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# Advances in Recycling of Waste Vulcanized Rubber Products *via* Different Sustainable Approaches

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## **Abstract**:

The recycling of waste vulcanized rubber (WVR) products is highly challenging due to the presence of a three-dimensional (3D) sulfur crosslinked network hindering natural degradation process. Traditional disposal approaches such as combustion, stockpiling, and landfilling create several environmental concerns by generating toxic fumes and gases causing serious health issues. Best approach to resolve these problems is to reuse/recycle waste materials using sustainable methods for minimizing the negative impact of the current waste handling systems. The recycling of WVR products requires the breaking of the 3D crosslinked sulfur network using environmentally benign devulcanization and/or depolymerization strategies. Pyrolysis is another important process to recycle the WVR products into value-added chemicals. It is important to adopt sustainable approaches to recycle the WVR products into new products. The present review covers various sustainable technologies with state-of-the-art development of recycling of waste tire and non-tire rubber products. Important processes such as physical, chemical, and biological devulcanization methods involving selective carbon-sulfur (C-S) and sulfur-sulfur (S-S) bonds breakage along with the depolymerization and pyrolysis are also discussed.

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# 1. Introduction

Rising life standards and a growing population are driver for significant increase in the consumption and demand for elastomers and rubber products worldwide.[1] The elastomers are classified as general-purpose rubber, special-purpose rubbers, specialty rubbers, exotic, thermoplastic rubbers and liquid processing rubbers. [2-3] The general-purpose rubber includes natural rubber (NR), styrene-butadiene rubber (SBR), and butadiene rubber (BR). The special purpose rubbers include ethylene-propylene rubbers (EPM, EPDM), butyl rubber (IIR), halogenated rubbers (HIIR), chloroprene rubber, nitrile rubber, etc. The examples of specialty rubbers are acrylic rubber, fluororubbers, silicone rubbers, epoxidized natural rubber etc. The exotic rubber includes perfluorinated rubber, polyphosphazene etc. and thermoplastic rubbers are styrene-butadiene-styrene, hydrogenated SBS, thermoplastic polyolefin rubber, etc. [2-3]

Industrial revolution accelerated urbanization leading to higher growth in the automobile sector. [4] Elastomers are a major component in auto industries and about 70% of globally produced rubber is consumed in the manufacturing of passenger and commercial vehicle tires. [5-6] The increasing demand for vehicles accelerates the production of new tires resulting in a huge ingestion of rubber in tires industries. [7] International Market Analysis Research and Consulting Services (IMARC) reported that about 2.3 billion units of new tires have been produced in the year 2022 and are expected to reach ~ 2.7 billion units by the year 2028. [8] On the other side, almost 1.5 billion waste tires are generated annually at the end-of-life cycle. [9] Majority of the waste tires and non-tire rubber products such as hoses, belts, and other rubber wastes undergo either accumulation or disposal processes. [10] A large number of waste tires are discarded except small percentage of waste tires are reused in building retaining walls, as guards for protecting boats, and products requiring weather resistance characteristics. [9-10] The current disposal system or simple accumulation of WVR products is hazardous and creates major environmental, health, and economic concerns. [10] The best approach for the disposal of WVR products is recycling to value-added products. [6, 9-12]

Recycling is a process of converting waste materials including WVR & WTR into new materials to mitigate the overall environmental pollution due to waste material dumping. Recycling of wastes involves different steps, including i) collection, ii) sorting, iii) processing, iv) manufacturing, and v) purchasing of recycled products. [10-11] Recycling of cured rubber products has been proven to be extremely difficult due to the presence of a three-dimensional sulfur crosslinked network structure resulting from the vulcanization of raw rubber. [11] Vulcanization is a process where the rubber becomes thermoset by crosslinking with sulfur and

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cannot be reformed or restructured into other products unlike thermoplastic materials. [10, 12] The vulcanizing agents are the combinations of crosslinking agents, accelerators, activators, and retarders. Sulfur was the first curing agent to vulcanize the commercial elastomer natural rubber. [2-3] Different curing systems for variety of elastomer are summarized in table 1. [2-3]

**Table 1.** Vulcanizing agents

| **Sr. No.** | **Elastomers** | **Class of curing agents** |
|---|---|---|
| 1 | DIENE (NR, SBR, BR, EPDM) | Accelerated sulfur and sulfur donor |
| 2 | Specially saturated types like silicone, EPR | Peroxides |
| 3 | Primary butyl rubbers | Resins (Hexamethylenetetramine (HMTA, phenolic resins, Resorcinol-formaldehyde (RF) resin, etc.) |
| 4 | Halogenated Elastomers | Metal oxides ($Fe_2O_3$, $Fe_3O_4$, $Ag_2O$, zinc oxide, etc. |

Cured elastomers are generally categorized in to WVR and WTR products. Over the past few decades, different methods and technologies for recycling of WVR and WTR products are reported. [9-11, 13] A variety of tires used in different types of vehicles such as passenger cars, trucks, buses, agricultural and off-the-road (OTR) instruments, involves different parts such as tire treads, sidewalls, and inner liner etc. The general composition of tires includes rubber along with filler, metal, textile, and other chemical additives. [14,18] and pose challenge for waste recycling system.[6, 9-10] The scrap tire problems can be resolved by following four basic choices, commonly referred to as the four Rs i.e. Reduce, Re-use, Recycle, and Recover. [15] The waste tires can be reused in the form of new products for multiple purposes such as playground, sports surfacing, rubber modified asphalts, [16] civil engineering applications, [17] doormats, gaskets, wheel chocks, and railroad crossing mates, etc. [7]

The traditional ways of recycling WTR are grinding, crumbling, re-treading, and combustion which has critical health and environmental issues. Thus, active researchers are working to develop new advanced strategies for recycling of WTR. [7] One of the environment-friendly strategies for recycling this type of material is to go through the selective breaking of the 3D crosslinked sulfur network in vulcanized rubber. [7, 9-10] This treatment is called devulcanization

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and can be defined as a process that causes the selective breakup of sulfur-sulfur (S-S) and the carbon-sulfur (C-S) chemical bonds without or minimum damaging of the carbon-carbon (C-C) backbone network. [9-10] Generally, in the recycling of WTR, some extent of energy needs to be supplied in the form of thermal and mechanical that boosts up the process to completely or partially break of three-dimensional crosslinked network formed during vulcanization. [14] Many devulcanization processes i.e. thermal, [19] mechanical, [20] chemical, [21] ultrasound, [22] thermosonic, [23] microwave, [24] thermomechanical, [25] mechanochemical, [26] thermochemical, [27] and biological, [28] are reported in the literature. [29] Along with these techniques, tire pyrolysis is another process where the crosslinked polymeric chains can be converted into small hydrocarbon molecules (tire pyrolysis oil) with the recovery of filler and steel used in tires. Present review covers waste tire and their disposal process including stockpiling, reuse and recycling. Various techniques such as physical, chemical and biological devulcanization and pyrolysis processes used for the recycling of WTR/WVR are also covered.

## 2. The current status and management of waste tires

As per the research by CMI team, the global tire recycling market is expected to record a CAGR of 3.7% from 2023 to 2032. The recycling market size is projected to reach a valuation of USD 8.32 billion by 2032. [30-34] The quantification and description of recycling processes can vary depending on the type and quality of the waste materials, the methods and technologies used, and the intended outcomes and benefits of recycling. [30]

The recycling and reuse of WTR is an essential and permanent solution to the waste tire disposal problem. However, a huge number (~1.5 billion Units) of waste tires are generated globally and a very limited number (100 million) of waste tires are recycled by using current technology. [9, 30] It is estimated that more than 50% of waste tires are discarded in landfilling or garbage without any treatment at the end of the service life. [9] According to estimation, around 4 billion units of waste tires are in landfills globally. In recent years, the research on developing new methods for recycling WTR has attracted immense interest from social, economic and environmental aspects also. Life cycle assessment (LCA), the environmental and economic impacts of recycling also compared to other waste management options, such as landfilling or incineration. [31, 33] Life cycle assessment (LCA), is a method that evaluates the environmental effects of a product or service throughout its life cycle, from raw material extraction to disposal. LCA measure energy consumption, greenhouse gas emissions, water use, resource depletion, and other environmental indicators associated with different waste management scenarios. LCA estimate the costs and benefits of recycling, such as the savings in raw materials, energy,

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and landfill space, or the revenues from selling recycled products. [31] China is majorly involved in the green tire disposal projects. One such major program called ZC Rubber Tire Recycling. Under this project, China has recycled around 400,000 waste tires, significantly reducing $CO_2$ emissions. [33,34] Another way to quantify recycling is by measuring the amount of waste materials that are diverted from landfills or incinerators and reused in new products. This can be expressed as a recycling rate, which is the percentage of waste materials that are recycled out of the total amount of waste generated. [33-34]

Tires are made of non-fusible or refractory elastomers, which take hundreds of years to break down to the point and affect the growth of plants in the soil. The utilization of waste tires in the form of crumb rubber or rubber powder used in heat energy or production of tire-derived fuel is the mainstream recycling method in the U.S. and EU. Japanese prefer to recycle tires in the form of thermal recycling for energy sources in paper manufacturing, chemical factories, cement factories, steel manufacturing, etc. Recycle process improvement and technological innovation are focus of attention by academic and industrial institution. [33-34]

