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A review paper on pyrolysis process of waste tyre

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Abstract
This paper reviews and discusses the waste tyre pyrolysis process and the applications of the derived products. The study reports the characteristics of used tyre materials and methods of recycling, types and principles of pyrolysis, the pyrolysis products and their composition. Pyrolysis is considered as a useful technique for recycling of scrap tyres by using which liquid, gases, carbon black and steel wires are obtained. This technology could not only reasonably and effectively dispose waste tyre and tube without pollution, but also is effective in producing fuel that can reduce energy crisis. The primary and secondary applications of oil, char, gas and steel wires are discussed.

Keywords: Pyrolysis, Proximate Analysis, Elemental Analysis, Incarnations, Retreading.

1. Introduction
The disposal of waste tyre has become a major environmental concern globally and this can be attributed to the increase in automobile usage as well as population especially in areas of large population and highly industrialized nations. The problems caused by the waste tyres is majorly because they are not biodegradable and can last for several decades if no proper handling is carried out. A number of studies related to tyre pyrolysis had been reported in the literature for its conversion into valuable compounds. Developed countries have been paying great attention to the effective utilization of discarded tyres to achieve the goals of protecting environment, recycling resources and preserving energy. For many reasons, recycling of waste rubber has received much attention in recent years all over the world, due to the present rate of economic growth in utilization of the fossil energy fuels like, crude oil, natural gas or coal without saving for the future. Waste tyres have a high content of volatile matters as well as fixed carbon that makes them an interesting solid as a fuel for energy production or hydrogenation processes and in pyrolysis processes to obtain different fractions of soild, liquid and gaseous products.

2. Need of Waste Tyre Recycling
On one hand, with the modernization of the society, rubber industry is developing at a rapid speed, rubber manufactures products are widely used, on the other hand, the pollutant of waste rubber is increasing day by day and its decomposing is very difficult, which is called as "Black Contamination". This has become a big threat to the environment. Compared to the developed countries, we are still lack of experiences in treating the pollution; the capital and the market are also big problems.
Nowadays, the output of tyre in India is more than 1.3 billion, i.e. the third in all over the world. The scrap tyres for each year are 65 million, and are increasing steadily year by year. So to set up a factory in each town, which could extract black carbon and tyre oil from 65-million scrap tyre, it is easy to find the raw material. The composition of passenger vehicle tyres is approximately 85% carbon, 10–15% fabric materials and 0.9–1.25% sulfur. The typical percentages of the rubber mix are 55% synthetic rubber (polybutadiene) and 45% natural rubber (latex) in passenger vehicle tyres. Thus, the abundant organic matter (OM) contents of tyres can be converted into useful products for energy sources.

3. Methods of Waste Tyre Recycling
Waste tyres are recycled in different ways which are:
1. Retreading
2. Landfills

3. using as construction Materials
4. Incarnations
5. Tyre Derived Fuel (Tyre Pyrolysis)

Retread is a manufacturing process designed to extend the lifespan of worn out tyres. The old tread is removed and a new tread is applied to the bare casing using specialized tools. This procedure is regularly carried out in airplane tyres as they are worn out very frequently and the necessity for them to be in good condition. On an average 4.5 gallons of oil is saved through this process compared to manufacture of a new tyre. In case of commercial vehicles, the savings can go upto 12.5 gallons of oil.
Land filling is the most common way of disposing waste tyres, accounting up to 53% of the total waste tyre generated. But it has a serious impact on land usage, fertility of land and is a potential hazard as it is prone to fires. Tyres are very difficult to extinguish when they catch fire. Citing this many countries have banned this form of disposal of waste tyres.
Incineration and TDF are two wastes to energy technologies that are available for the treatment of waste tyres. In incineration, energy recovery systems are used to recover the energy. TDF or tyre derived fuel the energy remains in a liquid form that can be used in combustors, IC engine etc.

4. Pyrolysis Process
Pyrolysis is one of the methods to derive alternative fuels, in which organic substances are converted into useful energy. It is a thermo chemical conversion process in which an irreversible chemical change is caused by the action of heat in absence of oxygen. This process yields value added products such as fuels or chemicals in the form of solid, liquid or gas. Without oxygen, the process splits the chemical bonds and leaves the energy stored in the organic substance. The main advantages of pyrolysis include compactness, simple equipment, low pressure operation, negligible waste product and high energy conversion efficiency of the order of 83%.
The oil obtained after pyrolysis is termed as Tyre Pyrolysis Oil (TPO). Pyrolysis of tyres yields liquid fuel, gases, carbon black and steel wires. Tyre Pyrolysis Oil can be directly used as fuel in Combustors and IC engines. Although using in such systems is effective, the complex composition poses huge challenges for use of TPO as a combustion fuel. Presence of Phenolic, Quinoline and PAH compounds leads to high emissions and high maintenance cost.

