields dropped most likely due to the complete decomposition of rubber at high temperature. At lower temperatures, the waste tyre was partly pyrolyzed to generate less oil and vaporized with maximal retention of substance in solid structure as char, according to the findings. Until a temperature of 500 °C, the thermal degradation of the tyre rubber rises (*i.e.* solid yield drops) and consequently increases liquid and gas yields.

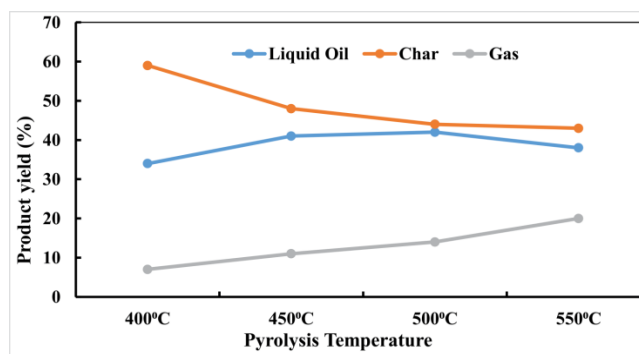


Fig. 3. Effect of temperature on the product yield during pyrolysis of waste tyres

Solid yield, mostly char, may contains carbon black, solid hydrocarbons, and small fraction of tyre rubber constituents e.g., sulfur, zinc, silica, clays, or metal oxides that comprise the solid char. Carbonaceous substances like char and coke were developed during pyrolysis by subsequent re-polymerization of the polymer-derived materials. Beyond 500 °C, the drop in liquid yields and the rise in gas yields were likely owing to the breakdown of certain oil vapors becoming permanent gases and subsequent re-polymerization and carbonization reactions of oil hydrocarbons into char. The char loss processes also contribute to the rise in gas

yields at elevated temperature¹⁴. Considering the above mentioned situations and waste tyre disintegration completion, the liquid yield was highest at temperatures between 450 - 500 °C for pyrolysis of waste tyres.

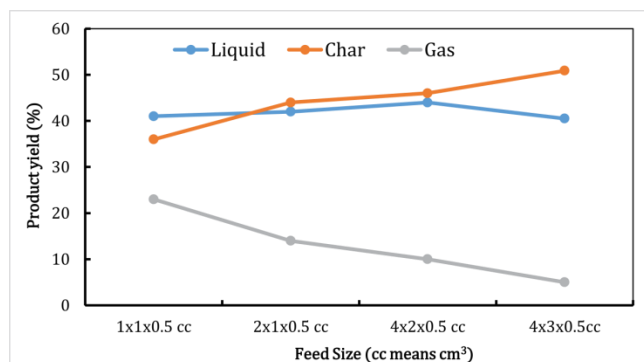


Fig. 4. Effect of waste tyres size on the product yield during pyrolysis at 500°C

Effect of Sample Size on Product Yield from Waste Tyres Pyrolysis

Figure-4 depicts the influence of sample size on the product yield during the pyrolysis of tyres at 500°C. The resulting weight fractions of char, TPO and gas is shown against the sample size. For a sample size of up to 4.0 cm³, TPO yield increased marginally, reaching a maximum of 42.0 wt%, and then decreased with increasing sample size.

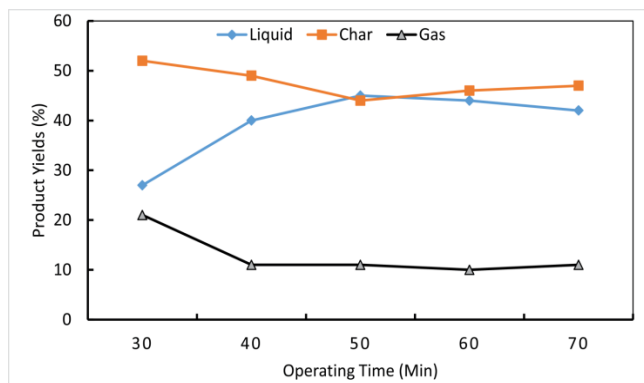


Fig. 5. Effect of operating time on product yield at 500°C of pyrolysis of waste tyre.