## 2.1 Environmental concern of waste tire disposal

The waste tire industry has grown at fast pace in the last 30 years. This also resulted in accumulation of waste tires.[31] Generally, WVR & WTR do not decompose and can release harmful chemicals and gases into the environment. Waste tires emit greenhouse and other harmful gases like methane when exposed to sunlight, contributing to global warming and climate change. Waste tires can catch sudden fire and produce toxic black smoke that contains chemicals used in tire manufacturing and also contaminates groundwater. To prevent these environmental problems, waste tires are recycled and reused in products such as rubber-modified asphalt, automotive products, tire composites, and tire-derived fuel. [31] Recycling tires can also save natural resources and reduce energy consumption. However, the demand for scrap tire recycling is not keeping pace with the supply, and more efforts are needed to find and develop new markets for recycled tire products. [31-32]

## 3. General methods of handling of WTR products

**3.1. Stockpiled and landfilling.** WTR has a long life and non-biodegradable behavior due to the highly cross-linked vulcanized network creating challenges, for the disposal.[7, 9-10] Tire biodegradability is very low and depends on several factors, such as the type and composition of rubber, the presence of additives, the degree of weathering, and the environmental

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conditions. [35] The biodegradation process can result in surface erosion and changes in the properties of tire particles. [35] Some tire constituents, such as natural rubber and treated distillate aromatic extracts, have higher biodegradability than others, such as synthetic rubbers and carbon black. However, the biodegradability of individual constituents is reduced when they are compounded into tires. Therefore, tire biodegradability is not a sufficient solution for the disposal of waste tires. Recycling and reuse of tire materials are preferred options for minimizing their environmental impact. [9-10, 35] In general, traditional methods for disposal of WTRs are stockpiling, dumping, or landfilling, which have very dangerous effects on human health and the environment. [35, 36] The stockpiled tires can become the perfect platform as breeding places for mosquitoes and other harmful insects/reptiles therefore creating health hazards. [35] On the other hand, in the landfilling process, these tires can consume large volumes of valuable space. The stockpile tires are also the major reason for fueling inextinguishable fires and due to sulfur crosslink generate toxic sulfur oxide gases along with $CO_2$/CO. Also, the harmful polymer chains and aromatics of WTRs are the major source of emission along with an increase in the zinc level in soil. [35] Besides these drawbacks, landfills and stockpiles of waste tires are also renowned for the leaching of toxic chemicals/gases into the earth, water, and surroundings as long-term effects. Also, at high temperatures, the rubber chains break down into oily petroleum products which are the major pollutants for the soil and groundwater.[15, 35-36] Therefore, several countries in North America and Europe have banned stockpiling and landfilling of whole tires and made recycling mandatory for these wastes. [15, 35]

**3.2. Combustion**. The combustion process directly uses WTRs as fuel in incinerators because these are excellent materials for energy recovery with high calorific values. The calorific value of tire reaches to 30-40 MJ/ KG which is higher than those of coal and other solid fuel. [37] The reduced power production cost and maximum heat recovery are the advantages of the tire combustion process. The demerits of the combustion process are no material recovery, capital investment is high, the need for flue gas cleaning, and the emission of various toxic gases with high operating costs.[38-39] Waste tires can be used as fuels in cement kilns. More attention is needed to ascertain the environmental impacts of this process, the emission of polycyclic aromatic hydrocarbon (PAH), which are well-known carcinogenic material. In addition to this, the heavily toxic smoke released from tire fires can cause poor air quality, result in the pollution of incredibly toxic gases, and reduce visibility in the surrounding area.[11, 37] W.-G. Pan et. al. reported the thermogravimetric and kinetic analysis of the co-combustion of waste tires and

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coal blends. [37] The combustion characteristics of the tire powder, bituminous coal and their blend co-combustion were studied. The combustion kinetics of tire powder shows that an increase in the ratio of tire powders with coal leads to a decrease in the activation energy in the temperature range of 349−465 °C. [37]

**3.3. Retreading of old tires.** In the tire industry, a lot of development has taken place for the manufacturing of high-standard tires using premium technologies, to continuously improve performance. [40] It is important to consider the use of high-quality tires frequently not only in 'first life', but in their second life too. To reuse tires in their second life the retreading tire industry is also growing, where the new treads are applied using specialized tools. [40] The retreading process is similar to the new tire manufacturing process with a lower (30-50%) consumption of the rubber material. The quality testing of retreaded tires revealed that it is quite safe and can be used in all kinds of vehicles such as taxis, trucks, school buses, military vehicles, etc. [40] Along with the reuse of old tires, the process is cost-effective as compared to the new tire and multiple times waste tires used for the retreading process. However, it is a labor-intensive process with compromises to the quality of the product.[41] On the other hand, the process is extremely hazardous to the worker due to the emission of volatile organic compounds (VOCs). [35, 42] The tire retreading can be achieved by hot and cold retreading process. [40] In the hot retreading process, the tire is placed in a suitable mould, and air pressure is maintained so that it expands uncured material at a temperature of 150 °C. In this process, for every size of tire, a new mould is required so it is a costly process. [40] In the cold process, no mould is used. In the cold process, a temperature of 100 °C used for replacing the tire lining. This is cost cost-effective process and increases the life cycle of the tire. [40]

## 4. Recycling Technologies

### 4.1. Pre-process treatment

Recycling of 'end of life tyres' (ELT) is a major environmental concern because of their large volume of production (15 billion units) and non-biodegradable properties. [43-45] The first pre-process treatment involves the separation of steel and the fabric components from WTRs. However, the process is extremely complicated and requires heavy machinery due to the tire's strong physical properties. [45] The present discussion is limited to only recovery of waste

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vulcanized rubber. After the removal of steel and the fabric components, the further sub step is the reduction of the size by grinding of WTR to produce ground tire tuber (GTR) using various techniques. Different methods for the grinding of WTR into fine particles are as follows.

**4.1.1. Ambient grinding.** It is simple mechanical process to reduce the particle size of the vulcanized rubber by mechanical forces at ambient temperature. In this process, the quality of the ground rubber is controlled by the number of grinding steps and the type of mills used. This process releases a huge amount of heat that can oxidize and degrade the crumb rubber. Also, in producing very fine mesh-size particles this process needs a huge cost. [44]

**4.1.2. Cryogenic grinding process.** It is a faster and cleaner way to produce rubber crumbs with smaller particle sizes. [46] This process is carried out at a very low temperature (liquid nitrogen) by first freezing the rubber followed by crushing the frozen rubber. The surface of the ground rubber obtained by the cryogenic process is relatively smooth with a broader range of particle size distribution than the ambient process.

**4.1.3. Wet grinding process.** In this method, very fine crumbs (10-20 μm) can be produced by grinding the rubber involving the addition of water as a lubricant and cooling agent. For milling highly resistant and large tires from trucks, the process consists of using a water jet that results in highly pure crumbs with a large specific surface area. This process can be considered as an environment benign method due to low energy consumption and recycling of water using in a closed-loop system. [47-48] The obtained grinded product further needs to dry.

## 4.2. Rubber devulcanization and depolymerization processes

Elastomers such as cured rubber have cross-linked C-S networks, which provide the strengths to the materials and obstacles to a simple recycling process in comparison to the thermoplastics. [49] Therefore, to recycle such types of cross-linked materials, the devulcanization process is required. In this process, mainly the cleavage of the carbon-sulfur (C-S, 273 kJ/mol) bond or sulfur-sulfur (S-S, 227 kJ/mol) bond takes place with retaining the carbon-carbon (C-C, (348 kJ/mol) bonds intact, in presence of specific chemicals or other driving forces such as thermal or mechanical methods under varying conditions. The selective cleavage of C-S or S-S bonds while keeping the C-C bond intact is highly challenging due to the very close energy difference between these bonds. [24] In vulcanized rubber, due to 3D crosslinked networks these vulcanizates become robust, hard, infusible, and insoluble in any solvent medium. [50] Successful devulcanization could be measured by analyzing the soluble content and crosslink density of

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the processed material. Hence, the precise degree of devulcanization or loss in crosslink density of vulcanizates can be measured by measuring the differences in crosslink density of rubber before and after treatment. Generally, the acceptable range of the degree of devulcanization is about 50-70%. [19] For providing sufficient energy to break selective bonds for the devulcanization of WTR various methods such as physical, chemical, and biological devulcanization processes have been used (Fig. 1). On the other hand, in the presence of suitable catalysts some extent of C-C bonds also undergoes for cleavage along with C-S and S-S bond, due to very low energy difference between C-S and C-C bonds. For depolymerization or degradation of polymeric chain, selective catalysts like Grubb's metathesis catalysts can be used that attack the double bond center and result in low molecular weight polymer. The depolymerization also results value-added products with reduced molecular weight.

