

Influence of process conditions on product yield of waste tyre pyrolysis- A review

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Abstract—Waste tyres have become a grave concern as their accumulation is aggregating every year. Not only the size of waste tyre has to be reduced, but also some useful energy has to be recovered out of it as the world badly requires energy from alternate sources. Pyrolysis is one such method to extract energy potential products from waste tyres. It is extensively used to generate carbon black (solid product), tyre-oil (liquid product) and syngas (gas product) from waste tyres. In that connection, this article discusses the effect of various parameters on the product composition of pyrolysis of waste tyres. The current usage of pyrolysis products and their typical characteristics are also discussed in this critique. Of late, extraction of high value added products, such as activated carbon from carbon black, and limonene from tyre-oil is gaining attention. The article also throws some light on the application and generation routes of activated carbon and limonene from waste tyres.

Keywords: Waste Tyre, Pyrolysis, Carbon Black, Tyre-oil, Limonene

INTRODUCTION

1. Scenario of Waste Tyre Accumulation

It cannot be over-emphasized that the advancement of science and technology has made daily lives easy and comfortable. However, the impact of this advancement on the environment is worrying. The usage of polymers and the progress in the polymer industry has been generating more scrap plastics, rubbers, tyres, etc. [1]. The production of plastics, rubbers and tyres cannot be halted or reduced as its need and demand is increasing day by day. However, the life period and performance of these goods can be prolonged. Furthermore, as these scraps are increasingly dumped; a suitable means of utilizing these wastes should be explored. Though these wastes are engaged in the recycling process, its proportion is meager considering the amount of accumulation of these scraps [2]. Hence, an appropriate mode of treating of these wastes in the context of energy recovery should be explored as the need for energy is doubling up. Thus, the need is to find out a way to recover useful energy from these wastes with minimal damage to the surroundings.

It has been estimated that every year 1.5 billion waste tyres are discarded all over the world [3,4]. Of that, only 15-20% of that waste is taken for reuse [5]. The remaining 75-80% of waste tyres are simply dumped into the earth. It is quite likely that this figure will shoot up as the demand for tyres is increasing every year. Particularly in countries like the US, Japan, European Union (EU), Australia, South Africa and South Korea where the usage of automobiles is greater, the generation of scrap tyres is expected to in-

crease [6-8]. Some developing countries like China, India, Brazil, Taiwan and Indonesia are also greatly contributing to the accumulation of waste tyres [9].

2. Problems of Scrap Tyres

Vulcanization is done on tyres to increase their flexibility. Anti-oxidants and anti-ozonants are added to tyres to extend their life time. It's because of the vulcanization process and addition of anti-oxidants and anti-ozonants that tyres are non-degradable [10]. Hence, waste tyres accumulate in large piles, often to be either incinerated or landfilled. When incinerated openly, they release toxic gases, which are prone to cause cancer and mutation disorder [11-13]. Strict pollution regulations all over the world have forced tyre incineration to operate in a closed system. However, closed incineration requires expensive air emission monitoring and control system.

Seventy-five % of a tyre is void space [14]. Hence, amassing of tyres occupies a large amount of valuable work space. Also, land-filled tyres react with methane gas and form a reactive mixture that can percolate inside the soil and pollute both soil and water. The waste tyres also become breeding sites for mosquitoes [15,16]. Mosquitoes, in-fact, are the carriers of many dreadful diseases like dengue, chickengunya, elephantiasis and malaria as well as viruses like Zika. These landfilled tyres also pose a high risk of fire [2,10,17-19]. Although waste tyres cannot be ignited easily, when ignited they are difficult to extinguish. Here are some examples of serious fire mishaps that have occurred due to landfilled tyres: Rhinehart tyre fire of Virginia, USA in 1983, the great Kuwait tyre fire of Jahra, Kuwait in 2012, the Watertown tire fire of Wisconsin, USA in 2005 and the Westley tire fire of California, USA in 1999. It took several months to put out these fires. Not only did the waste tyre fire pollute the atmosphere, but it was also reported that water bodies in the nearby vicinity were contaminated with lead and arsenic.

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That illustrates the seriousness of waste tyre fires.

3. Recycling of Waste Tyres

Waste tyres are commonly incinerated to generate electricity, and in some cases to generate process steam. The steam is also used to heat and air-condition buildings [2]. In industries such as cement, steel and paper, waste tyres are used as a secondary fuel with coal. Researches on co-treatment of waste tyres with coal in power plants are also underway [20].

Apart from generation of useful heat, waste tyres are also recycled for other purposes. Since waste tyres have good acoustical properties they are used as sound proofing materials. They are also used as flooring medium in the construction of indoor stadiums, pavements *etc.* [21]. They are also employed in the laying of road and rail foundations [22].

Of all the recycling methods, reclaiming of tyres is the most environmentally benign mode of tyre reuse [9]. Reclamation is the process of recovering useful materials from the waste. Waste tyres are shredded into fines and are mixed with some reclaiming agents to yield reclaimed tyres. Nonetheless, it is reported that only 5% of the total waste tyres is reclaimed [2,23]. Even though the waste tyres are used for various applications as discussed above, the proportion of waste tyres employed for recycling is insignificant. The above applications are also restricted by limited market demand for the recycled goods.

CHARACTERISTICS OF WASTE TYRES

The typical composition of various tyres is provided in Table 1

Table 1. Typical composition of various tyres

Components	Tyre 1 composition (wt%)	Tyre 2 composition (wt%)	Tyre 3 composition (wt%)	Tyre 4 composition (wt%)	Tyre 5 composition (wt%)
Rubber	38.0	50.5	50.0	51.0	62.1
Fillers	30.0	25.5	25.0	26.0	31.0
Reinforcing agents	16.0	13.4	10.0	Small amount	Small amount
Plasticizers	10.0	5.5	Small amount	13.0	1.9
Vulcanization agents	4.0		2.0	3.0	3.0
Antioxidants	1.0		Small amount	Small amount	Small amount
Miscellaneous substances	1.0	4.7	Small amount	7.0	1.9
Reference	Nkosi and Muzenda [24], JATMA [25] Muzenda [10]		Aranda et al. [26]	Bajus and Olahová [27]	Amari et al. [28]

Table 2. Typical elemental and proximate analysis composition of biomass, coal and various tyres

Elements	Biomass	Coal (Anthracite)	Tyre 1	Tyre 2	Tyre 3	Tyre 4	Tyre 5
	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)
Carbon	38.00-57.00	91.80	86.40	85.03	77.30	77.22	85.16
Hydrogen	5.00-6.50	1.40	8.00	7.65	6.20	6.72	7.27
Nitrogen	0.00-1.00	0.60	0.50	0.47	0.60	1.44	0.38
Oxygen	35.00-46.00	5.30	1.70	5.25	7.10	1.08	0.54
Sulphur	0.00-0.10	0.90	2.40	1.60	1.80	1.34	2.30
Reference	Basu [29]	Liu [35]	Nkosi and Muzenda [24], Muzenda [10]	Aranda et al. [26]	Portofino et al. [30]	Gu et al. [31]	Galvagno et al. [32]
Elements	Biomass	Coal (Anthracite)	Tyre 1	Tyre 2	Tyre 3	Tyre 4	Tyre 5
	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)	Composition (wt%*)
Moisture	4.00	3.30	1.30	0.64	1.16	0.70	0.71
Volatile matter	70.40	4.00	62.10	64.46	61.30	62.60	62.58
Fixed carbon	21.40	53.70	29.40	30.02	33.47	30.10	30.07
Ash	4.20	39.00	7.10	4.88	4.36	6.60	6.64
Reference	Basu [29]	Lee et al. [36]	Nkosi and Muzenda [24], Muzenda [10]	Aranda et al. [26]	Galvagno et al. [32]	Martínez et al. [33]	Aylón et al. [34]

*Moisture and ash free basis

[10,24-28]. Rubber is the main component in tyres. Both natural and artificial rubbers are used for tyre manufacturing. Fillers such as carbon black, carbon chalk are added to impart color to the tyres. Carbon black is also used to remove heat from the tread and belt to minimize thermal damage to tyres. Some reinforcing materials like steel, rayon and nylon are added to provide support and strength to the tyre components. Plasticizers such as oils and resins are added for the easy shaping and molding of tyres. Sulfur, zinc oxide and some chemicals are added as vulcanizing agent. These agents improve elasticity and offer strength, hardness to tyres. Anti-oxidants are added to avoid separation of tread and belt during the long run of tyres.

The typical elemental and proximate analysis composition of biomass, coal and various tyres is given in Table 2 [10,24,26,29-36].