4.1 Types of Pyrolysis
Pyrolysis process can be performed under different operating conditions which can be used in classifying it. They are differentiated by residence time of the pyrolysed material in the reactor, process temperature, feed particle size, heating rate etc. These include the following

4.1.1 Slow Pyrolysis
The solid residence time(s) in the reactor is 450–550s, heating rate is 0.1–1, and feed particle size (mm) is 5–50 with temperature (ºC) of 550–950. This process enhances char production and is unlikely to be unsuitable for high quality bio-oil production. Also, due to high residence time secondary reaction is favorable as cracking of primary product occurs which could adversely affect bio-oil yield and quality.

4.1.2 Fast Pyrolysis
Fast pyrolysis involves the rapid heating of the feed material to a high temperature in the absence of oxygen with a short residence time of the condensable vapor in the reactor. Its operating parameters are solid residence time between 0.5 and 10s, heating rate of 10–200 ºC, feed particle size less than 5 mm, and reaction temperature of 550–1200 ºC. The technology has received much popularity in producing liquid fuels and a range of specialty and commodity chemicals. Typically on weight basis, fast pyrolysis yields 60%–75% pyro oil with 15%–25% compared to other processes; it has reasonably low investment costs and high energy efficiencies particularly on a small scale.

4.1.3 Flash Pyrolysis
This process is characterized by residence time of less than 0.5 s, high heating rate of more than 200 ºC, particle size of less than 0.2 mm, and high reaction temperature of more than 1000 ºC. However, the major technological challenge of the process is poor thermal stability, solids in the oil, and production of pyrolytic water.

4.1.4 Catalytic Pyrolysis
Catalytic pyrolysis is a pyrolysis process that includes the use of a catalyst. The catalyst helps enhance the pyrolysis reaction kinetics by cracking down higher molecular weight hydrocarbon compounds to lighter hydrocarbon products. It has been reported that the use of catalyst in tyre pyrolysis systems can greatly influence the composition, quality, and yield of products. Examples of catalysts used in tyre pyrolysis include Na_2CO_3, NaOH, MgO, $CaCO_3$, aluminium-based catalyst, perlite, CaC_2, $Cu(NO_3)_2$, etc. Operating conditions can determine different product distribution for different catalysts. Pyrolysis catalyst can be grouped based on their method of application. The first group is when the catalyst is added to the feedstock before being fed into the reactor. The second group is when catalyst is added after the feed is already heated up in the reactor allowing it to have immediate contact with vapors, solid, and char. The third group is when the catalyst is placed in another reactor located downstream from the pyrolysis reactor.