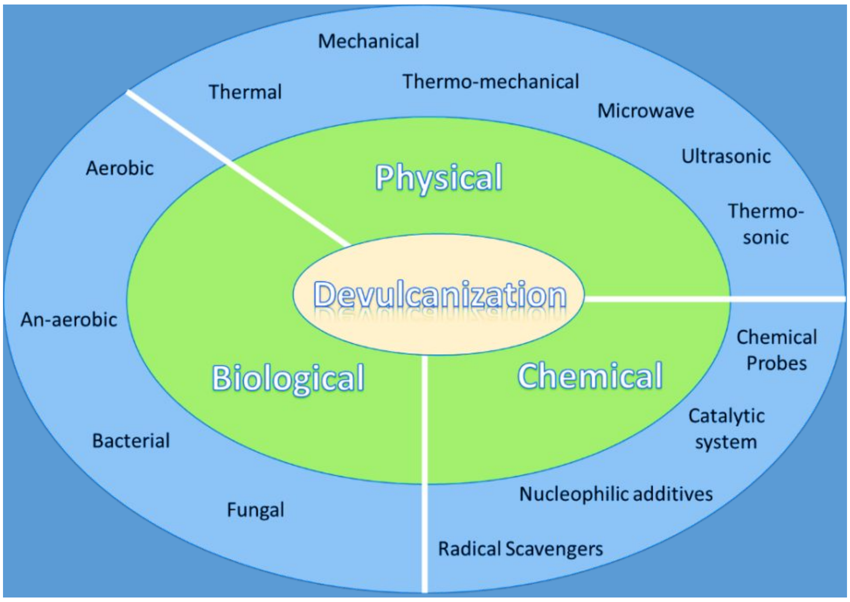

**Fig. 1**. Various methods used for the devulcanization of waste tire rubber.

### 4.2.1. Physical devulcanization technology

The disposal and accumulation of WTR have a significant negative impact on the development of a circular economy and sustainable environment. [51] Due to several difficulties in recycling waste tires, most tire industries are not showing interest in devulcanization technologies which obstacle to the commercialization of the methods. For reaching the goal the selective breakage of carbon-sulfur linkage in waste tire rubber without or with little polymeric scission is crucial

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and may be performed in the presence of physical forces such as thermal, mechanical, thermo-mechanical, microwave, ultrasonic, and thermosonic methods. [51]

**4.2.1.1 Thermal devulcanization processes.** The techniques that require heat as an energy source to break the S-S and C-S linkage are known as thermal devulcanization methods. As discussed earlier the types of bonds present in vulcanized rubber and their bond energies are crucial for effective devulcanization, where only C-S and/or S-S bonds are cleaved. [9-10, 51] Various scientific efforts are made to develop a method for recovering WTR or WVR by thermal methods without breaking C-C bonds in the chain. New processes for the devulcanization of cured rubber have been patented by Goodyear tire & Rubber Company. [52-53] The invention suggested that cured styrene butadiene rubber (SBR) can be devulcanized by heating at different temperatures ranging from 150 to 350 °C under high pressure of 21 Megapascal (MPa) in presence of a suitable solvent like alcohols. [53] The devulcanization process carried out below 300 °C temperature resulted in a high molecular weight of devulcanized rubber and did not significantly change the microstructures. The results revealed that devulcanization in 2-butanol at 300 °C showed a maximum conversion of up to 93% over other alcoholic solvents (Table 2). In addition, the recovered rubber can be compounded with virgin rubber and is used for the preparation of useful articles in substantially the same way as for the original rubber.

**Table 2**. The percentage conversion of cured SBR to devulcanized SBR in different alcohols & temperatures. [53]

| **Examples** | **Alcohol** | **150 °C** | **200 °C** | **250 °C** | **300 °C** |
|---|---|---|---|---|---|
| 1 | 2-Butanol | 38% | 82% | 90% | 93% |
| 2 | Methanol | 2% | 3% | 4% | 7% |
| 3 | Ethanol | 2% | 4% | 9% | 20% |
| 4 | 1-Propanol | 3% | 16% | 43% | 69% |
| 5 | 2-Propanol | 2% | 7% | 13% | 25% |
| 6 | 1-Butanol | 4% | 19% | 57% | 86% |
| 7 | Isobutyl alcohol | 2% | 10% | 44% | 74% |
| 8 | 1-Pentanol | 3% | 11% | 42% | 89% |
| 9 | 4-Methyl-2-pentanol | 2% | 11% | 33% | 68% |

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Further, Wang and coworkers have developed a thermal-oxidative reclamation process for recycling and reuse of GTR by using a newly designed dynamic reclamation reactor. This reactor has an adjustable pulse air input at 200 °C for four different oxidative periods, 5 min, 10 min, 15 min, and 20 min which resulted in recovered GTRs (RGTRs) with four reclamation degrees. [54] The results revealed that cross-linked network can be effectively destructed by this process in the presence of air at 200 °C. The sol fractions of RGTRs were measured with a Soxhlet extraction method using toluene as the solvent. The analysis suggested that sol fraction increases, while molecular weight and PDI decrease significantly on increasing the stirring time. The reclamation via either cross-link network scission or main chain scission has been confirmed by theoretical Horikx's method. The analysis showed that experimental points are all positioned above the main chain scission curve, meaning that the reclamation is dominated by main chain scission under high temperatures. [54] This process is catalyst-free and carried out in the complete absence of any chemical reagent. The RGTR with a high reclamation degree showed good dispersibility and reinforcement in natural rubber (NR) compared with other traditional reclaimed rubber. The addition of 10 to 40 wt% of RGTR in NR had no adverse effect on the mechanical properties, instead improved the thermal aging resistance of NR. [54]

**4.2.1.2 Mechanical devulcanization processes.** The mechanical process for devulcanization of WTR/WVR is a crucial technique to get the devulcanized rubber under high shear strain, at a given temperature in either the presence or absence of chemical reagent. The process can be carried out in a high-pressure internal mixer or extruder machine. Some additives such as oils or reclaiming agents could be added during the process. In the last decade, various research groups have investigated the thermomechanical and mechano-chemical devulcanization processes for different types of waste rubbers. [55-58] Suzuki et.al. and Mouri et. al. have performed thermomechanical recycling of ethylene-propylene-diene-monomer (EPDM) in an extruder. [6] They proposed a mechanism for the thermomechanical devulcanization process where the energy required to break the mono-sulfur links is greater than that required for poly-sulfur links. On applying heat to vulcanized rubber inside the extruder, the poly-sulfur links are broken first and convert the structure to mono-sulfur links. Further, energy increases on applying the shear stress to break the mono-sulfur links too. However, the S-S bond breaking is not selective, so some main chains have also been broken by the shear stress action. [55-58] The process leads to the formation of carbon disulfide ($CS_2$), sulfur dioxide ($SO_2$) and hydrogen sulfide ($H_2S$) gases. Further, Seghar et. al. has carried out the recycling of natural rubber

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industry waste by thermo-mechanical devulcanization process in a twin-screw extruder with different barrel temperatures range from 80 - 220 °C. [24]

Various analytical tools such as crosslink density, soluble fraction, Mooney viscosity and Horikx diagram showed the extent and quality of devulcanization. The results revealed that the best devulcanization quality with more selective sulfur bond scission is achieved at a lower input temperature. [24]

Recently, Simon et. al. have used a co-rotating twin-screw extruder for thermomechanical devulcanization of GTR. The results revealed that at lower temperature, selective cross-link scission is observed, while increase in temperature results degradation of polymer chains. In addition, this recovered devulcanized GTR (dGTR) is compounded with NR that showed a decrease in tensile and tear strength that agree with Horikx's analysis, i.e. the greater the degradation of dGTR, the more mechanical properties were impaired. [59]

In addition, the mechanochemical devulcanization of a ground rubber vulcanizate is carried out in the presence of a dual-function devulcanizing agent bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT). It is a well-known silica-coupling agent for the dispersion of silica filler but is also treated as a devulcanizing agent in the recovery of waste tires during mechanical treatment. Ghosh et al. have developed a cradle-to-cradle approach to simultaneous devulcanization and chemical functionalization of waste styrene butadiene rubber vulcanizate (SBR) using a thermo-mechanical-method in the presence of sulfide-based multifunctional devulcanizing agent. [60] The devulcanized SBR (DeVulcSBR) is prepared by the treatment of ground SBR (GSBR) vulcanizate with TESPT as a multifunctional disulfide-reclaiming agent in an open two-roll mill. The resulting material showed a significant reduction in cross-link density with an increase in sol content in devulcanized styrene butadiene rubber (DeVulcSBR) from GSBR. The FT-IR spectral analysis (600-4000 $cm^{-1}$ range) revealed that homolytic scission of S-S bonds (bond energy 22.8 Kcal/mol) takes place along with the attachment of fragmented TESPT with DeVulcSBR. The characteristic FT-IR peaks of TESPT for Si-O stretching appeared at 1165 $cm^{-1}$, 1071 $cm^{-1}$, 955 $cm^{-1}$ and 1242 $cm^{-1}$ for symmetric Si-C-H bending. [60] In DeVulcSBR, absorption peak appears at 1165 $cm^{-1}$, 1078, 965 $cm^{-1}$ for Si-O stretching and 1242 $cm^{-1}$ for symmetric Si-C-H bending, indicating the chemical attachment of fragmented TESPT in DeVulcSBR. [60] The resulting compound reinforced with nano-silica is re-vulcanized-to-prepare-new rubber composite (SBR/$SiO_2$-DeVulcSBR). The curing and processing characteristics and mechanical performance are further compared with those of conventional silica-based green tire formulations. The performance studies of SBR/$SiO_2$-DeVulcSBR composite suggested that 30 phr silica-loaded composite showed superior