Tyres predominantly consist of nearly 86% of carbon. This indicates their high calorific value. Appreciable amount of hydrogen indicates that tyres contain more volatile content. The nitrogen and

Table 3. Comparison of calorific value of tyres with some common fuels

Fuel	Higher heating value (MJ/kg)
Waste tyre	28.0-38.0
Anthracite coal	34.0
Diesel	43.4
Gasoline	44.4
Methane	50.0

Table 4. Analysis pertaining to tyres, carbon-black and tyre-oil

Analysis	Standard	Referred test method
Elemental analysis	ASTM D3176-89	Standard practice for ultimate analysis of coal and coke
Heating value	ASTM D2015-96	Standard test method for gross calorific value of coal and coke by the adiabatic bomb calorimeter
Proximate	ASTM D3173-87	Standard test method for moisture in the analysis sample of coal and coke
	ASTM D 3174-04 (2010)	Standard test method for ash in the analysis sample of coal and coke from coal
	ASTM D3175-07	Standard test method for volatile matter in the analysis sample of coal and coke
Rubber identification by pyrolysis gas chromatography	ASTM D3452-93(1988)	Standard practice for rubber-identification by pyrolysis-gas chromatography
Sulfur content	ASTM D-1619-03	Standard test methods for carbon black-sulfur content
Analysis pertaining to carbon black		
Analysis	Standard	Referred test method
Elemental analysis	ASTM D3176-89	Standard practice for ultimate analysis of coal and coke
Heating value	ASTM D2015-96	Standard test method for gross calorific value of coal and coke by the adiabatic bomb calorimeter
Proximate	ASTM D3173-87	Standard test method for moisture in the analysis sample of coal and coke
	ASTM D 3174-04 (2010)	Standard test method for ash in the analysis sample of coal and coke from coal
	ASTM D3175-07	Standard test method for volatile matter in the analysis sample of coal and coke
Carbon black-Ash content	ASTM D-1506-99	Standard test methods for carbon black-ash content
Pelleted- Pour density	ASTM D 1513-05	Standard test method for carbon black, pelleted-pour density
Extractable transmittance of toluene extract	ASTM D1618-99 (2011)	Standard test method for carbon black extractable transmittance of toluene extract
Mass loss of the pyrolytic and commercial carbon black	ASTM D-1509-95 (2007)	Standard test methods for carbon black- heating loss
Oil adsorption number	ASTM D 2414-11	Standard test method for carbon black- oil absorption number (OAN)
pH value	ASTM D 1512-15	Standard test methods for carbon black- pH value
Sieve residue	ASTM D-1514-01	Standard test method for carbon black- sieve residue
Oil absorption number (OAN)	ASTM D 2414-96	Standard test method for carbon black- oil absorption number (OAN)
Tint strength	ASTM D-3265-11	Standard test method for carbon black- tint strength

Table 4. Continued

Analysis pertaining to tyre-oil		
Properties	Standards	Referred test method
Acid number	ASTM D664-11a	Standard test method for acid number of petroleum products by potentiometric titration
Aromatic hydrocarbons	ASTM D6591 - 11	Standard test method for determination of aromatic hydrocarbon types in middle distillates- high performance liquid chromatography method with refractive index detection
Ash content	ASTM D482-03	Standard test method for ash from petroleum products
Boiling range distribution	ASTM D2887-15	Standard test method for boiling range distribution of petroleum fractions by gas chromatography
Calorific value	ASTM D240-09	Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter
Carbon Conradson residue	ASTM D524-04	Standard test method for ramsbottom carbon residue of petroleum products
Carbon residue	ISO 10370: 2014	Determination of carbon residue by micro method
Cetane index	ASTM D976-91	Standard test methods for calculated cetane index of distillate fuels
Cetane number	ASTM D7668-10	Standard test method for determination of derived cetane number (DCN) of diesel fuel oils-ignition delay and combustion delay using a constant volume combustion chamber method
Chrome	ASTM D5185-05	Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES)
Cold filter plugging point	ASTM D6371-05 (2010)	Standard test method for cold filter plugging point of diesel and heating fuels
Colour	ASTM D 1500-12	Standard test method for ASTM color of petroleum products (ASTM color scale)
Density	ASTM-D1298-85 (1990)e1	Standard practice for density, relative density (specific gravity), or API gravity of crude petroleum and liquid petroleum products by hydrometer method
Density, relative density (specific gravity) or API gravity	ASTM D1298-99	Standard test method for density, relative density (specific gravity), or API gravity of crude petroleum and liquid petroleum products by hydrometer method
Distillation	ASTM-D86-12	Standard test method for distillation of petroleum products at atmospheric pressure
Distillation characteristics	EN ISO 3405:2011	Determination of distillation characteristics of petroleum products at atmospheric pressure
Elemental analysis	ASTM D5291-96	Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants
Flash point	ASTM D92-01	Standard test method for flash and fire points by Cleveland open cup
Gas chromatography (GC) conditions for simulated distillation	ASTM D2887-89	Standard simulated distillation protocol for the separation of petroleum fractions over the boiling points range of 55.5 to 538 °C

sulfur content of tyres is comparatively higher than biomass, however lower than some high sulfur coals. Tyres contain a significant proportion of volatiles, which indicates that upon thermal decomposition a considerable yield of tyre-oil could be obtained. Significant quantity of fixed carbon indicates that tyres possess considerable heating value potential. Small ash content of tyres indicates that they have limited inorganic inert, which can be easily disposed, upon

thermal degradation.

Heating value of some common fuels is presented in Table 3 [5]. Tyres have a heating value greater than the best quality coal. Hence, the co-combustion of tyres with low grade coal offers a tremendous scope. However, the heating value of tyres is lower than of diesel, gasoline and methane. Analysis involved in the determination of properties of tyres is given in Table 4 [4,13,37].

Table 4. Continued

Analysis pertaining to tyre-oil		
Properties	Standards	Referred test method
Insoluble	ASTM 893-05	Standard test method for insoluble in used lubricating oils
Iron, Nickel	ASTM D5185-05	Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES)
Karl Fischer water	ASTM D6304-07	Standard test method for determination of water in petroleum products, lubricating oils, and additives by Coulometric Karl Fischer titration
Kinematic viscosity	ASTM D445-65	Standard method of test for viscosity of transparent and opaque liquids (kinematic and dynamic viscosities)
Lubricity	ISO 12156-2:2007	Assessment of lubricity using the high-frequency reciprocating rig (HFRR)
Oxidation stability	EN 15751	Oxidation stability of biodiesel
Pour point	ASTM D97-05	Standard test method for pour point of petroleum products
Specific gravity	ASTM D4052-96	Standard test method for density and relative density of liquids by digital density meter
Sulfur content XRF	ASTM D5453-12	Standard test method for determination of total sulfur in light hydrocarbons, spark ignition engine fuel, diesel engine fuel, and engine oil by ultraviolet fluorescence
TAN	ASTM D 664-11a	Standard test method for acid number of petroleum products by potentiometric titration
Total Particles	EN 12662	Determination of contamination in middle distillates
Water content- Coulometric Karl Fischer Titration	ASTM D4928-12	Standard test method for water in crude oils by Coulometric Karl Fischer titration
Water content- Volumetric Karl Fischer method	ASTM E203-96	Standard test method for water using volumetric Karl Fischer titration

ENERGY RECOVERY FROM WASTE TYRES

Currently, there are three modes of energy recovery from waste tyres [38]. All the three modes are concerned with thermal decomposition of waste tyres: Pyrolysis gasification and liquefaction.

Pyrolysis is the simplest method of converting waste tyres into useful products. Since there are three types of pyrolysis, such as slow, fast and flash, based on the demand of the products (carbon black, tyre-oil and syngas), a suitable pyrolysis mode has to be chosen.

In gasification, the impetus is given to convert waste tyre into more gaseous products. The gasifying agent can be air, O₂, steam, CO₂ or any mixture of these. The quality and the proportion of gaseous product yield largely depend on the gasifying agent. Factors such as temperature, heating rate, residence time, nature of feedstock, type of reactor also have a profound influence on the product distribution.

On the other hand, liquefaction focuses on decomposing waste tyre into liquid products. The process takes place at lower temperature in the presence of catalyst. Liquefaction can be done through pyrolysis, gasification and hydrothermal treatment. In hydrothermal processing, waste tyres are converted into oily substances by treating with water at a temperature between 300-350 °C for a pressure of 12-20 MPa for certain period of time [29].

The operating parameters of waste tyre pyrolysis, gasification

and liquefaction are provided in Table 5 [10,29,39]. The choice of the these processes depends on the product demand. For generation of carbon black, slow pyrolysis can be preferred. If the intended product is syngas, then gasification is the best choice. For the want of liquid fuels, fast pyrolysis and liquefaction could be an ideal option. Yet, the selection of conversion processes also relies on the economics, market demand of product, environmental regulations, topography, resources of the place, manpower, *etc.* [40,41].