4.2 Pyrolysis Process Detail
The procedure is simply depicted below in figure 1

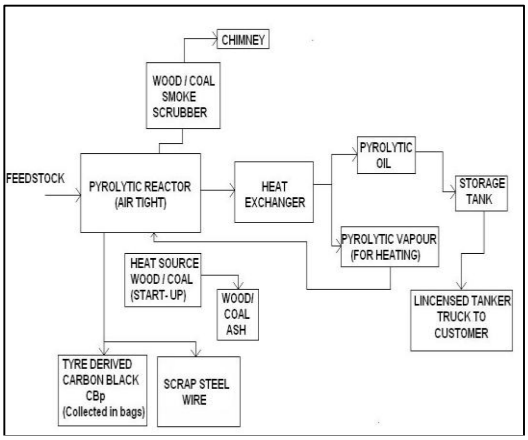

Fig 1: Pyrolysis Process of Waste Tyre

The waste tyres are collected and segregated. Then the tyres are cut into small pieces and steel wires, fabric fibers were removed. Thick outer edges of the tyres were divided into small slices. These tyre slices were washed, dried and then filled in the pyrolysis reactor vessel and initial heat is provided with the help of wood, gas, coal or oil under controlled conditions of temperature and pressure. Conventional pyrolyis was performed under N_2 environment and ambient pressure. Most tyre pyrolysis processes operate within a temperature range of 250–500ºC, although some processes are reported to operate at upto 900ºC. At temperatures above approximately 250 ºC shredded tyres release higher amounts of liquid oil products and gases, while above 400 ºC, the yield of oil and solid tyre-derived char may decrease relatively to gas production The process will bring about molecular restructuring of the rubber and convert into the vapors and gases. This vapors and gases will flow into vapor gas separating tank. Then, these vaporized gases are passed through heat exchanger and convert that vapor into liquid in the form of Tyre oil during the process, carbon black and steel are also generated.
The heat exchanger use water for cooling as a condensing Medium and this water is re-circulated through process.

The thermal efficiency of this process is approximately 70%, and can increase to 90% with the use of pyrolytic products as fuel. The use of tyre chips instead of whole tyres may also increase the efficiency of the process by 20-30%. The speed of the process and rate of heat transfer also influences the product distribution. Slow pyrolysis (carbonization) can be used to maximize the yield of solid char. This process requires a slow pyrolytic decomposition at low temperatures. Rapid quenching is often used to maximize the production of liquid products, by condensing the gaseous molecules into liquid.

4.3 Pyrolysis Product Details

4.3.1 Fuel Oil (40% to 45%)

The main product produce by pyrolysis plant is tyre oil (industrial fuel oil). This is used in many industries as a fuel. There are 2 types of oil we get from the process, one is normal Tyre oil and other is heavy oil. Heavy oil is about 5% to 7% of Tyre oil. The final percentage of oil is about 40% to 45% depends on tyre quality. Nowadays there is a great demand of fuel oil in the market, as every industry requires fuel for heating purpose.

Table 1: Pyrolysis Oil Specification Report

S. No	Specifications	Units	Test Results	Standard Value (LDO) BIS:1460
1.	Kinematic Viscosity At 40°C	CST	9.00	2.4– 15.7
2.	Acidity, Total	mgKOH/gm	0.01	NIL
3.	Ash	% BY WT	0.005	0.02
4.	Flash Point, Coc	°C	40	66 MIN.
5.	Water Content	% BY WT	NIL	1.0 MAX.
6.	Pour Point	°C	+ 6	12 – 18
7.	Density At 27°C	gm/cc	0.907	TO REPORT
8.	Sediments	% BY MASS	0.02	0.10
9.	Total Sulphur	% BY MASS	0.65	1.80
10.	Copper Strip Corrosion Test For 3 Hrs At 100°C	NO UNITS	1b	1 MAX.
11.	Gross Calorific Value	KCAL/KG	10,200	ABV.10000

Applications of pyrolysis oil- (Used in the industries where burning process is required.)
1. Steel Industries.
2. Rolling Mill Industries.
3. Chemical Industries.
4. Used in the Boilers for the heating purposes.

4.3.2 Carbon Black (30% to 35%)

The second product of tyre pyrolysis plant is carbon black. The quantity of carbon black is about 30% to 35% according to tyre quality. The carbon black can be used as a chemical strengthener in rubber industries and coloring agent in pigment industries. This carbon black price is very competitive compare to petroleum carbon black.

Table 2: Carbon Black Specification Report

S. No.	Carbon Black Specification Report Total (condition)	Method	Unit	Specified Value	Observed Value
1.	Ash Content	ASTM D 1506	%	--	9.44
2.	Pour Density	ASTM D 1513	Kg/m3	--	244
3.	pH Value	ASTM D 1512	--	--	6.60
4.	Loss on Heating	ASTM D 1509	%	--	0.41
5.	Solvent Extractable	ASTM D 4527	%	--	7.60
6.	Iodine Adsorption	IS 7498	gm / Kg	--	81.14
7.	Surface Area by BET Method	ASTM D 1993	m2 / gm	--	27.51
8.	ICP Analysis Cu Fe Mn	IRMRA/CHEM/ SOP/08	PPM	--	11 954 14

Applications of carbon black
1. Used in steel industries for burning process.
2. Used in footwear industries to make rubber soles.
3. Used in polish industries.
4. Used in ink industries.
5. Used in color industries as pigment.
6. Used in Iron industries.

4.3.3 Steel Wire Scrape (10% to 15%):-

The third product of tyre pyrolysis plant is steel wire, the quantity of steel wire is about 10% to 15% according to tyre quality.