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properties over other composite ratios. The tensile strength and elongation at break of silica-30 vulcanizate are 10.34 MPa and 451% respectively, whereas the respective values of silica-30(control) vulcanizate are 4.34 MPa and 336% respectively. Dynamic mechanical analysis reveals that room temperature storage modulus increases and the highest tan δ at Tg decreases with silica loading in silica-30 vulcanizate due to strong rubber-filler interaction. [60]

Further, Ghorai et. al has also demonstrated a devulcanization process of natural rubber (NR) vulcanizate in an open roll mixing mill by using TESPT, a novel devulcanizing agent. First Grounded NR (100 g) was mixed with various proportions of TESPT in presence of spindle oil and kept the mixture for 24 h for soaking prior to devulcanization in an open two roll mill for different time intervals. [61] The characterizations revealed that the degree of devulcanization is depend on devulcanization time and concentration of TESPT. The TESPT concentration is optimized as 6 mL/100 g for the high extent of devulcanization and vulcanizate is designated as DeVulcNR-6. The extent of devulcanization was monitored by various analytical measurements such as sol and gel content, crosslink density, molecular weight and Mooney viscosity of devulcanized rubber. [61] In addition, DeVulcNR is prepared using 6 mL TESPT and designated to optimize the devulcanization time. Differential scanning calorimetry (DSC) analysis revealed that with sol content the fraction of immobilized polymer chains decreases due to increasing molecular weight between crosslinks. In addition, DeVulcNR is used in re-vulcanization with or without silica filler as a reinforcement agent. The resulting compounds showed that the mechanical properties e.g. modulus at 50% and 100% elongation, tensile strength, and elongation at break increase with devulcanization time up to 40 min. [61]

**4.2.1.3 Microwave assisted devulcanization processes.** The devulcanization of waste rubber using the microwave irradiation process is one of the most explored and crucial methods. In this method, the molecules absorb the microwave radiation when allowed to keep under the microwave's electromagnetic field radiations with specified wavelength (from 1 to 1,000 mm) and frequency (300 MHz to 300 GHz) respectively, [19, 62] and convert the radiations to heat or thermal energy to cleave the target bond. For the selective cleavage of bonds, the material's ionic conductivity or material polarity plays a crucial role. [29] Microwave-assisted devulcanization process is one of the most efficient processes having several advantages like uniform heating in comparison to traditional heating methods, [63-65] no chemicals treatment, [66] high productivity of devulcanized rubber, [67] and easy modification of the process parameters. [68] The devulcanization degree increases with microwave energy employed up to 1.389 KJ Kg$^{-}$

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[1]. The maximum devulcanization degree reached to 95% (high yield). [67] In the traditional pyrolysis process, heating carried out from the outside to inside the tire materials. On the other hand, in this process, irradiation of microwaves and corresponding magnetic field occurs uniformly inside & outside of material simultaneously. Moreover, microwave irradiation reduces the activation energy required for the thermal decomposition by loosening the bond. The advantage of microwave assisted pyrolysis over conventional heating is direct transfer of heat into material, allowing for consistent heating of irregular waste fragments. This causes the high productivity of devulcanized rubber. [31] Microwave-assisted devulcanization has first time introduced by Goodyear Tire & Rubber Co. as a patented document, [65] where GTR with 6-10 mm particle size has been treated under microwave with the frequency range of 0.915 or 2.45 GHz. The temperature of the process is rapidly increased from 260 to 350 $^{o}$C, which may be associated with the polarity of carbon black filler, instead of the GTR. Aoudia et al. reported a method of devulcanization of GTR to break the S-S and C-S bonds resulting in devulcanized GTR (DGTR) using microwave electromagnetic energy. [67] Crosslink densities of the devulcanized materials have been analyzed by swelling analysis that showed a significant degree of devulcanization. Further, the cleavage of bonds has been confirmed by FT-IR (400-4000 cm$^{-1}$). FT-IR analysis in the range from 750 to 400 cm$^{-1}$ revealed a strong decrease of peak heights of C-S and S-S bonds confirming the breakage of vulcanization link. [67] The resulting DGTR has been used to prepare the epoxy-based composites. The mechanical property analysis results that the epoxy composites compounded with DGTR showed superior behavior over the GTR-compounded epoxy composite. [67]

Further, deSousa et al. has explored GTR devulcanization by microwave treatment with different exposure times (3.0-5.5 min). [68] The thermal stability of devulcanized samples and the revulcanization behaviour were correlated to structural modifications that occurred during the devulcanization process, where four similar degradation steps take place those are temperature dependent. In the first step of heating from 25 to 300 °C, decomposition of the processing oil and additives followed by decomposition of NR over the temperature range of 300 to 400 °C. [62] While the decomposition of SBR taken much higher temperature range from 400 to 550 °C. Finally, in the fourth step, the carbon black degradation appears at the highest temperature of 550 to 800 °C. All these steps occur under an oxidizing atmosphere on the microwave exposure at different times. [62]

Further, Saron and co-workers have vulcanized the SBR in the presence of various vulcanization agents with variable amounts of carbon black (0-100 phr). [69] The vulcanized rubber was treated under microwave irradiation for devulcanization and analyzed the chemical

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modifications. The microwave treatment causes cross-link breaks mainly in the polysulfidic bonds as well as the decomposition of chemical groups containing sulfur attached to the chemical structure of SBR, while the chemical bonds of higher energy such as monosulfide bonds remain preserved. [69] Also, the results suggested that only SBR containing high carbon black content shows some portion of devulcanized material, while the SBR with lower carbon content shows an increase in cross-link density. [69]

### 4.2.2. Chemical devulcanization technology

Besides the physical methods of waste rubber recycling, the chemical devulcanization process is another essential technique, where the waste rubber is treated with active chemicals, catalysts as devulcanizing agents to cleave the C-S & S-S linkage in the cured rubber network. Along with the C-S / S-S bond cleavage, the scission of the polymeric chain in the presence of appropriate catalysts is also important for the recovery of waste elastomers. [51] Chemical devulcanization generally requires thermal and mechanical energy to accelerate the treatment. [51,70] A synergistic improvement has been observed in the performance of chemical treatment due to these additional (thermal & mechanical) processes. Compared to other devulcanization techniques, chemical devulcanization appears to be the most common technique as it provides a large selection of possible promising agents. Generally, organic/inorganic chemicals such as aliphatic, alkyl phenolic sulfides, amine, aromatic mercaptans, zinc salts, di-sulfide and other unsaturated compounds are used for the chemical devulcanization process. [70]

Chemical devulcanization and thermochemical pyrolysis both are very important recycling processes. In normal condition, WVR can not be melted and reused due to their three-dimensional mono-, di-, and poly-sulfidic bonds that are formed during vulcanization. Thus, in chemical devulcanization, there is selective breaking of sulphur bonds and breakdown of cross-link structure of WVR. This allows the reuse of rubber reprocessed and form the new rubber products. The devulcanization process is particularly important for recycling tire-derived rubber, which is challenging to repurpose due to its composite nature. [30-32] On the other hand, in thermochemical pyrolysis, waste vulcanized tires (WVR) decomposed at higher temperature (300-600 $^{o}$C) under inert condition. The final products of the process are tire pyrolysis oil, carbon char and the gases.[30-32] These products are used as energy sources and starting material for other valuable products.

In chemical devulcanization, the disulfide and mercaptans are the important sulfur-containing reagents that are frequently used for waste rubber devulcanization. In this way, De et. al.

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devulcanized GTR in a two-roll mill using tetra-methyl-thiuram disulfide (TMTD) as a devulcanizing agent and resulting vulcanizates were blended with virgin NR and studied the physical and mechanical properties.[71] The blending of GTR at 20% showed a slight reduction (7%) in tensile strength that reaches up to 46% further increasing the GTR ratio to 60%. In addition, blending of GTR with virgin SBR,[72] showed an increase in Mooney viscosity on increasing the GTR content. The mechanical properties such as modulus, tensile strength, and elongation at break were increased due to the blend's higher resistance to swelling.