In contrast, the char yield raised and the gas yield decreased in the case of all sizes from 1 to 6 cm³. Small sized raw materials resulted in a larger surface area for reaction, which allowed a faster heating rate and premature disintegration of the waste tyres during pyrolysis. For the case of particle size of lesser than 4.0 cm³, during pyrolysis at the set temperature, the oil vapor received sufficient time in the reactor for secondary reaction, resulting in a rise in gas yields and a drop in liquid and char yields. Conversely, for the particle size larger than 4.0 cm³, since the thermal conductivity is reduced the heating rate became slower and

heat can only go so far in the limited pyrolysis time before the rubber core gets carbonized, leading to higher char yields and lower liquid and gas yields¹¹. At the optimal reactor temperature, the decomposition of tyre parts at a feed size of 4.0 cm³ is found to be optimal and less likely to cause secondary cracking.

Effect of Reaction Time on Product Yield

Figure- 5 illustrates the influence of reaction time on the product yield. At 500 °C, with the increase of reaction time, the gas yield decreased and the liquid TPO increased till 50 min operation time. Afterward, the char yield increased. Due to the lower operating time necessary to accomplish the conversion, higher oil and lesser char are produced. There are none readily apparent reasons for gas deficit as a function of operation time. Additionally, it was discovered that low temperature and extended running time promote secondary pyrolysis of primary products, resulting in less oil and more char products¹¹.

Comparison of pyrolysis liquid oil (TPO) with conventional diesel fuel

A comparison of waste tyre-derived TPO fuel characteristics to that of the commercial diesel fuel is shown in Table 2.

Table 2. Comparison of the properties of tire pyrolytic oil with conventional diesel fuel

Properties	Crude Tire oil	Conventional Diesel Fuel
Density (kg/m ³) at 15°C	936.4	830-860
Viscosity (at 40°C, cSt)	4.6	3.5-4.5
Flash point (°C)	49	65
Fire point (°C)	95	228
Carbon Residue, (%)	0.54	0.7
Ash Content, (%)	0.031	0.01
Pour point (°C)	-6	-30 ~ -40
Calorific value, MJ/Kg	40.4	44.83
pH	4.9	5
Sulphur Content (%)	0.24	0.045
Color	Brownish black	Green tea liquor

The density of TPO was found 936.4 kg/m³ at 15 °C, which is greater than that of commercial diesel (830-860 kg/m³) and that of gasoline (is 700-800 kg/m³). TPO showed a density almost close to that of furnace oil (850 - 950 kg/m³) which may be due to the fact that the pyrolysis oil contains

heavier hydrocarbons. The viscosity of TPO (4.6 cSt @40°C) was found near closer to that of the diesel fuel (3.5 to 4.5 cSt @ 40°C) but significantly less than same type of furnace oil (45 cSt@40°C). The low viscosity of any fuel is a beneficial characteristics for handling and transferring the liquid.

The flash point of the TPO was found 49°C and that for conventional diesel fuel is 65°C. With compared to other petroleum-based fuels, TPO has a lower flash point. The fire point of TPO was found 95°C and that of traditional diesel fuel is 228 °C, which is much higher than that of TPO. The Carbon residue in the TPO was estimated 0.54 % (w/w) and that of conventional diesel fuel was reported 0.7 wt. % which indicates that the combustion of TPO will give less carbon deposition. The pour point of the TPO was estimated -6 °C whereas that of diesel was reported -30 °C. The calorific value of TPO was 40.4 MJ/Kg which is comparable to other commercial fuel indicating the possibility of using tyre produced oils as fuel. However, the sulphur content in TPO was found higher (0.24%) than that of diesel and other types of fuel oil, owing to contaminations from waste tyre vulcanization.

Boiling point distributions

Fig. 6 shows the boiling point distribution (performed by distillation process) of hydrocarbons in the TPO collected at 500°C. The percentage of various fractions collected based on distillation temperature are compared with the distillation simulation results of commercial kerosene and commercial diesel. The TPO has a broad range of boiling points; initial boiling point (IBP) of TPO was found at 30°C, approximately 35% of the TPO (mainly light fractions in TPO) distilled out at 30 –160°C, 15% distilled out at 160 - 200 °C and the rest was found in 200 - 300 °C. All these stand for the bound boiling points of light naphtha, heavy naphtha and middle distillate, correspondingly.