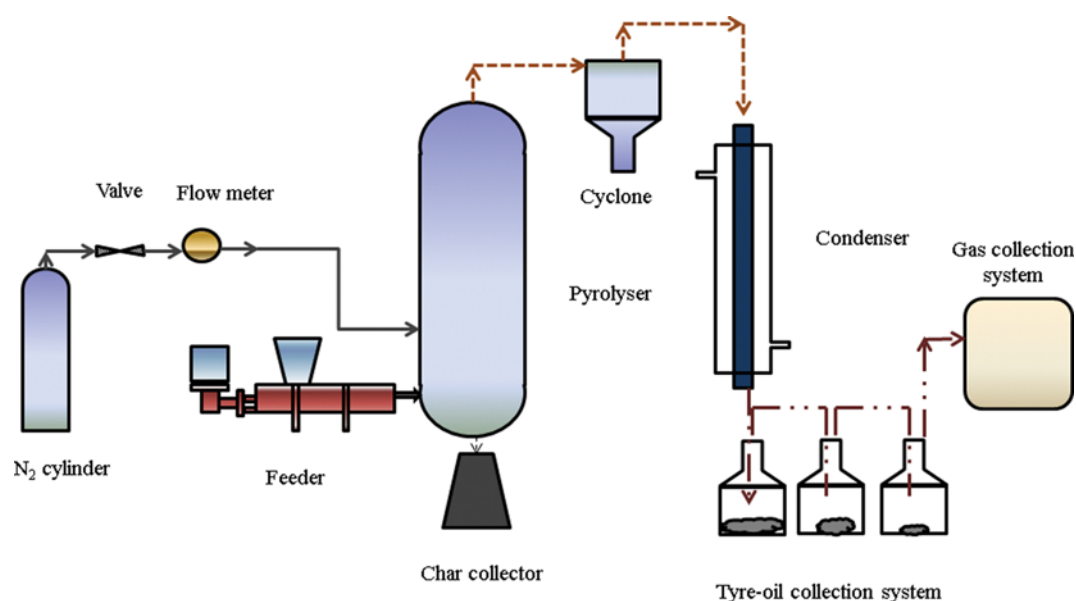
PYROLYSIS

Through pyrolysis, waste tyres can be converted into convenient solid, liquid and gaseous fuels. The solid residue or solid product is called 'carbon black'. The liquid product is referred to as 'tyre-oil'. The gaseous product is termed 'syngas'. The proportion of these products depends on various factors. Primarily, slow and fast pyrolysis is employed to convert waste tyres into useful products.

Fig. 1 presents schematics of waste tyre pyrolysis [19,42]. The pyrolysis setup entails a heating source, reactor, condensers and a gas collection system. Since the pyrolysis process has to be in an inert atmosphere, usually N₂ gas is passed into the system before and after the pyrolysis process. The solid product of pyrolysis, carbon black, can be collected from the reactor. The volatiles which condense in the condensers are accumulated as tyre-oils. Based on

Table 5. Operating conditions of the tyre conversion processes

Variables	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis	Gasification	Liquefaction
Intended product	Carbon black	Tyre-oil	Tyre-oil	Syngas	Tyre-oil
Temperature (°C)	300-600	300-700	350-600	350-900	250-330
Pressure	Atmospheric pressure	Atmospheric pressure	Atmospheric pressure	Atmospheric pressure	5-20 MPa
Heating rate (°C/min)	5-50	15-50	700-1,100 °C/s	High	Medium
Particle size (mm)	1-4	~4	0.3-1.18	0.4-2.0	0.5-4.0
Solid residence time (min)	30-60	15-60	<1 s	15-60	60-120
Gasifying agent	Not essential	Not essential	Not essential	Essential	Not essential
Equivalence ratio	0.14-0.18	0.14-0.18	0.14-0.18	0.20-0.40	0.14-0.18
Water requirement	Not essential	Not essential	Not essential	Not essential	Essential
Catalyst	Not essential	Not essential. However, catalyst improves oil yield and quality	Not essential. However, catalyst improves oil yield and quality	Not essential. However, catalyst improves gas yield	Essential
Syngas composition	H ₂ S, CO, CO ₂ , CH ₄ , alkanes, alkenes			H ₂ , CO, CO ₂ , CH ₄ , ethane, ethylene and acetylene	H ₂ , CO, CO ₂ , alkanes, alkenes and H ₂ S

**Fig. 1. Schematics of waste tyre pyrolysis.**

the necessity of the process, either single condensers or multiple condensers are employed. The gases escaping from the condensers are collected in a suitable gas collection system.

Table 6 details some earlier works on the pyrolysis of waste tyres [19,43-45]. The table indicates that researchers have studied pyrolysis employing different reactors. The products of pyrolysis have been studied by varying parameters such as temperature, heating rate, feedstock particle size, solid residence time and catalyst.

Although a few articles focus on the influence of parameters on the products of waste tyre pyrolysis, they either focus on the aspect of generating tyre-oil or carbon-black [7,21,46,47]. Hence, in this article we present the effect of essential parameters such as temperature, heating rate, feedstock, feedstock particle size, residence

time, reactor configuration and catalyst on all products of waste tyre pyrolysis. The emphasis is not on a single product but on all products: carbon black, tyre-oil and syngas. Also, we discuss the application of these pyrolysis products in various industries and their necessity in the near future. Further, the properties of all pyrolysis products and the analysis associated with it are well presented. We also emphasize the need to generate activated carbon from carbon black and to extract limonene from tyre-oil. The scope of activated carbon and limonene is also discussed.

VARIABLES OF WASTE TYRE PYROLYSIS

Temperature, heating rate, feedstock, particle size, residence time,

Table 6. Previous works on pyrolysis of waste tyres

Reactor	Parameter of study	Operating conditions	Product composition (wt%)	Findings	Inference	Reference
Conical bed spouted reactor	Temperature	Feedstock- 2 g of tyre, Temperature- 425 and 500 °C	At 400 °C: Carbon black- 35.0, Tyre-oil ~ 64.0, Gas ~ 1.0 At 500 °C: Carbon black- 34.0, Tyre-oil ~ 63.0, Gas ~ 3.0	Increase in temperature from 425 to 500 °C decreased tar yield from 29.3 to 25.7%	Increase in pyrolysis temperature increases gas yield. Increase in pyrolysis temperature reduces tar yield.	Olazar et al. [43]
Conical bed spouted reactor	Temperature and Catalyst	Feedstock- 2 g of tyre, Catalyst- HZSM5, Catalyst quantity- 15 g catalytic bed Temperature- 425 and 500 °C.	At 425 °C: Carbon black- 34.0, Tyre-oil ~ 58.0, Gas ~ 8.0 At 500 °C: Carbon black- 45.0, Tyre-oil ~ 35.0, Gas ~ 20.0	In presence of HZSM5 catalyst, increase in temperature from 425 to 500 °C increased char yield from 34.0 to 45.0% and gas yield from 8.0 to 20.0% Addition of HZSM5 catalyst decreased tar yield significantly from 28.8 to 14.9%	Introduction of HZSM5 catalyst reduces tar yield drastically. HZSM5 catalyst encourages gas yield.	Olazar et al. [43]
	Temperature and Catalyst	Feedstock- 2 g of tyre, Catalyst- HY, Catalyst quantity- 15 g catalytic bed, Temperature- 425 and 500 °C	At 425 °C: Carbon black- 33.0, Tyre-oil ~ 64.0, Gas ~ 3.0 At 500 °C: Carbon black- 35.0, Tyre-oil ~ 62.0, Gas ~ 3.0	With the presence of HY catalyst, increase in temperature from 425 to 500 °C, slightly increased carbon black yield. However, a small decrease in tyre-oil yield from 64.0 to 62.0% was noted. With respect to gas yield, no change was observed. With regard to tar yield, increase in temperature from 425 to 500 °C significantly reduced tar yield from 42.7 to 32.5%.	HY catalyst induces carbon black yield. Introduction of HY catalyst significantly reduces tar yield.	

reactor configuration are some essential factors which decide the product distribution of pyrolysis [48-50]. The factors affecting the yield of tyre pyrolysis products are discussed in detail below.

1. Effect of Temperature

Temperature is the most influential factor on the product yield of pyrolysis. In general, low temperatures (300-450 °C) favor carbon black yield, medium temperatures (450-600 °C) support liquid yield, while high temperatures (>600 °C) tend to favor gas yield. Some works on the effect of temperature on product yield are discussed below.