Besides the devulcanization of WTR and WVR, depolymerization is also a crucial process, where the carbon backbone chain also undergoes cleavage along with C-S bonds. In this regard, Abbas et. al. have developed a chemical-initiated method for the recycling of waste natural rubber via a degradation/de-polymerization approach. [73] First, the vulcanized NR was degraded following the cross-metathesis process with ethyl acrylate acting as a cross-metathesis agent in the presence of Grubbs' catalyst-producing enolate end-capped oligo-cis-isoprene. The resulting liquid oligomer contains a highly active single electron-deficient double bond, which undergoes further transformations. The electron-deficient oligomers underwent a cycloaddition reaction with cyclopentadiene resulting in norbornenes via ring-opening metathesis polymerization (ROMP). The characterization data of the main-chain unsaturated polymer bearing oligo-1,4-cis-isoprene side chains suggested the thermal stability of the polymer with a glass transition temperature of -60 °C. Further, the polymer degradation product, corresponding norbornene derivative and resulting polymer Poly2 have been characterized by $^1$H NMR spectral studies. [73]

In addition, Ionic liquid (IL) as a solvent has been explored for various polymerization processes and more particularly executed for ring-opening metathesis polymerization (ROMP) reaction. Dez and coworkers has used IL for the depolymerization of natural rubber. [74] They reported a controlled degradation process for NR depolymerization by olefin metathesis reaction in IL medium i.e. trihexyl(tetradecyl)phosphonium chloride (Cyphos101) and N, N-dioctyl imidazolium bromide ($C_8C_8$ImBr). The results revealed that the low dispersity acetoxy telechelic polymer are produced in high yield under low ruthenium (Ru) content. The reaction is feasible in IL phase under low temperature, low IL quantity, and shorter the reaction time. [74]

Moreover, Gutierrez et. al reported cross-metathesis reactions to the synthesis of terpene-terminated oligomers from NR using alpha-pinene with a high yield ranging between 80 and 90%. [75] The metathesis reaction was carried out in the presence of ruthenium-based second-

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generation Grubbs catalyst under solvent-free conditions. The molecular weight of the product has been controlled by changing the alpha-pinene and NR ratio. [75]

Further, Smith et. al. have demonstrated a new method for the reprocessing of cross-linked rubber by catalytic disassembling of polymer chains. [76] In polybutadiene (PB) rubber, the crosslinked network has been cleaved using first and second-generation (G1 and G2) Grubbs' ruthenium catalysts resulting in a soluble product via cross-metathesis (CM) reaction. Generally, the polymer reacts with another olefin, such as a diester (e.g. dimethyl maleate), accelerate which is known as chain transfer agent in presence of Grubbs' catalyst to scission polymer chain at the double bond position. The analytical results suggested a significant reduction in molecular weight to around 2000 g mol$^{-1}$ with a breakdown of the cross-linked networks. More interestingly, the reaction can be performed at RT within 2.5 h, while increasing the reaction temperature and time increases the extent of polymer chain cleavage. Similarly, the reaction has also been performed and analyzed properties for cured SBR which is a major component in tire manufacturing. [76]

Periodic acid is a strong oxidizing agent and can be used for the degradation of polymeric chains. Phinyocheep et. al. has demonstrated a process for epoxidized natural rubber (ENR) degradation in the latex phase using periodic acid at 30 °C. [77] First NR was epoxidized in the latex phase using performic acid, generated in situ by the reaction of hydrogen peroxide and formic acid. The resulting ENR latex was subsequently degraded into low molecular weight epoxidized liquid natural rubber using periodic acid. The results revealed that increasing the concentration of periodic acid showed a faster reduction in the molecular weight. Based on $^1$H NMR spectral analysis showed that the epoxide content in both the epoxidized liquid natural rubber (ELNR) and ENR obtained was about the same. Further, the carbonyl formation is confirmed by the FT-IR analysis with an increase in the carbonyl signal on increasing the reaction time or increasing the amounts of periodic acid employed. [77]

Hassan et. al. reported an eco-friendly method for reclaiming of GTR at low-temperature oxidation under the swollen action of soybean oil (SBO). SBO contains double bonds in structure so it can not only participate in the swelling of GTR but also be involved in crosslinking. [78-79] The highly reclaimed rubber with a high degree of reclamation can be obtained by swollen action of SBO, GTR in situ reclaimed GTR followed by curing into a reactive plasticizer (RP) through a free-radical chain reaction between activated molecular rubber chains and soybean oil. [80] Further blending and curing of reactive plasticizers with

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SBR/silica compound explored its re-vulcanization ability and multifunctional additive behavior.

Among the chemical methods, the supercritical carbon dioxide ($ScCO_2$) jet pulverization methods a new technology using a green and efficient reaction medium for WTR/WVR devulcanization or foaming. This method showed an environment benign strategy because of the chemical inertness, non-toxicity, and inflammability of used $CO_2$.[81-85] Wang et. al. represented reclamation of WTR using $ScCO_2$ jet pulverization technology. The analysis revealed that devulcanized GTR with smaller particle size and rough surfaces can show selective breakage of crosslinks in larger reaction time with low jet pressure in $ScCO_2$ jet pulverization. Thus, this process can be an excellent choice for WTR reclamation concerning both size reduction and rubber devulcanization. [86]

The other chemical devulcanizing agents are disulfides, polysulfides, TESPT, amines etc. The organic reagents can be act as initiators for crosslinks cleavage. The devulcanization carried by either through radical or via nucleophilic mechanism. [132] In this, de-crosslinking of sulfur linkage in partially or total homolytic cleavage of mono-, di-, and polysulfide crosslinks which generate macromolecular free radicals. To prevent the recombination of these radicals, various chemical agents like diphenyl disulfide (DPDS) are added during reclaiming of rubber. [132] The various devulcanizing agents via radical mechanism and nucleophilic mechanism are reported in Table 3 & 4. [132]

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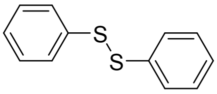
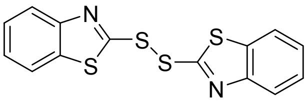
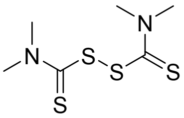
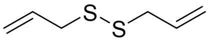
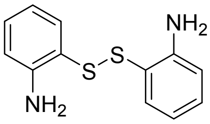
**Table 3.** Chemicals reagents for chemical devulcanization via radical mechanism[132]

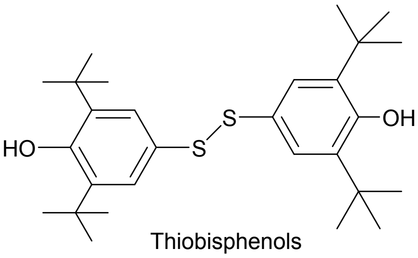

Diphenyl disulfide (DPDS)

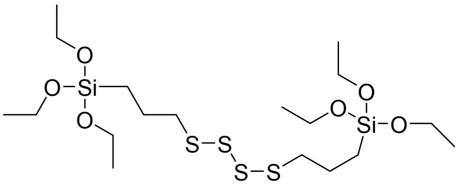

2,2'-Dithiobis(benzothiozole) (MBTS)


Tetramethylthiuram Disulfide (TMTD)


Diallyl disulfide (DADS)


Di(2-aminophenyl)disulfide (APDS)


Thiobisphenols


bis[(3-triethoxysilyl)propyl]
tetrasulfide (TESPT)

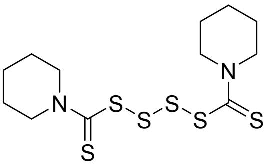
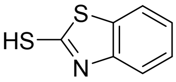
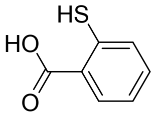
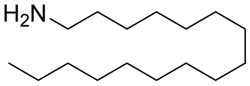
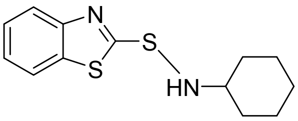

Bis(pentamethylene)thiuram
tetrasulfide (DPTT)

**Table 4.** Chemicals reagents for chemical devulcanization via nucleophilic mechanism [132]


Ercaptobenzothiazole (MBT)


Thiosalicylic acid


1-Hexadecylamine (HDA)


N-Cyclohexyl-2-
benzothiazolesulfenamide (CBS)

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The other chemical methods include the oxidation of sulfur bonds using benzoyl peroxide, nitric acid ($HNO_3$) were also studied for effective devulcanization processes. [56]

### 4.2.3. Biological devulcanization technology

Tire biodegradability is the process of tire materials being broken down by microorganisms into simpler substances. Tire biodegradability is important for reducing the environmental impact of waste tires, which can pollute the air, soil, and water with harmful chemicals and microplastics. [35] Vulcanized elastomers (WTR & WVR) are considered resistant to microbial attack. However, in limited cases, devulcanization can be achieved through microorganisms such as bacteria and fungi via selectively breaking the S-S bonds. [28-29, 51] Biological desulfurization by microbes is considered one of the safe environment friendly and economical alternative processes, which results in more selective devulcanization over the chemical and physical processes. [28-29] However, this emerging process has several advantages but due to slower reactivity, it is not considered as the preferred method by the industries. In this process, a maximum amount of 4.7% of sulfur can be removed in a 40-day process. [51, 87] Various methods of bacterial devulcanization on different elastomer latex are reported in the literature in aerobic or anaerobic environments with different strands of bacteria. In anaerobic bacterial devulcanization, sulfur-reducing bacteria are incorporated, while in aerobic conditions, sulfur produces sulfone groups on the elastomer surface. [88-89]

Raghavan et al. have first time performed a bio-based bio desulfurization of rubber material containing 15.5% of sulfur by Thiobacillus ferrooxidans and T. thiooxidans microorganism. [88] The sulfate concentration in rubber samples after experiments is measured as 350 ppm.