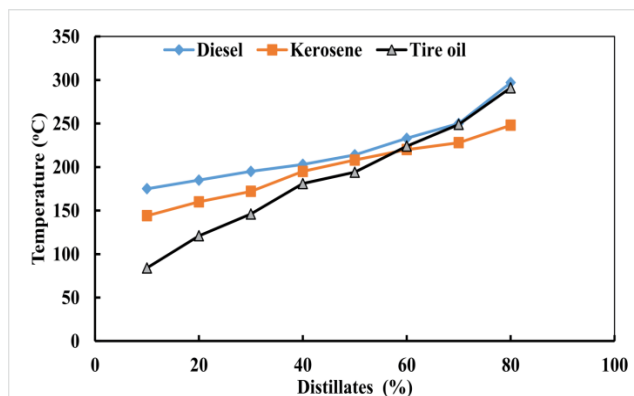


Fig. 6. Comparison of boiling point distribution of the TPO with diesel and kerosene

The existence of a greater proportion of middle distillates indicates the possibility of TPO use in a broader range of applications e.g., as diesel fuels, heating oils. The light

fractions from distillation of TPO are highly comparable to those obtained from truck waste tyres¹⁵. Additionally, the residual product (with a boiling point span of 150 to 300 °C) obtained during distillation of TPO, which accounts for approximately 50% of total volume, are critical to contemplate for use as diesel fuels. Therefore, the liquid portions of tyres in the boiling range of 150 - 300 °C may be atomized efficiently, allowing the combustion to begin at a lower temperature. On the other hand, the fraction at 300 °C or above contains heavier HCs compounds e.g., polycyclic aromatics, which is suitable as heating oil¹² but restricted for use as automobile fuels.

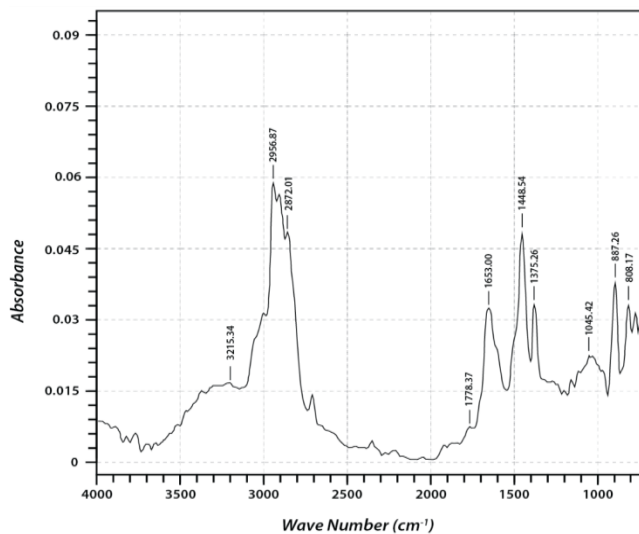


Fig. 7. FTIR spectra of Tyre Pyrolysis Oil (TPO)

Fourier Transform Infra-Red (FTIR) Spectroscopy analysis of TPO

The FTIR spectroscopic analysis of TPO was carried out to investigate the functional group of various components present in the TPO. Fig. 7 shows the FTIR spectra of the TPO which mainly contains functional groups of aromatics alkanes, alkenes, ketones, alcohols and aldehydes.

The absorbance peak of the C-H stretching at 3000 – 2850 cm⁻¹, the C-H bending at 1520 – 1200 cm⁻¹, the C = C stretching at 1035 – 845 cm⁻¹ and CH₂ bending at 731 cm⁻¹ indicating the existence of alkanes functional groups. Besides, the presence of alcohol groups was observed by the molecular motion of the O-H stretching between 3200 – 3400 cm⁻¹ and the C-O stretches between 1200 – 1050 cm⁻¹. The peak at 900 – 1600 cm⁻¹ (for C = O stretching) suggested the incidence of aldehyde groups. The FTIR analysis also confirms the presence of small amount of sulphur compound and carbon dioxides groups. The functional groups of these are quite similar to that of diesel oil found in other studies. The existence of hydrocarbons like C- H, C = C and alcohols in the liquid implies that the TPO has the capacity to be utilized as a fuel.

IV. Conclusions

In this study, commercially usable pyrolysis oil was produced from discarded tyres. The optimum temperature, particle sizes etc. parameters have been studied for the production of TPO during pyrolysis. At a temperature of 500 °C and a tyre geometry of 2 cm × 1 cm × 0.5 cm, the maximum production of TPO from the discarded tyres was 42.0 wt%. The physico-chemical properties e.g., calorific value, density, viscosity, carbon and hydrogen percentage of the pyrolytic oil are commensurate with that of commercial diesel and other conventional fuels. However, higher sulphur content and lower flash point of TPO should need to take into consideration during application. The novel process for the removal of the sulphur and in details study of the fractionated products from TPO will be studied in future. The application of TPO and its derived fuel will bring a drastic change in fuel economy, will ensure the proper management of tyre wastes and reduce the environment pollutions.

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