Unapumnuk et al. studied the influence of temperature on carbon content of pyrolysis products of TDF in a laboratory scale pyrolysis reactor [13]. About 3-4 g TDF was taken for the study. An inert

atmosphere was provided by supplying N₂ at a flow rate of 0.47 l/min. The study was carried out at different temperatures of 600, 800 and 1,000 °C, maintaining a heating rate of 5 °C/min. Only the carbon content of carbon black and tyre-oil was determined; the carbon content in gas was calculated by mass balance. With the increase in temperature from 600 to 800 °C, a decrease in carbon content of carbon black from 0.48 to 0.44 g (g denotes g of carbon in 1 g of TDF sample) was obtained. Beyond 800 °C, the carbon content of carbon black remained constant. In the case of tyre-oil, an increase in temperature decreased the carbon content from 0.24 to 0.14 g. For gas, an increase in temperature increased the gas yield from 0.07 to 0.22 g. The carbon content was the highest in carbon black. Maximum carbon content of carbon black of

Table 6. Continued

Reactor	Parameter of study	Operating conditions	Product composition (wt%)	Findings	Inference	Reference
Pyrex glass batch reactor	Catalyst	Temperature- 350 °C, Pressure- Atmospheric condition, Solid residence time- 2 hr, Catalyst- MgO & CaCO ₃	For MgO: Carbon black- 35.8, Tyre-oil ~ 39.8, Gas ~ 24.4 For CaCO ₃ : Carbon black- 35.2, Tyre-oil ~ 32.2, Gas ~ 32.5	MgO catalyst favored generation of tyre-oil and yielded a maximum tyre-oil yield of 39.8%. On the other hand, CaCO ₃ supported generation of gas and yielded a maximum gas yield of 32.5%.	The MgO catalyst is effective for tyre-oil generation while CaCO ₃ is efficient for gas yield.	Shah et al. [44]
Fixed bed reactor	Temperature	Feedstock- 10 g, Heating rate- 10 °C/min, Atmosphere- N ₂ , Solid residence time- 60 min Temperature- 375, 400, 425, 450, 475 and 500 °C	At 375 °C: Carbon black- 50.7, Tyre-oil ~ 46.2, Gas ~ 3.0 At 400 °C: Carbon black- 40.0, Tyre-oil ~ 51.0, Gas ~ 6.0 At 425 °C: Carbon black- 30.0, Tyre-oil ~ 60.0, Gas ~ 9.0 At 450 °C: Carbon black- 27.0, Tyre-oil ~ 58.0, Gas ~ 12.0 At 475 °C: Carbon black- 26.4, Tyre-oil ~ 57.0, Gas ~ 16.0 At 500 °C: Carbon black- 26.4, Tyre-oil ~ 54.1, Gas ~ 20.2	Increase in temperature from 375 to 500 °C decreased char yield from 50.7 to 26.4%. Tyre-oil increased from 46.2 to 60.0% when the temperature was increased from 375 to 425 °C. Nonetheless, when temperature was further increased from 425 to 500 °C, a decrease in tyre-oil yield from 60.0 to 54.1% was noted. Whilst, increase in temperature from 375 to 500 °C increased gas yield from 3.0 to 20.2%.	Maximum oil yield is obtained at medium pyrolysis temperatures (425-450 °C).	Kar [19]

0.48 g was obtained at 600 °C. Maximum carbon content of tyre-oil of 0.24 g was obtained at 600 °C. Maximum carbon content of gas of 0.22 g was obtained at 1,000 °C.

Pradhan and Singh investigated the effect of temperature on product yields [51]. Experiments were conducted using bicycle tyres in a batch reactor. The temperature effect was studied between 450 to 650 °C. A heating rate of 20 °C/min was maintained and a particle of size of 1 cm was considered. A significant decrease in carbon yield was obtained when the temperature was increased from 450 to 600 °C. However, after 600 °C only a slight decrease in carbon black yield was observed. No significant difference in yield of carbon black was observed between 600 to 700 °C. In case of tyre-tyre-oil, a steady increase in yield was noticed till 600 °C. However, above 600 °C no significant change in oil yield was observed. With the increase in temperature, there was a slight increase in gas yield

till 550 °C. However, after 600 °C the trend got reversed: only an increase in gas yield was noted. Maximum carbon black yield of 68.6% was obtained at 450 °C. Maximum tyre-oil yield of 49.6% was observed at 600 °C. Maximum gas yield of 11.5% was noted at 550 °C.

From the above studies, it can be seen that increase in pyrolysis temperature decreases carbon black yield. In case of tyre-oil, initially an increase in temperature increases yield. Nonetheless, after a certain temperature the yield of tyre-oil decreases irrespective of the temperature increase. For gas, increase in temperature always increases the yield.

2. Effect of Particle Heating Rate

Next to temperature, the heating rate plays a vital role in controlling the product yield of pyrolysis. In general, when waste tyres are heated at a higher heating rate, it yields less carbon black; how-

Table 6. Continued

Reactor	Parameter of study	Operating conditions	Product composition (wt%)	Findings	Inference	Reference
Fixed bed reactor	Catalyst	Feedstock- 10 g, Temperature- 375 °C, Heating rate- 10 °C/min, Atmosphere- N ₂ , Solid residence time- 60 min, Catalyst- Expanded perlite, Catalyst addition- 5, 10, 15, 20 and 25%	For 5% catalyst: Carbon black- 28.0, Tyre-oil ~ 62.0, Gas ~ 8.0 For 10% catalyst: Carbon black- 27.0, Tyre-oil ~ 65.0, Gas ~ 8.0 For 15% catalyst: Carbon black- 28.0, Tyre-oil ~ 61.0, Gas ~ 11.0 For 20% catalyst: Carbon black- 27.0, Tyre-oil ~ 59.0, Gas ~ 18.0 For 25% catalyst: Carbon black- 27.0, Tyre-oil ~ 58.0, Gas ~ 19.0	At 375 °C, addition of 5% expanded perlite catalyst improved tyre-oil yield from 46.2 to 62.0%, gas yield from 3.0 to 8.0%. Nevertheless, a decrease in char yield from 50.7 to 28.0% was observed with the addition of catalyst. Increase in catalyst composition from 5 to 25% did not change the char yield. In case of tyre-oil, increase in catalyst composition from 5 to 10% increased tyre oil yield from 62.0 to 65.0%. However, further increase in catalyst composition decreased oil yield. This indicated that with regard to tyre-oil yield catalyst underwent saturation after 10% catalyst composition. With regard to gas yield, increase in catalyst composition from 5 to 25% increased gas yield from 8.0 to 19%.	The introduction of catalyst increases tyre-oil and gas yield while decreasing carbon black yield. The addition of catalyst initially increases oil yield. However, the effect of catalyst saturates after certain composition of catalyst. Increase in composition of catalyst drastically improves gas yield.	Kar [19]
Fluidized bed	Temperature	Pressure- 101.325 Pa, Solid residence time- 12-20 min, Temperature- 350, 500 and 600 °C.	At 350 °C: Tyre-oil ~ 42.0 At 500 °C: Tyre-oil ~ 38.0 At 600 °C: Tyre-oil ~ 18.0	Increase in temperature from 350 to 600 °C decreased tyre-oil yield from 42.0 to 18.0%. Yield of tyre-oil was significant (38.0-42.0%) only at medium temperatures (350-500 °C).	Yield of tyre-oil is maximum at medium pyrolysis temperatures.	Araki et al. [45]

ever, it supports for more tyre-oil and gas yield.

The effect of heating rate on product yield was observed by Unapumnuk et al. [13]. The study was performed on tyre-derived fuels (TDF) in a laboratory scale pyrolysis reactor. TDF of quantity 3-4 g was fed into the reactor. N₂ was supplied into the reactor to offer

an inert atmosphere. The study looked at different heating rates of 1, 5 and 10 °C/min, varying temperatures between 400 to 1,000 °C. It was observed that the tyre-oil yield was highest at ~550-600 °C for the heating rate of 5 °C/min. The maximum tyre-oil yield was 0.4 g/g of TDF sample.

Su and Deng conducted TGA on Chinese waste tyre powder of particle size 100 mesh at three different heating rates, 10, 20 and 40 °C/min, to study the pyrolysis characteristics of samples [5]. The experiment was conducted between room temperature to 800 °C and at N₂ atmosphere of flow rate 20 ml/min. It was found that a high heating rate developed some resistance during pyrolysis. At high heating rates, the surface of particles liquefies and hinders the release of volatiles, and hence the pyrolysis process is affected at high heating rates. It was suggested to conduct pyrolysis at small heating rate to overcome heat resistance. It was also observed that initial temperature, final temperature and peak temperature for mass loss were comparatively low at 10 °C/min. Initial temperatures correspond to the minimum temperature at which degradation of components starts. Final temperature corresponds to the temperature at which degradation of components undergoes completion. Peak temperature is the temperature at which maximum weight loss is occurring. The study indicates that at low heating rates initial, final and peak temperatures of components are low.