In 2011, Li and coworkers demonstrated the microbial desulfurization of ground tire rubber (GTR) by Thiobacillus ferrooxidans, obtained from the soil of an iron mine having a strong sulfur-oxidizing capacity. [89] The desulfurization process GTR has been carried out in a modified Silverman medium for 30 days during the cultivation of T. ferrooxidans. The increasing concentration of sulfate ions in the medium clearly indicated that the sulfur available on the surface of GTR is oxidized. The NR composite with desulfurized GTR (10-40 phr loading) showed superior mechanical properties with lower crosslink density in compare to the non-desulfurized GTR composite. [89]

Further, Yao et al. selected a microbe named Alicyclobacillus sp. with the desulfurizing capability to recycle waste latex rubber (WLR) and observed the microbial desulfurization

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activity towards WLR, and explored the tentative mechanism.[90] Alicyclobacillus sp. microbe is sensitive towards the rubber additives in WLR, so the concentration of WLR optimization is an important parameter to receive good results. The Optimization of the effect of the amount of WLR on the growth of Alicyclobacillus sp. was studied. The 2% and 5% (w/v) of WLR concentration in the medium showed the best growth of microbes.[90]

The devulcanization of WLR reported by Tatangelo et al. using Gordonia desulfuricans DSM44462 and Rhodococcus sp. AF21875 bacteria. [51, 91-92] The treatment was performed in salt medium at 30 °C for 1 day. The strand DSM44462 was more effective than AF21875, as it resulted in a higher sol content. [91-92] Similarly, Kaewpetch et al., investigated the devulcanization of natural rubber using Bacillus cereus TISTR 2651 bacterial strain. It was observed that bacteria can selectively cleave sulfide bonds in the first 10 days. [93] Furthermore, a white rot basidiomycete, Ceriporiopsis subvermispora can degrade WVR on a wood medium. [94]The desulfurization process depends on the time, if the time increases the swelling value of desulfurized waste latex rubber (DWLR) increases, with a reduction in crosslink density. Further, significantly improved mechanical properties of natural rubber (NR)/DWLR composite have been observed over those of the NR/WLR composite. Though biological devulcanization processes are Safe, economical, and environmentally friendly, still far from being applied industrially, due to the low devulcanization ratio, and the risk of bacteriological contamination.[20, 51, 95]

## 4.3. Pyrolysis of waste tires

In tire pyrolysis, the molecular breakdown of waste tires occurs under oxygen free environment where the heat is supplied to the reactor to drive the thermal decomposition of tires. [32, 96-98] The optimum temperature for pyrolysis is between in the range of 250-600 ℃ depending upon the condition of pyrolysis resulting in various crucial products. [7, 9] In some cases, the pyrolysis carried out up 1000 °C. The conditions of pyrolysis process (temperature, heating rate, residence time, pressure etc.) depends upon the characteristics of feedstocks (composition of tire, particle size & source of material) and final characteristics of products. For example, the pyrolysis of tire without catalyst and chemicals occurs at higher temperature range of 350-600 ℃. On the other hand, pyrolysis under catalytic condition achieved at lower temperature of 300-450 ℃. Similarly, microwave assisted, chemical devulcanization, hydrothermal pyrolysis process at high pressure carried out at lower temperature. [32] The final product of tire pyrolysis

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generally converted into liquid or pyrolytic oil, solid residue, and combustible gases with the recovery of steel.

The major product of pyrolysis is thermal pyrolysis oil (TPO) achieved in 40-60 wt% and can be used as alternative fuel or preparation of carbon nanotubes (CNTs). [7, 9, 51] The second major component is thermal pyro-char (TPC, 30-40 wt%) containing high carbon content and can be used to make porous activated carbon, useful in various energy purposes like Na or Li-ion batteries, super capacitors etc. [99] One another product is thermal pyro-gas (TPG, 5-20 wt%) containing mainly non-condensable gases i.e. $H_2$, CO, $CO_2$, $C_2H_4$, and $C_3H_6$, having high gross heating value and can be used as a fuel source to heat the pyrolysis reactor. [99-100] The properties of end product of pyrolysis of waste tire is depend upon the operational parameters such as pressure, temperature, feed particle sizes, heating rate, catalysis, type of reactor, residence time, and flow rate of inert carrier gas. These parameters affect the pyrolysis process in terms of product distribution and quality of end products. [96-98]

## 4.3.1. Factors affecting the pyrolysis process and product

Pyrolysis of the waste tire is a crucial process and is mainly influenced by several parameters like temperature, pressure, heating rate, and the presence or absence of catalysts. The used temperature and heating rate can significantly affect both the quantity and the quality of pyro-products. Usually, the pyrolysis process for WTR is carried out in the range of 400 to 500 °C, while varying the temperature affects the quality and percentage yield of the products i.e. tire pyrolysis oil (TPO), tire pyrolysis gas (TPG), and tire pyrolysis char (TPC). From various researchers, it is observed that the lower temperature yields higher TPO while obtaining high yield of TPG at higher temperatures. Cunliffe and Williams has carried out pyrolysis of WTR at different processing temperatures from 450 and 600 °C and observed that lower temperature favors the production of TPO while high-temperature process favors the production of gases. [100] The results revealed that the process yields the highest TPO (58.2 wt%) at 475 °C which reduces to 53.1 wt% at 600 °C. In addition, pyrolysis in the range of 450 to 650 °C with a heating rate at 5 °C $min^{-1}$ for 2 h resulted in TPO 55% having higher viscosity and higher sulfur content compared to diesel fuel. [101] On the other hand, the heating rate also influences the yield of the product. At a lower heating rate, TPC is higher and, at a higher heating rate, TPG yield is higher. It has also been observed that increasing the heating rate from 5 to 35 °C $min^{-1}$ increases the TPG yield up to 33.8 wt% while decreasing the TPO yield to 35.1 wt% at 400 °C without any catalysts. In addition, like temperature and heating rate, the pressure of the reactor can also affect the product yield. [102] Under vacuum condition TPO yield is higher than the

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atmospheric pyrolysis process, while TPG and TPC yield is lower. On pyrolysis of WTR at 415 °C it has been found that under vacuum TPO yield obtained 55%. [103] Williams et. al. have investigated the effect of heating rate on pyrolysis products at 720 °C. [104] The results suggested, that TPG yield increases from 6.6 wt% to 14.8 wt% on increasing heating rate from 5 °C $min^{-1}$ to 80 °C $min^{-1}$. Further, an increase in temperature from 375 to 500 °C has resulted in an increase in TPC yield from 2.99 to 20.22 wt%. [105]

### 4.3.2. Effect of catalyst on waste tire pyrolysis product

Catalysts play a significant role in all the chemical reactions. In the pyrolysis of WTR, the catalysts are important in enhancing the pyrolysis rate by improving the product quality and composition of product. Various types of metal catalysts like $CaC_2$, MgO, ZSM-5, Cu/HBETA, $MgCl_2$, $Ca(OH)_2$, Zeolite, Al-MCM-41, Al-SBA-15, $Al_2O_3$, $SiO_2$, $Ca(OH)_2$, and $AlCl_3$ are used in the tire pyrolysis process. [96] The selection of the catalysts, amount, and their ratio with the tire affect the quality and yield of the products. Zeolite-based catalysts having larger pore size and high surface activity resulted in higher yield of TPG and TPC while lower yield of TPO on WTR pyrolysis. [106] SanMiguel et. al. [107] have observed that TPO obtained from WTR pyrolysis in the presence of zeolite catalysts contain higher aromatics compounds. In addition, the zeolite USY (ultra-stable Y) catalyst resulted in a significant reduction in TPO yield and an increase in TPG product. [108] Further, increasing the catalyst amount increases the light fraction, hence increasing the TPG yield and reducing the TPO yield because of the increased cracking activity of a catalyst. [108] Further incorporations of noble metals on catalysts significantly affected the pyro-products. Immobilizing Ru clusters on SBA-1 has improved the TPG yield by around two times that of the thermal pyrolysis. [109] The major effect of ruthenium clusters is to improve the product quality as light oil has lower hydrocarbons and hence low boiling point. In the presence of a catalyst, the heavy hydrocarbon TPO is cracking down into low molecular weight TPO. On the other hand, 5% $Ca(OH)_2$ catalyst in the process and concluded to achieve the highest yield of the liquid product with reduced sulfur content. [110, 111] The effect of catalyst on pyrolysis process are summarized in table 5.