4.3.4 Pyrolytic Gases (About 10 %):-

We get pyrolytic gases during process about 10% of waste tyre. The main component of these gases is methane (CH4), so we cannot condense and store these gases. We use this gases to heat the reactor and we can use exceed gases for other heating application.

5. Characteristic Analysis of Tyres

Tyres are produced by more than 100 different species. The composition of different tyre parts like the tyre sidewall or the tyre tread varies due to the different desired characteristics of product. Tyres are composed of rubber compounds and textile or steel cords. Rubber compounds generally consist of elastomers (natural or synthetic rubber), carbon black, hydrocarbon oils, zinc oxide, sulphur and sulphur compounds and other chemicals such as stabilizers, antioxidants, anti-ozonants, etc. The rubbers mostly consist of blends of two or three rubbers together with tyre additives. Because of these complex mixtures, the pyrolysis of tyres seems to be a complicated process involving a large number of chemical reactions and complex interactions of the single components. In order to determine feedstock characteristics, analyses suitable for solid materials characterization are used such as proximate and elemental analyses.

5.1 Proximate Analysis

Proximate analysis separates the products into four groups:

1. Moisture
2. Volatile matter, consisting of gases and vapors driven off during pyrolysis
3. Fixed carbon, the nonvolatile fraction of coal
4. Ash, the inorganic residue remaining after combustion.

5.2 Elemental Analysis

A complementary method to proximate is the ultimate analysis. Its scope is the determination of the carbon and hydrogen in material, as found in gaseous products of feedstock's complete combustion, determining also the content of sulphur, nitrogen, and ash in the material as a whole, and oxygen content by difference. Table 3 shows the proximate analysis of scrap tyres declared by various authors. The elemental analysis of waste tyres found in the literature is presented in Table 4.

Table 3: Proximate Analysis of Scrap Tyre Rubber

Author	Volatile (wt %)	Fixed Carbon (wt %)	Moisture (wt %)	Ash (wt %)	Steel (wt %)
M. Juma *et al*. Z	61.61	22.66	1.72	14.01	_
Rodrigues *et al*. *	58.8	27.7	_	3.9	9.6
Jong Min Lee *et al*.	67.3	28.5	0.5	3.7	_
Yu Min Chang *et al*.	62.32	26.26	1.31	10.29	_
Gonzales *et al*.	61.9	29.2	0.7	8.0	_
Chen *et al*.	93.73**	_	0.54	5.3	_
Loresgoiti *et al*. *	59.3	27.6	_	3.5	9.6
Orr *et al*.	68.7	23.3	0.4	7.6	_
Williams and Bottrill	66.5	30.3	0.8	2.4	_

*- Based on reinforced tyre with steel cords **- Including fixed carbon

Table 4: Elemental Analysis of Scrap Tyre Rubber

Author	C (wt %)	H (wt %)	N (wt %)	S (wt %)	O (wt %)	Ashes (Inorganic)
M. Juma *et al*. Z	81.24	7.36	0.49	1.99	8.92	_
Rodrigues *et al*. *	74.2	5.8	0.3	1.5	4.7	13.5
Jong Min Lee *et al*.	83.8	7.6	0.4	1.4	3.1	3.7
Yu Min Chang *et al*.	74.4	6.96	0.21	1.6	5.02	10.21
Gonzales *et al*.	86.7	8.1	0.4	1.4	1.3	2.9
Chen *et al*.	81.16	7.22	0.47	1.64	2.07	7.44
Loresgoiti *et al*. *	74.2	5.8	0.3	1.5	5.1	13.3
Orr *et al*.	81.3	7.3	0.3	1.5		1.4
Williams and Bottrill	85.8	8.0	0.4	1.0	2.3	2.4

6. Waste Tyre Pyrolysis Plant Advantages

1. We get valuable outputs from the process and that are fuel oil, carbon black powder, scrap steel & gas.
2. It is feasible technology with small amount of investment, high availability of raw materials, short recovery period.
3. There is 100% recycling of waste tyres, no disposable materials are left at the end of the process.
4. The output products have its demand in the market.
5. Access to best technology available in India at best price.
6. It is a pollution free process, thus making eco-friendly environment.
7. For the waste Tyre pyrolysis plant the main raw Materials are waste tyres & plastic scrap, which can be easily available in any part of the world.
8. The raw material is cheaper.

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