González et al. studied the effect of heating rate in shredded waste tyre pyrolysis [49]. Experiments were conducted in a cylindrical stainless steel atmospheric pressure reactor over a range of 350-700 °C and at different heating rates of 5, 10, 15 and 20 K/min. It was noted that with the increase in heating rate, a decrease in carbon black yield was observed. Liquid yield exhibited an increase when heating rate was increased up to 15 K/min. However, at 20 K/min a decrease in liquid yield was observed. On the other hand, a steady increase in gas yield was obtained when heating rate was increased. It was also noted that carbon black obtained at higher heating rate exhibited high surface area. Maximum carbon black yield of 40.9% was obtained at 5 K/min, maximum liquid yield of 55.4% was noted at 15 K/min, while maximum gas yield of 6.6% was observed at 20 K/min.

The above studies indicate that low heating rates favor carbon black yield, while high heating rates support gas yield. It can also be seen that at low heating rates effective decomposition of waste tyres is occurring.

3. Feedstock

Leung and Wang studied the kinetics of scrap tyre pyrolysis and combustion using TG and DT analysis [52]. Three materials, such as tyre rubber powder, tyre fiber and wood powder, were investigated. Experiments were performed at different heating rates of 10, 30, 45 and 60 °C/min. It was observed that there was a significant difference in reaction time and total weight loss in feedstocks. This indicates that different feedstocks exhibit different kinetics during thermal decomposition. Also, it can be understood that feedstocks influence on the kinetics of pyrolysis and combustion.

The influence of tyre formulation on the products of pyrolysis was examined by Lopez et al. [53]. The study was carried out in a conical spouted bed reactor in the temperature range of 425-600 °C. Two kinds of tyre materials with varying compositions of natural and synthetic rubber were used. It was found that products of pyrolysis were not affected by the tyre composition; however it influenced the properties of products drastically.

The above studies indicate that different feedstocks undergo thermal degradation differently. It also implies that feedstock influences the product yield and product properties as well.

4. Feedstock Particle Size

Oyedun et al. conducted an optimization study of particle size in waste tyre pyrolysis [54]. The study is more of a simulation study aimed to compare the influence of particle size on the process completion time and overall energy requirement during the decomposition. The particle sizes were studied at varying heating rates and operational strategies. The study confirmed that small particles reached completion within a short span of time, while larger particles consumed less energy. The study validated that the particle size has a profound influence on process operation and product yield.

Barbooti et al. conducted pyrolysis in a fixed bed batch reactor heated by an electrical furnace [55]. The effect of particle size (2, 6, 10, 16 and 20 mm) was studied at an optimum nitrogen flow rate of 0.35 m³/h and at various temperatures between 400-460 °C. It was found that solid residue yield increased when the particle sizes were increased. However, beyond 16 mm the carbon black yield remained constant, which indicates that large particles have less impact on carbon black yield. The difference in carbon black yield of larger particles (16 and 20 mm) was insignificant. The yield of tyre-oil decreased, initially corresponding to the increase in particle size of feedstock up to 10 mm. However, beyond 10 mm, an increase in the tyre-oil yield was observed. In general, when the particle size is increased, carbon black and tyre-oil yield decreases. The large sized particles block the release of volatiles, and hence more carbon black is generated. Due to reduced availability of volatiles, the generation of tyre-oil is reduced. For to this reason, an increase in carbon black yield and a decrease in tyre-oil yield were observed when the particle size was increased from 2 to 10 mm. However, after 10 mm (larger size particles) mass transfer limitations come into effect and hence a reversing trend in the yields of carbon black and tyre-oil was noted.

Leung and Wang investigated the effect of particle size on kinetics of scrap tyre pyrolysis and combustion [56]. The kinetics of the process was determined using TGA. Tyre powder of sample sizes 8-16 (between), 16 and 40 mm was taken and their thermal degradation kinetics were determined between the temperature range of 450-610 °C. For all sample sizes, no change in kinetic energy and frequency factor was found. This indicated that particle size has less impact on decomposition kinetics.

From the above studies, we note that small particles favor for effective conversion. Also, an increase in particle size increases carbon black yield, but it decreases tyre-oil yield. Also, particle size has insignificant influence on the kinetics of pyrolysis and combustion.

5. Residence Time

Nkosi and Muzenda reported that liquid and carbon black yield decreased with an increase in vapor residence time [24], but they noted an increase in the gas yield. This could be due to the secondary decomposition of tyre-oils into gases. It was also found that long contact time between carbon black and volatiles decreased the carbon black yield.

The investigation indicated that when vapor residence time is increased, the yield of carbon black and tyre-oil is decreased. Yet, with the increase in residence time, gas yield increases.

6. Reactor Configuration

Several reactors such as autoclave, kiln, auger type, fixed bed,

spouted bed, entrained bed, fluidized bed, rotating cone, vortex type, plasma type, free fall, vacuum pyrolyzer and ablative type have been employed to pyrolyze waste tyres [15,57]. Some prominent works are discussed below.

Martinez et al. conducted co-pyrolysis of forestry wastes and waste tyres in a continuous auger reactor [58]. The thermal inlet power capacity of the reactor was 150 kW_{th}. Experiments were conducted at a pyrolysis temperature of 500 °C. An inert atmosphere was provided by supplying N₂ at a flow rate 5 l/min. Though the reactor was capable of handling 15 kg/h of waste tyres, the reactor was operated at a waste tyre feed rate of 5 kg/h. The study was conducted varying biomass to tyre ratio of 100/0, 90/10, 80/20 and 0/100. The reactor could be able to deliver carbon black yield between 24.97 to 48.31%, tyre-oil yield between 38.38 to 56.01% and gas yield between 15.88 to 26.54%. Maximum carbon black yield of 48.31% was obtained at biomass-to-tyre ratio of 0/100. Highest tyre-oil yield of 56.01% was obtained for the biomass to tyre ratio of 100/0. At biomass-to-tyre ratio of 80/20, maximum gas yield of 26.54% was attained. It was concluded that the auger reactor yielded tyre-oil of improved quality.

Helleur et al. employed an ablative reactor to pyrolyze used tyres [59]. Experiments were performed at a pyrolysis temperature of 550 °C under N₂ atmosphere. The reactor was designed in such a way that the heating of feedstock to the desired temperature (550 °C) was accomplished within 1 sec. This was done to avoid secondary polymerization and condensation reactions. The reactor was successful in achieving complete decomposition and recovering primary pyrolysis products. The generated carbon black had an ash content of 15.2%. When analyzed, it was found that the carbon black was similar to other carbon blacks generated through other pyrolysis technologies. However, it was observed that the carbon black cannot be used in recycling for tire manufacturing and but can be employed in rubber compounding.

An autoclave reactor was attempted by Rodriguez et al. to carry out waste tyre pyrolysis [41]. The volume of the reactor was 3.5 dm³. N₂ gas was passed into the system so as to provide an inert atmosphere. Tyre pieces of size 2-3 cm were selected for the study. For experimental runs, about 175 g of tyre pieces was used. The investigation was performed for various pyrolysis temperatures of 300, 400, 500, 600 and 700 °C. A heating rate of 15 °C/min and a solid residence time of 30 min were maintained throughout the study. The products were obtained in the following range: carbon black yield 43.7-84.7%, tyre-oil yield 4.8-38.5% and gas yield 7.7-19.3%. It was found that at pyrolysis temperature of 500, 600 and 700 °C, the decomposition of tyres was complete. Also, a pyrolysis temperature of 500 °C was the optimum temperature for generation of tyre-oil. At that temperature, the disintegration of tyres was complete and also the pyrolysis process consumed less energy.

Day et al. employed a commercial kiln system for pyrolyzing automobile shredder residue [60]. The commercial system had the capacity to handle 200 kg/h of waste tyre. The pyrolysis study was done at 500 °C and a solid residence time of 15 min. The reactor could deliver a carbon black yield of 43.0%, tyre-oil yield of 31% and gas yield of 26%. It was concluded that commercial valuable products could be generated from waste tyres.

A conical spouted bed reactor was employed by Lopez et al. for

performing continuous pyrolysis of waste tyres [53]. The intention of the study was to investigate the effect of tyre formulation on the composition of pyrolysis products. The study was done using two feeds, such as natural and synthetic rubber. In this study, the pyrolysis temperature was varied at 425, 500 and 600 °C. Feedstock was fed at a rate of 300 g/h. An inert atmosphere was ensured by equipping N₂ at a flow rate of 30 l/min. The natural rubber yielded products in the following composition: carbon black 35.36-38.30%, tyre-oil 54.88-62.83% and gas 1.81-6.81%. The product composition of 33.91-35.81% for carbon black yield, 33.91-35.81% for tyre-oil yield and 1.81-8.26% for gas yield was obtained for synthetic rubber. It was concluded that temperature and tire composition had an insignificant effect on product composition. Nonetheless, both parameters exhibited significant influence on product quality. Further, it was found that the carbon black generated at 600 °C displayed high surface area and was suitable to be employed as activated carbon.