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**Table 5.** Effect of catalyst on pyrolysis process

| Sr. No. | Pyrolysis process | Catalyst | Significance |
|---|---|---|---|
| 1 | Pyrolysis process with catalyst | Metal catalyst | Type, amount, and ratio of catalyst with tire affect the quality and yield of pyro products |
| 2 | WTR pyrolysis using zeolite having a large porous area | Zeolite | Higher yield of TPG and TPC while lower yield of TPO |
| 3 | WTR pyrolysis using zeolite | Zeolite | TPO with higher aromatics |
| 4 | WTR pyrolysis using zeolite USY | zeolite USY (ultra-stable Y) | Significant reduction in TPO yield and an increase in TPG |
| 5 | Pyrolysis with an increase in the catalyst amount | Metal catalyst | Increases the light fraction, hence increasing the TPG yield and reducing the TPO yield |
| 6 | WTR pyrolysis using ruthenium catalyst | Ruthenium catalyst | Improvement in the TPG yield and improved product quality of TPO (heavy hydrocarbon TPO is cracking down into low MW TPO) |
| 7 | WTR pyrolysis using 5% $Ca(OH)_2$ | 5% $Ca(OH)_2$ catalyst | Highest yield of the liquid product TPO with lower sulfur content |

Moreover, the summary of pyrolysis processes under different catalytic conditions given in table 6. The various operating parameters, catalysts used, and their product yield are summarized in the table 6. [96]

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**Table 6.** Catalytic pyrolysis conditions, catalyst characteristics and fraction yield.[96]

| Catalyst type | Catalyst spec. | Quantity/ratio Catalyst /Tire (CT) | Operating parameters | | | | | Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Tire size | Temp Range (°C) | Reaction time (min) | Heating rate (°C / min) | Inert gas flow (ml / min) | Oil (TPO) | Gas | Char | coke |
| ZSM-5 | n. r. | n. r. | 6 mm | 450–500 | 55–65 | 11 | $N_2$ | 30 | 25.5 | 44.8 | - |
| | | 0.1 | 0.75 $cm^3$ | 300-600 | n. r. | n. r. | $N_2$ | 35.8 | 12.1 | 47.1 | - |
| | | 0.15 | 0.75 $cm^3$ | 300-600 | n. r. | n. r. | $N_2$ | 35.6 | 15.2 | 49.7 | - |
| | Si/Al ratio: 30; $S_{BET}$: 541 $m^2/g$; pore size: 5.6 Å | CT = 1.5/150 (g) | 20-100 mesh | 500 | 30 | 15 | $N_2$; 400 | 55.6 | 6.5 | 37.9 | - |
| ZSM-22 | Si/Al ratio: 58; $S_{BET}$: 350 $m^2/g$; pore size: 5.6 Å | CT = 1.5/150 (g) | 20-100 mesh | 500 | 30 | 15 | $N_2$; 400 | 55.1 | 10.4 | 34.4 | |
| USY | Si/Al ratio: 5.4; SBET: 432.5 $m^2/g$; pore size: 7.8 Å | CT = 1.5/150 (g) | 20-100 mesh | 500 | 30 | 15 | $N_2$; 400 | 53.5 | 9.97 | 36.5 | - |
| $Al_2O_3$ | n. r. | n. r. | 6 mm | 450–500 | 55–65 | 11 | $N_2$ | 32.5 | 30.0 | 37.4 | - |
| $CaCO_3$ | n. r. | n. r. | 6 mm | 450–500 | 55–65 | 11 | $N_2$ | 39.8 | 23.6 | 37.4 | - |
| $Na_2CO_3$ | n. r. | 10% catalyst | n. r. | 400-600 | 45 | n. r. | n. r. | 49.2 | - | - | - |
| MgO | n. r. | n. r. | 6 mm | 450–500 | 55–65 | 11 | $N_2$ | 42.5 | 17.0 | 40.3 | |
| Regenerated $NiMoS/Al_2O_3$ | $S_{BET}$: 198.75 $m^2/g$; Pore volume: 0.42 $cm^3/g$; Pore width: 8.86 Å | | 8-18 mesh | 500 | 90 | 10 | $N_2$ | 33.1 | 21.2 | 40 | 8 |
| Y-Zeolite | Pore size: 7.8 Å; Si/Al ratio: 5.4 | 1:1 | 1–1.4 mm | 430-600 | 60 | 10 | $N_2$ | 32.2 | 21.8 | 38.0 | 8 |
| ZSM-5 | Pore size: 5.6 Å; Si/Al ratio: 40 | 1:1 | 1–1.4 mm | 430-600 | 60 | 10 | $N_2$ | 34.6 | 20.0 | 38.0 | 7.6 |
| HY/MCM-41 core shell composite | $S_{BET}$: 790 $m^2/g$; pore volume: 0.85 $cm^3/g$; pore size: 29 nm | catalyst: 7.5 g | 20–40 mesh | 350-500 | 120 | N.R. | $N_2$ :30 | 42 | 9.1 | 41.2 | 4.3 |
| Cu/HBETA | $S_{BET}$: 413 $m^2/g$; pore volume: 0.200 $cm^3/g$ | CT (g) = 7.5:30 | 20-40 mesh | 350-500 | 90 | 10 | 20-40 mesh | 39 | 11 | 40.5 | 7.1 |
| Cu/HY | $S_{BET}$: 488 $m^2/g$; pore volume: 0.256 $cm^3/g$ | CT (g) = 7.5:30 | 20-40 mesh | 350-500 | 90 | 10 | 20-40 mesh | 40.1 | 12 | 40.5 | 5.0 |
| Fe/HMOR | $S_{BET}$: 352 m2/g; pore volume: 0.176 cm3/g; pore width: 6.50 Å | TC ratio = 4 | - | 350-500 | 120 | 10 | $N_2$ :30 | 41 | 13.5 | 40.7 | 2.0 |
| Fe/HBETA | $S_{BET}$: 406 $m^2/g$; pore volume: 0.234 $cm^3/g$; pore width: 6.59 Å | TC ratio = 4 | - | 350-500 | 120 | 10 | $N_2$ :30 | 42.2 | 12.1 | 40.7 | 4.51 |

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Finally, we have summarized the different methods of devulcanization discussed previous sections, their advantages and disadvantages with applications (table 7).

**Table 7**. Summary of different methods devulcanization process and their advantages and disadvantages.

| **Sr. No.** | **Devulcanization Methods [Ref]** | **Advantages** | **Disadvantages** | **Application of Recycled Materials** |
|---|---|---|---|---|
| 1 | **4.2.1. Physical devulcanization technology** | | | |
| | 4.2.1.1 Thermal process [52, 53, 33] | a. Catalyst & Chemical free process.<br>b. The RGTR with a high degree of reclamation. [35,36] | a. High temperature & pressure process<br>b. High energy process | Good dispersibility and reinforcement in NR (10-40%) compared to traditional reclaimed rubber. [33,54] |
| | 4.2.1.2 Mechanical process [55-58] | a. Low-temperature process<br>b. With or without chemical reagents | a. High-energy process in the extruder (mechanical & thermal energy) with additional. chemical silane reagents<br>b. Hazardous gas generation as a side product. [24] | a. DeVulcNR for revulcanization with or without silica filler as a reinforcement agent. [60]<br>b. Performance studies of SBR/$SiO_2$-DeVulcSBR composite showed superior properties over other composite ratios. [60] |
| | 4.2.1.3 Microwave process [63-67] | a. Uniform heating in comparison to traditional heating methods. [63-67]<br>b. No chemical treatment. [66]<br>c. High productivity and easy modification of the process parameters. [67] | a. High cost for industrial microwave reactor.<br>b. Difficulty in uniform mixing and heating. | Devulcanized product used in silica composites shows good properties. [60] |
| 2 | Chemical devulcanization technology [71-86] | a. Low catalytic process<br>b. Solvent-free conditions.<br>c. Low temp (RT) process | a. May cause environmental problems due to chemical disposal.<br>b. Low degree of devulcanization compared to thermal process. | The blending of GTR with virgin SBR showed improvement in mechanical properties. [90] |
| 3. | Biological devulcanization technology [87-90] | a. Safe, economical, and environmentally friendly approach.<br>b. Selective devulcanization over the chemical and physical processes. [88-90] | a. With slower biological reactivity (4.7% sulfur removal in 40 days), it is not the preferred method by the industries. [87]<br>b. Biological contamination of product. | a. Desulfurized waste latex rubber significantly improved the mechanical properties of natural rubber (NR)/DWLR composite.<br>b. Landfilling, Road construction etc. |

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| | | | | |
|---|---|---|---|---|
| 4 | Pyrolysis process [99-111] | a. It improves the conversion efficiency of devulcanization.<br>b. It can easily separate the different components of WTR & WVR. | High temperature (300-500 $^{o}$C) and pressure process | a. The TPO can be used as an alternative fuel.[103, 118]<br>b. Thermal pyro-char (TPC) can be used to make porous activated carbon, for various energy purposes like Na or Li-ion batteries, and supercapacitors. [120, 125]<br>c. Thermal pyro-gas (TPG) can be used as a fuel source to heat the pyrolysis reactor. [115-116] |

### 4.3.3. Value-added products from pyrolysis of waste tire rubber

The first lightest product of WTR pyrolysis is TPG having high gross heating value 2900 J/g with an enthalpy of pyrolysis process about 270 J/g. TPG contains a mixture of olefins, carbon oxides, hydrogen and small content of sulfur and nitrogen based gases. [112] Due to very high hydrogen content TPG can be used to produce an efficient and environmentally benign hydrogen gas containing high energy density, carbon-free energy and zero greenhouse emission. [113-115] Another pyrolysis product is TPO, having broad range higher molecular weight aromatic and aliphatic with polar and heteroatom structure. Based on boiling point (bp) TPO can be characterized into three categories: 1) lightest part with low bp liquid ranging from 45 to 205 °C, 2) component having bp in range of 205–300 °C, 3) heaviest oil having bp >300 °C. The chemical composition of TPO is complicated having a mixture of critical hydrocarbons like, benzene, Toluene, xylene, limonene and styrene those are useful for chemical industry. [116] However, TPO has potential applications in diverse areas but the presence of sulfur impurity generated by sulfur crosslinks in vulcanized rubber has critical environmental concern. On direct combustion TPO can releases $SO_2$ that cause serious environmental problems. Thus, to overcome this challenge some sulfur releasing treatment need to be done before combustion of TPO. Thus, TPO on treatment with formic acid (pH 4.0) in presence of 25 vol% of hydrogen peroxide ($H_2O_2$) can significantly remove the sulfur from pyro-oil. [117] Further research indicated that the pyro-oil can be used as diesel fuel in small engines after proper distillation. [118] Murugan et al. demonstrated the pyro-oil as fuel in single cylinder direct injection diesel engine by blending it with diesel fuel in 10%, 30%, and 50% ratio and studied the performance, emission and combustion characteristics. [103]