Roy and Chaala used vacuum pyrolysis of automobile shredder residue in a vacuum pyrolyzer [61]. The reactor was of the following dimensions: volume 15 l, length 3 m and diameter 0.6 m. The reactor was attached to three condensers for effective condensing of volatiles. A feed rate of 50 kg/h was maintained. The experiments were conducted at a pyrolysis temperature between 496 to 536 °C and at pressure between 1-5 kPa. The composition of the products was carbon black 52.5%, organic liquids 27.7%, pyrolytic water 13.3% and gas 6.6%. It was concluded that vacuum pyrolysis offers high flexibility with regard to energy recovery.

Kaminsky and Mennerich conducted pyrolysis of synthetic tire rubber in a laboratory scale fluidized-bed reactor [62]. Quartz sand of particle diameter 0.3-0.5 mm was used as fluidized bed medium. The study was performed at pyrolysis temperatures of 500, 550 and 600 °C with a gas residence time of 2.6-3.0 s. With N₂ as fluidizing gas, the reactor generated a carbon black yield of 30.00-40.00%, tyre-oil yield of 51.24-65.59% and gas yield of 5.0-9.2% respectively. The study was also conducted with steam as fluidizing gas at 500 °C. It contributed 31.0% of carbon black yield, 65.0% of tyre-oil yield and 3.5% of gas yield. It was found that the quality of the carbon black greatly improved with increase in temperature. The quality of the carbon black was quite good at 600 °C. Also, it was concluded that N₂ and steam contributed for the same products (carbon black, tyre-oil and gas) yield.

A laboratory scale entrained flow reactor was experimented by Wojtowicz et al. [63]. The study aimed to generate carbon black from waste tyre pyrolysis oil. The reactor was made of quartz and was heated externally. Four oil samples were tested. Oil droplets of size $d < 20 \mu\text{m}$ was sprayed through a spray nozzle assembly. The reactor was maintained at a temperature of 1,100 °C. Experiments were conducted at carrier gas flow rates of 2,000 and 500 ml/min. Oils were supplied at a flow rate of 0.10-0.16 cm³/min. The system generated carbon black yield between 25.0 to 60.0%. It was found that the generated carbon black was well within the range of ASTM carbon black.

The above literatures indicate that the configuration of reactors also influence the decomposition of waste tyres. The yield and composition of the pyrolysis products are also influenced by the reactor design. Notwithstanding, during the selection of the reactors fac-

Table 7. Properties of carbon black from various tyres

Properties	Carbon black 1	Carbon black 2	Carbon black 3	Carbon black 4	Carbon black 5
C		80.30	83.50±0.50	87.37	83.00
H		1.30	0.60±0.040	0.66	
N		0.30	0.30±0.070	0.31	
S		2.70	2.40±0.10	2.63	2.60
Zn		3.80			4.20
O					6.00
Si					1.60
Ca					2.40
HHV (MJ/kg)		29.30 MJ/kg	28.80±0.60		
Specific gravity	1.70				
Bulk density	519.00 kg/m ³				
Particle size	40-50 microns				
BET surface area	40.00 m ² /g	83.00		82.00	
CTAB (cetyltrimethylammonium bromide adsorption methods) surface area	85.00 m ² /g				
Void volume DBP (dibutyl phthalate method)	85.50 ml/100 g				
Total pore volume (cm ³ /g)				0.40	
Total micropore volume (cm ³ /g)				<0.01	
Average pore size (nm)				50	
Pellet hardness	23.00 g/pellet				
Toluene discoloration	90.00				
Effective thermal diffusivity			9.00*10 ⁻⁸ m ² /s		
Specific heat capacity			1,500 J/kg K		
Thermal conductivity			0.10 W/mK		
Reference	CIWMB [11]	Olazar [43]	Rodriguez [41]	Aranda et al. [26]	Nkosi and Muzenda [24]

tors such as economics, nature of feedstock, desired products, available resources, *etc.* should also be well thought out.

7. Catalyst

Williams and Brindle studied the effect of catalyst on scrap tyre pyrolysis [64]. Pyrolysis was performed in a semi-continuous fluidized bed reactor at varying temperatures of 450, 500, 550 and 600 °C. Y-type zeolite and zeolite ZSM-5 catalyst were investigated in this study. In case of tyre-oil yield, the addition of catalyst decreased its yield. At low temperatures of 450 and 500 °C, CBV 400 catalyst favored tyre-oil yield, while at high temperatures of 550 and 600 °C ZSM5 favored tyre-oil yield. The addition of catalyst obviously improved gas yield significantly at all temperatures. It was found that CBV 400 effected more gas yield than ZM5 catalyst. Also, the addition of catalyst did not yield any significant change in carbon black yield.

The influence of zeolite USY catalyst on the yield of products was studied by Boxiong et al. [65]. Pyrolysis was carried out in a fixed bed reactor. The result indicated that increasing catalytic temperature and catalyst/tyre ratio, gas yield increases at the expense of tyre-oil yield. The increase in catalyst/tyre ratio from 0.25 to 1.0 increased gas yield from 30.5 to 49.9%. Nonetheless, it decreased tyre-oil yield from 31.6 to 12.7%. No significant change in carbon black yield was noticed with the addition of catalyst.

The above studies indicate that the introduction of catalyst improves gas yield. Nevertheless, catalyst addition reduces tyre-oil yield. It can also be noted that catalyst has no influence on carbon black yield.

PYROLYSIS PRODUCTS

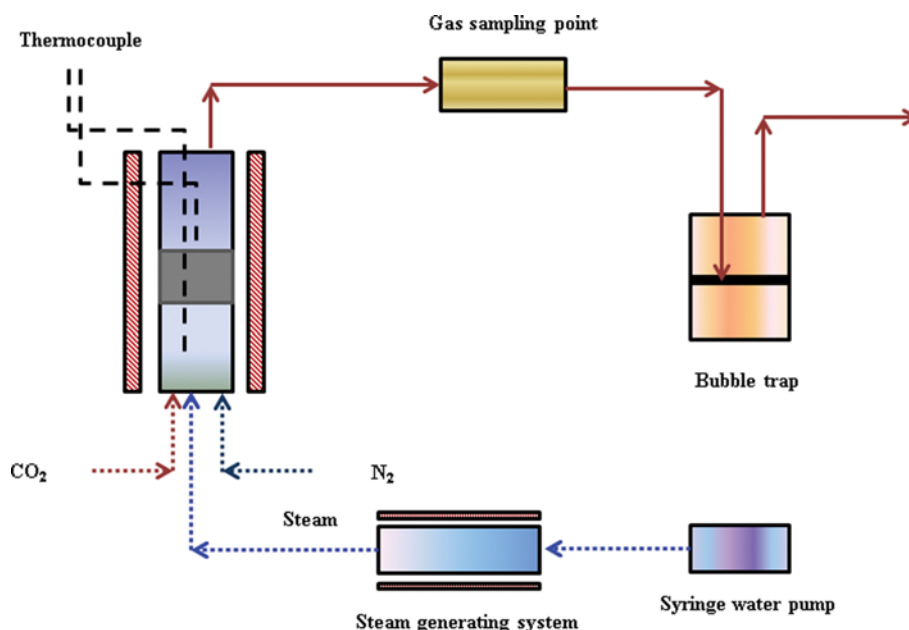
1. Carbon Black

The properties of carbon black from various tyres are presented in Table 7 [24,26,38,41,43]. The standard analysis pertaining to the determination of properties of carbon black is given in Table 4 [13,23,37,41,66,67]. Carbon black, as such, has the potential to be used as fuel. Generally, carbon black is used as fuel, adsorbent and precursor to generate activated carbon. In some power plants, carbon black is made into slurry and used as fuels. As adsorbent, tyre derived carbon black is very effective in eliminating pollutants such as chromium, lead, copper, dyes and phenol from industrial liquid effluents [17,40,68-71]. It is also used to capture industrial gaseous effluents such as SO₂ [24,72]. Furthermore, carbon black is used as fillers and pigments for making printing inks, tyres, *etc.* [73].

Table 8 presents some literatures on the generation of activated carbon from waste tyre pyrolysis [74-76]. Compared to carbon

Table 8. Works on generation of activated carbon from waste tyre pyrolysis

Reactor	Parameter of study	Operating conditions	Output	Findings	Reference
Activation: TG	Particle size	Temperature- 900 °C, Heating rate- 30 °C/min, Atmosphere- He mixture, Feedstock- 170 mg piece and granulated piece of diameter less than 300 µm	Char yield (Granulated tyres)- 36%, Surface area 99 (m ² /g) for 0% burn-off, 124 (m ² /g) for 30% burn-off, 188 (m ² /g) for 50% burn-off Char yield (170 mg)- 34%, Surface area 97 (m ² /g) for 0% burn-off, 423 (m ² /g) for 30% burn-off, 732 (m ² /g) for 50% burn-off	The efficiency of activation process is more for large sized feedstock.	Teng et al. [74]
Pyrolysis: Quartz tube reactor	Temperature	Feedstock- Natural rubber tyre, Feed- 1 g, Atmosphere- Helium, Solid residence time- 1 hr, Water feed rate- 0.75 mg of water/g of sample/s, Temperature- 700 and 900 °C	For temperature 700 °C: Carbon residue surface area ~100 m ² /g For temperature 900 °C: Carbon residue surface area- 1260 m ² /g	Increase in temperature increases the surface area of char residue.	Ogasawara et al. [75]
Cylindrical stainless steel atmospheric pressure reactor	Activation agent	Feedstock- 20 g, Temperature- 750-900 °C, Activation time- 1-3 h, Activation agent- steam and CO ₂	Activated carbon- 1317 m ² /g at 900 °C in steam Activated carbon- 496 m ² /g at 850 °C in CO ₂	Activation using steam generates activated carbon with narrow micropores and large surface area.	Gonzalez et al. [76]

**Fig. 2. Schematic illustration of generation of activated carbon from carbon black.**

black, activated carbon has a good commercial market. The commercial potential of carbon black can be improved by converting carbon black into activated carbon, which can be done through chemical activation. A schematic of carbon black conversion into

activated carbon is presented in Fig. 2 [77]. Even though activation agents such as steam or carbon dioxide are used, the carbon generated from steam displays good surface area [73,77]. When steam is used as activating agent, it reacts with carbon of carbon

Table 9. Properties of activated carbon from various tyres

Properties	Activated carbon 1	Activated carbon 2	Activated carbon 3	Activated carbon 4	Activated carbon 5
C	87.00	80.25	84.90	96.80	
O	5.90	7.62	13.60	<0.10	
H			0.08	0.22	
N			0.80	0.22	
Si	0.60	4.13			
S	1.80	1.01	0.60	5.85	
Zn	2.90				
Ca	1.80				
Fe		3.11			
Surface area	800	400 m ² /g		373 m ² /g	1317 m ² /g
Meso volume					1.25 cm ³ /g
Macro volume					0.47 cm ³ /g
Reference	Nkosi and Muzenda [24]	Belgacem et al. [78]	López et al. [79]	Wójtowicz et al. [80]	González et al. [76]

black and generates hydrogen, carbon monoxide, carbon dioxide and methane. With carbon dioxide as agent, the activation process releases carbon monoxide. The reaction between carbon black and agent generates gases by disintegration of carbon black particles, thereby increasing the surface area of carbon black.

Table 9 presents properties of activated carbon [24,76,78-80]. Activated carbons are mostly used as adsorbents to adsorb phenols, basic dyes, metals, p-chlorophenols, butane, natural gas, *etc.* [24,81,82]. They are also effective in the removal of organic as well as inorganic substances from industrial effluents. Specifically, KOH activated carbon is used to remove halogenated hydrocarbons and pesticides from drinking water [24,47,81]. Of late, activated carbon

is applied in gas phase applications too [18,24,58,76,81]. They find their application in the separation, storage and catalysis of gaseous species. They are also used for the transportation of flammable gases such as acetylene, *etc.*

2. Tyre-oil

Tyre-oil is dark brown and has an acrid smell. The property of the oil is presented in Table 10 [4,19,44,83,84]. The standard analysis concerned with the determination of properties of tyre-oil is given in Table 4 [1,4,15,16,42,47,83,85-88]. The oil can be directly used as fuel in furnaces, steam boilers, gas turbines, IC engines, *etc.* [24]. Oil can be treated to derive some important chemicals such as benzene, xylene, toluene and D-limonene [57,64,73,89].

Table 10. Properties of tyre-oil from various tyres

Proximate analysis	Tyre-oil 1	Tyre-oil 2	Tyre-oil 3	Tyre-oil 4	Tyre-oil 5
Ultimate analysis					
Carbon	86.5			84.09	60.32
Hydrogen	10.8			9.75	6.94
Nitrogen	0.5			0.39	0.35
Sulfur	0.8	0.6	0.55	1.37	0.14
Ashes	Traces				
Oxygen	2.2			4.40	32.25
Cl (ppm)	130				
Heating value					
LHV (MJ/kg)		43.1	41.0@25 °C		
GCV (MJ/kg)	43.7	45.9	42.1@25 °C	41.31	25.6
Physical properties					
Carbon conradson residue	1.3				
Density (kg/m ³)	950@20 °C	840	872.7	994.7@15 °C	876.3@15 °C
Viscosity 40 °C (cs)	9.7@50 °C	2.35	5.2	6.61@50 °C	1.99@40 °C
Flash point (°C)	28	38	64		<30
Freezing point (°C)			-11.5		
Boiling range (°C)		110-300	80-320		
Diesel index			49		
Reference	Roy et al. [83]	Shah et al. [44]	Shah et al. [84]	Kar [19]	Uçar and Karagöz [86]

These chemicals are important feedstock for manufacturing plastics, resins, fibers, dyestuffs, pesticides, solvents, surfactants, *etc.* [47]. Upon upgradation, tyre-oil can also be converted into useful transport fuel.

Earlier studies on recovery of Limonene from tyre-oil are presented in Table 11 [57,72,90-92]. D-limonene is one such essential chemical which can be derived from tyre-oil. The schematic of D-limonene recovery from tyre-oil is illustrated in Fig. 3 [16]. Recently, the generation of D-Limonene from tyre-oil has been picking up.

D-Limonene has become an inevitable commodity in the formulation of many solvents, resins, adhesives, *etc.* [42,64,93,94]. It is used as a dispersing agent in pigments and fragrance agent in cleaning products [42,94,95]. It is used in pharmaceutical industry in the formulation of drugs used for curing cancer, bronchitis *etc.* [19]. In food industry, it is employed as a flavoring agent in making beverages and chewing gum. Due to its increased usage in industries such as pharmaceutical, chemical and cosmetic, its demand is increasing every year [24,90]. The extraction of D-Limonene from

Table 11. Works on recovery of Limonene from tyre-oil

Reactor	Operating conditions	Output	Findings	Reference
Multiple hearth vacuum pyrolysis unit	Pyrolysis: Temperature-510 °C, Pressure-1 kPa, Feed- 3.5 kg/h Distillation: Pressure- Atmospheric, Temperature- 204 °C.	Tyre-oil- 55.0% Limonene- 95.0% purity	High purity Limonene can be generated from tyre-oil	Pakdel et al. [72]
Continuous ablative reactor	Pyrolysis: Temperature- 550 °C, Residence time- 0.6 s, Atmosphere- Nitrogen, Feed size- 1 cm Distillation: Temperature- 190 °C.	Limonene- 16.3% (Vacuum distillation) Limonene- 32.0-37.0% (Re-distillation)	Vacuum distillation is the apt method to purify Limonene.	Stanculescu and Ikura [92]
Fixed-bed fire tube heating	Pyrolysis: Temperature- 375, 425, 475, 525 and 575 °C, Heating rate- 15 °C/min, Atmosphere- N ₂ , Feed size- 4 cm ³	Highest liquid yield- 475 °C Limonene- 50.86%	The property of tyre-oil is very similar to petroleum derived fuels.	Rofiqul et al. [91]
Analytical pyrolyzer with GC/MS	Pyrolysis: Temperature- 500, 550, 600, 650 and 700 °C, Heating rate- 20 °C/ms, Feed size- less than 100 mesh, Residence time- 20 s	Maximum Limonene yield- 22.9%	Maximum Limonene yield is possible at temperatures less than 500 °C.	Ding et al. [57]
Semi-continuous pilot plant reactor	Pyrolysis: Temperature- 440-570 °C, Feed rate- 21 and 42 kg/h	Maximum Limonene yield- 50.0%	Beyond 500 °C Limonene is decomposed.	Pakdel et al. [90]

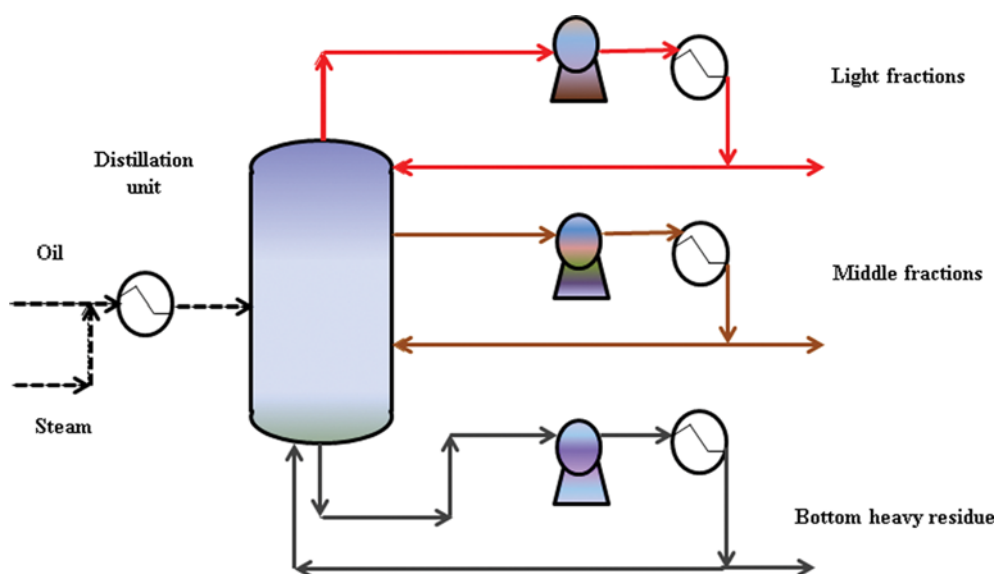


Fig. 3. Recovery of D-Limonene from tyre-oil.