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Besides TPG and TPO, another important product of waste tire pyrolysis is thermal pyro char (TPC) that can be converted into activated carbon (AC) by physical or chemical treatments. To activate TPC steam, $CO_2$ based treatment are considered as physical activation process while treatment with acid or base i.e. $H_2SO_4$, KOH, $H_3PO_4$ known as chemical activation methods. After activation, the properties such as a surface area, porosity, electrical conductivity of TPC can be improved. One of the vital applications of AC or char is the removal of organic/inorganic pollutants from industrial wastewater and air. [119] The activated carbon can also be used for various purposes like waste water treatment, purification of various materials by absorption/adsorption of impurities, and used as electrode materials for Li, K, Na-ion battery, supercapacitor and electrocatalyst (ORR). In other applications the waste tire recovered AC can be used for better adsorption capacity for methylene blue compared to commercial AC. [120] Tire-derived activated carbon has been used for oxygen reduction reaction. [121] TPC has also been used as electrodes in double layer super capacitors after the chemical activation by $H_3PO_4$, [122] and steam-based activation. [123] Li et al. [124] reported the synthesis of disordered carbon from pyrolysis of $H_2SO_4$-treated tires and showed its application in sodium-ion batteries. Sharma and co-workers activated tire-derived carbon by KOH and demonstrated for Li-ion battery and displayed a high specific capacity of ~880 mAh/g (at 50 mAh/g) with nearly 80% capacity retention after 100 cycles. [125]

Pan and coworkers developed dual N-doped material (ACBp-oN) for supercapicitor application with superior rate performance and satisfactory specific capacitance of 335 F $g^{-1}$ (1 A $g^{-1}$) along with long cycle life in three-electrode system. [126] First, in-situ aniline is polymerized with o-phenylene-diamine (OPD) on activated pyro-carbon black (CBp) to results CBp/ polyaniline (PANI) composite denoted as ACBp-oPANI with enhanced N content. Due to enhanced N doping and enriched channel structure this material showed rapid electron transport and ion diffusion on charging/discharging. In addition, ACBp-oN showed superior properties like excellent energy density of 68.9 W.h $kg^{-1}$ as cathode material along with electrodeposited Zn anode.

### 4.3.4. Handling of devulcanized rubber in tire-tread compounding

Tire compounding is a process that involves the blending of different materials to create rubber compound used for tire manufacturing with specific properties and performance. [52, 57, 127] Rubber from waste tires through devulcanization can be used as a partial replacement for virgin rubber (NR, SBR) in tire compounding. [127] Recycled rubber (RTR) from waste tires can

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be obtained by different methods, such as mechanical grinding, chemical regeneration & pyrolysis produces from ground tire rubber (GTR) as discussed in above sections. [51, 127-128] The GTR with different particle size can be blended with virgin rubber to improve the rolling resistance, wet grip, and self-healing ability of the tire compounds. [127-128] Pyrolysis converts waste tires into oil, gas, and carbon black, which can be used as raw materials for rubber and other industries. [96-98] Chemical regeneration produces regenerated tire rubber (RTR) by breaking the crosslinks and restoring the elasticity of the waste tire rubber, which can be mixed with virgin rubber to enhance the mechanical and rheological properties of the tire compounds. [127-128] Table 8 presents a list of the works performed on the compounding of GTR and RTR with different grades of rubbers like natural rubber (NR), NBR, and SBR at different ratios (table 8). [127] The mechanical properties of the composites studied for tensile strength, elongation at break, tear strength, abrasion resistance etc. [127, 129-131]

**Table 8.** GTR/RTR rubber blends and their mechanical properties [127]

| Blends | GTR/RTR (Loading) | Tensile Strength (MPa) | Elongation at Break (%) | Tear Strength (N/mm) | Abrasion Resistance (cc/h) | Compression set (%) | Resilience (%) |
|---|---|---|---|---|---|---|---|
| NR / RTR | 20 | 15 | 610 | 27 | 10.6 | 18 | 58 |
| | 40 | 12.5 | 580 | 29 | 10.7 | 25 | 52 |
| | 60 | 12 | 60 | 30 | 10.7 | 25.2 | 50 |
| NR / GTR | 20 | 15.9 | 500 | - | - | - | - |
| | 40 | 13.4 | 417 | - | - | - | - |
| | 60 | 11.6 | 260 | - | - | - | - |
| NBR / RTR | 20 | 2.5 | 320 | 27.9 | 2.5 | 18 | 30 |
| | 40 | 3.0 | 380 | 27.5 | 5 | 21 | 29 |
| | 60 | 5.5 | 500 | 27.3 | 8 | 26.5 | 28 |
| NBR / GTR | 20 | 4 | 325 | 22 | 4 | 15.5 | 30.5 |
| | 40 | 6 | 310 | 27 | 7 | 17.5 | 27 |
| SBR / RTR | 20 | 2.5 | 350 | 13 | 14.5 | 4.5 | 46 |
| | 40 | 3.8 | 525 | 17 | 19 | 5.0 | 45 |
| | 60 | 5.5 | 600 | 21 | 20 | 6.2 | 38 |
| SBR / RTR | 20 | 17.5 | 350 | - | - | - | - |
| | 40 | 14.8 | 317 | - | - | - | - |
| | 60 | 8.7 | 260 | - | - | - | - |

- GTR = Ground Tire rubber; RTR = Regenerated Tire Rubber
- NR = Natural Rubber; SBR = Styrene Butadiene Rubber; NBR = Nitrile Butadiene Rubber

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Using recycled rubber from waste tires in tire compounding can have several benefits, such as reducing the environmental impact of waste tire disposal, saving the cost and energy of producing virgin rubber, and improving the performance and durability of the tire products. [134] However, there are also some challenges and limitations, such as the compatibility and dispersion of the recycled rubber in the rubber matrix, the quality and consistency of the recycled rubber, and the optimal formulation and processing conditions for the tire compounds. Therefore, further research and development are needed to overcome these issues and optimize the use of recycled rubber from waste tires in tire compounding. [127-128]

## 5. Conclusion and future perspective

Since the demand and consumption of new tires are continuously increasing in auto industry, a huge number of waste tires generated per annum after the end of life. Hence, the systematic disposal of the waste tire is a major concern in both the environmental and economic terms. These actions need enormous attention from scientific and technical community globally. Currently, there are several disposal techniques are being used i.e. stockpiled and landfilling, combustion of waste tires as fuel and these methods has various environment, health and economic issues. On the other side, reuse of old tires by retreading after end of their first life is another important technique to reduce waste tire and be useful to circular economy. However, the inferior quality of second life product and health hazards to workers is not appreciating this process. In addition, another best way of recycling and reuse of GTR is the conversion of WTR into value added products with different purposes such as preparation of rubber asphalt, tiles, footwear, conveyor belts, playground mats, shock resistance reinforcement in buildings, and many other applications. But these disposal and reuses techniques are not sufficient as the huge number of the WTR are produced annually. The researchers and industries have made lot of sustainable and environmentally benign efforts to handle the WTR and other waste vulcanizate materials to reprocessed materials that possess the capability to be turned into high value-added products.

In this direction, the devulcanization and depolymerization techniques play an important role for recovering and recycling of WVR products to the value-added products or blend of devulcanized rubber with virgin rubber. In current review, we focus on the devulcanization and depolymerization process for the recycling of WVR products. The

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devulcanization process mainly carried out by breakage of C-S and S-S bonds in the cured rubber network and can be carried out through thermal, mechanical, chemical, microwave and ultrasonic methods. While on chemical treatment the C-C bonds also undergo for the cleavage along with the C-S and C-C bond and results low molecular weight products known as depolymerization process. We also discussed the extent of devulcanization and the revulcanization of the recovered rubber with the virgin rubber for further compounding process. Further, the effect of the different oxidizing agents and catalysts i.e. Grubbs' catalyst on different grade of vulcanized rubber and GTR has also been summarized. The role of different ratio of GTR with virgin rubber has been monitored by the studies of the curing properties and mechanical behavior such as, tensile strength, elongation at break and modulus. This review also considers the conversion of WTR into value added product by thermal pyrolysis process, where the thermally generated TPO and TPC can be used for various industrial purposes.

For the systematic recycling of WTR the researchers and industries may have to focus on the further studies on efficient and economical methodologies for recycling. The major focus of this type of recycling should be on economically feasible process having an outcome of value-added products. Minimum effluent generation is also another area where further work can be done. Rubber technologist may further look into the devulcanized rubber product, which can be used as rubber compounding ingredients like plasticizer, process aids, stabilizer, compatibilizing agents etc. More focus to be given to complete use of recycled rubber in addition to the carbon black filler in the composites, which also creates lot of nuisance to the environment. Even the policy makers should look into the legal enforcement for all vulcanized rubber goods manufacturer for maximize the recycling of elastomers.

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## Data Availability Statement

All the supporting data ( Tables and Figures) of the article are included in the manuscript

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