Table 12. Composition of tyre-syngas reported in literatures

Constituent	Tyre-syngas 1		Tyre-syngas 2		Tyre-syngas 3		Tyre-syngas 4		Tyre-syngas 5	
	(Vol%)	(Wt%)	(Vol%)	(Wt%)	(Vol%)	(Wt%)	(Vol%)	(Wt%)	(Vol%)	(Wt%)
H ₂	6.5	0.66	2.3	0.14	10.097	0.179	20.0	1.78		
CO (%)	1.3	1.84	43.9	37.19	0.382	0.095	29.0	35.93	11.94	7.86
CO ₂ (%)	1.6	3.56	41.8	55.63	1.177	0.460			8.39	8.67
CH ₄ (%)	10.8	8.77	9.6	4.66	5.427	0.771	1.7	1.21	1.94	0.73
C ₂ H ₆ (%)	4.3	6.54	0.9	0.82	1.557	0.415			10.00	7.06
C ₂ H ₄ (%)	4.5	6.39	0.9	0.76	1.152	0.286			5.81	3.83
C ₂ H ₂ (%)					0.000					
C ₃ H ₈ (%)	5.1	11.38	0.6	0.80	0.660	0.258			3.55	3.68
C ₃ H ₆ (%)	4.8	10.22			0.872	0.325				
C ₄ H ₁₀ (%)					0.165	0.085			5.16	7.04
C ₄ H ₈ (%)					0.102	0.050				
Isobutylene (%)					2.090	1.039				
Butadiene (%)					0.120	0.057				
Cis-pentene (%)					0.035	0.022				
n-Hexane (%)					0.040	0.030				
Cyclohexane (%)					0.355	0.264				
Benzene (%)					0.083	0.057				
Isobutane									0.00	0.00
Isobutene									0.65	0.86
1,3 Butadiene									37.74	47.95
2-Butene									9.35	12.32
H ₂ S	0.5	0.86								
Heating value	11.4 MJ/Nm ³				6.4 MJ/Nm ³					
Reference	Martínez et al. [15]		Martínez et al. [33]		Berruero et al. [96]		Martínez et al. [58]		Olazar et al. [43]	

tyre-oil offers a tremendous scope.

3. Gas

The gas contains good heating value and is used to supply process heat [38]. Composition of tyre-syngas reported in the literature is presented in Table 12 [15,33,43,58,96].

WASTE TYRE RECYCLING PLANTS

There are many waste tyre recycling plants all over the world. Table 13 details some of the commercial waste tyre recycling plants in the world. Lately, new plants are being commissioned in fast grow-

Table 13. Some commercial waste tyre recycling plants of the world

Plant	Location	Product	Purpose	Capacity* (T/yr)
Lakin Tire East/West	California, USA	Crumb rubber	Tyre derived aggregate, rubberized asphalt, tyre derived fuel, recycled consumer products	387600
Laking General Corporation	Chicago, USA	Tyre derived fuel (TDF), Crumb tyre	Automotive parts, mats, Fuels	306000
Emanuel Tire, LLC	Maryland, USA	Crumb rubber	Civil engineering materials, rubber reclaim industry material, septic system material, sound wall material, horse arena footing, playground material, tyre derived fuel	173400
Liberty Tire recycling	23 Facilities across USA	Crumb rubber, TDF, rubber mulch	Mats, rail road ties, anti-fatigue mats, acoustical underlay, portable speed bumps, weightlifting plates, Astroturf, Fuel, automotive parts, paints and coatings, house foundation, landscaping and playground applications	113500
Genan	Houston, Texas, USA	Rubber powder	Asphalt, Bitumen	100000

Table 13. Continued

Plant	Location	Product	Purpose	Capacity* (T/yr)
Genan	Viborg, Denmark	Rubber powder	Asphalt, Bitumen	70000
Genan	Kammlach, Bayern, Germany	Rubber powder	Asphalt, Bitumen	70000
Genan	Oranienburg, Berlin, Germany	Rubber powder	Asphalt, Bitumen	65000
Genan	Dorsten, NRW Germany	Rubber powder	Asphalt, Bitumen	65000
Eldan recycling	Al ain, Abu Dhabi, UAE	Granulate	TDF	57600
Crumb rubber manufacturers	California, USA	Crumb rubber	Rubberised asphalt, sports tracks, mulch, rubber molded products	51000
Champlin Tire recycling, Inc.	Concordia, USA	Crumb Tyre	Park benches and picnic tables	40800
Entech, Inc.	White pigeon, USA	Crumb rubber	Molding, extrusion, rubberized asphalt, equestrian markets, mulch and playgrounds	36320
L & S Tire Company	Washington, USA	TDF, Crumb tyre	Fuel, tyre bales, tyre treads, retreads	35700
Tire disposal & Recycling Inc.	Portland, USA	TDF, crumb tyre	Fuel, civil engineering applications, grading of casings for re-use	10200
AngloEnvironmental Engineering & Construction Limited	Essex, UK	Tyre blocks	Civil construction	1500
S & J Granulate Solutions Pvt. Ltd.	Gujarat, India	Rubber granulates	Flooring- Sports stadium, Insulation, Hoses-irrigation	1500

*Capacity calculated based on one piece of tyre is equivalent to 10.2 kg of tyre chips

ing developing countries.

CONCLUSION

This review paper addresses the nuisances of and need to treat these waste tyres. The article emphasis is on the energy recovery routes from waste tyres. Even though three means of energy recovery exist, only pyrolysis and gasification are largely employed to generate carbon black, tyre-oil and syngas from waste tyres. Variables such as temperature, heating rate, feedstock, feedstock particle size, residence time, reactor configuration, catalyst, majorly influence the product composition of pyrolysis. There exists a huge potential to generate value added products, such as activated carbon and limonene.

FUTURE SCOPE

➤ Tyres upon thermal decomposition are prone to release pollutants such as SO₂, H₂S, HCl, HCN, dioxins (C₄H₄O₂) and polycyclic aromatic hydrocarbons (PAH). Hence, future research should focus on arresting these pollutants.

➤ Carbon black from waste tyres is considered of low quality as they contain impurities as high as 10%. Hence, suitable treatments to reduce the impurities need to be explored.

➤ Though activated carbon from waste tyres satisfy the criteria of commercial activated carbon (surface area close to 500 m²/

g), its market demand is not that much sound. Henceforth, some appropriate upgradation techniques to increase the surface area of activated carbon have to be established.

➤ The economics involved in the extraction of limonene from tyre-oil is expensive. The production cost can be brought down by optimizing operating conditions such as usage of apt reactors, temperature, heating rate, vapor residence time, catalyst, *etc.* Further research should investigate on these parameters to optimize the cost of production of limonene.

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NOMENCLATURE

API : American petroleum institute
 ASTM : American society for testing and materials
 BET : brunauer emmett teller
 CTAB : cetyltrimethylammonium bromide adsorption methods
 DBP : dibutyl phthalate method
 DCN : derived cetane number

DT : derivative thermogravimetric
 EN ISO : european union ISO
 ER : equivalence ratio
 EU : european union
 GC : gas chromatography
 GC/MS : gas chromatography/mass spectrometry
 HFRR : high-frequency reciprocating rig
 HHV : higher heating value
 HTR : high temperature reactor
 IC : internal combustion
 ICP-AES : inductively coupled plasma atomic emission spectroscopy
 ISO : international organization for standardization
 Ltd. : limited
 OAN : oil absorption number
 PAH : polycyclic aromatic hydrocarbons
 Pvt. : private
 TAN : total acid number
 TDF : tire derived fuel
 TG : thermogravimetric
 UAE : United Arab Emirates
 UK : United Kingdom
 USA : United States of America
 XRF : X-ray fluorescence

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