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Pyrolysis Char from Waste Tyres its Characteristics, Upgrading and Application

ABSTRACT

The pyrolysis of waste tyres can recycle energy and produce reusable products (oil, char and gas). Although there are many reviews in the literature in regard to the pyrolysis characteristics of waste tyres, but this paper critically looked as pyrolysis char as one of the useful product. Its physical characteristics include pore diameter, pore volume, specific surface area, and composition. The common detection techniques of the physical characteristics include elemental analysis, proximate analysis, SEM, EDS, TGA, XRF, BET, and Raman spectroscopy. The chemical characteristics of tyre char mainly include calorific value, the surface functional groups (i.e phenols, alcohols, carboxylic acid and C-O/C-O-C chemical structures) which can be determined by FT-IR, XRD. The higher sulfur retention on the surface of tyre char is obtained at low temperature compared with that obtained at high temperature. Tyre char could also be directly used as a catalyst material to decrease the operational cost, and improve the quality of pyrolysis oil and gas. The modified tyre char with high specific surface area and lower ash content could be used as an activated carbon adsorbent material, catalyst and catalyst support, capacitor electrode to create higher commercial value, as an adsorbent, in batteries and so on. It is suggested that the recycling applications of tyre char should be developed, which can create a high level of potential economic prospects for the waste tyre pyrolysis industry.

Keywords: *Pyrolysis, Waste tyres, Char, Modification, Carbon black.*

1. INTRODUCTION

Over time, pyrolysis technology has advanced and become sufficiently refined to be considered a quick and effective means of addressing the environmental issues arising from waste tyres. Pyrolysis oil, char, and gas are the three primary products that are derived from pyrolyzing tyres under mild conditions. Nevertheless, the direct use of these products as energy sources is constrained by their high sulfur concentration and composition [1]. The pyrolysis process yields nearly no waste byproducts, and the steel, rubber, carbon black, additives and other components present in the discarded tyre may be recovered [2].

Fig. 1 illustrates the products and by-products from waste tyre pyrolysis. Improving the quality of pyrolysis products is the primary obstacle to the full-scale development of the waste tyre pyrolysis process, even with appropriate processing and modification. Numerous large-scale tyre pyrolysis projects have reportedly failed to achieve complete commercial success because of the low value of the goods that are produced [3].

In the realm of waste tyre treatment, pyrolysis is a promising technique for recycling and recovering energy and fuels. It has the potential to satisfy the three pillars of solid waste treatment: pollution mitigation, resource recovery, and reduction. In contrast to alternative therapeutic approaches (i.e. com-

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bustion, retread, and landfill) [4-6]. Since pyrolysis reduces secondary pollutants in the environment and has the potential to increase product economic value, it has been extensively studied as a recovery technique. In order to produce gases and condensable oil, the procedure breaks down the organic components of discarded tyres, and solid char [7,8].

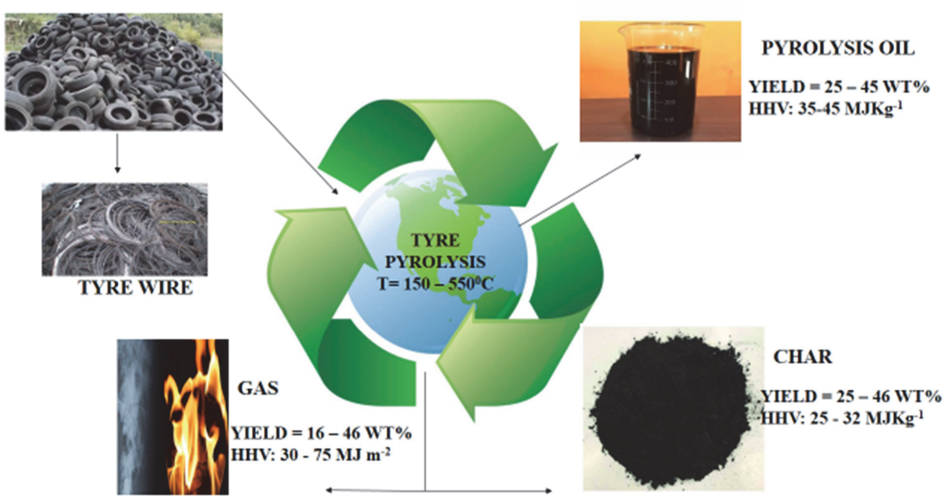

Fig. 1: The pyrolysis product of waste tyres

Thus, it is possible to utilize fewer conventional fossil fuels when waste tyres are converted to alternative fuels. For this reason, waste tyre pyrolysis has been shown to be a practical method of indirectly reducing greenhouse gas emissions [9]. Furthermore, the tyre's steel reinforcing can be extracted from the leftover char and recycled back into the iron and steel sector [10].

1.1 Pyrolysis Tyre Char

One of the primary byproducts of pyrolysis made from used tyres is tyre char, whose marketability is essential to the ongoing growth of waste tyre pyrolysis commerce [11]. Tyre pyro-char is a carbon-rich solid material that is produced during pyrolysis. It is a black porous substance that contains high amounts of carbon, and low amounts of volatiles and ash [12,13]. It is a solid residue obtained from pyrolysis that can be used as a soil amendment, carbon sequestration, or fuel. It has high carbon content water retention, and reduce greenhouse gas emissions [14]. It can also be used as a fuel, as it has a high calorific value and burns cleanly [12,13]. (Fig: 2)

So many reviewed work have been focusing on pyrolysis oil been one of the product obtained during the process, but in this paper will focus on pyrolysis char as one of the important product obtained during pyrolysis so as to highlight its characteristics, application and further possible modification of the char.

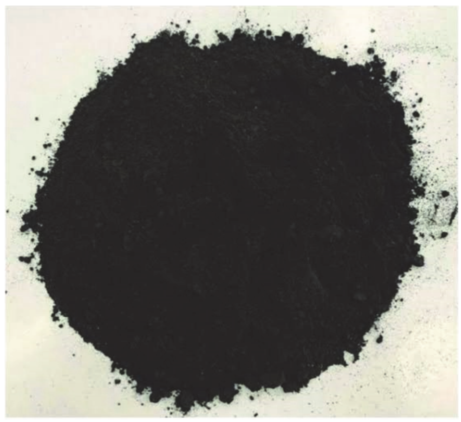

Fig. 2: Pyrolysis char from waste tyres

2. STRUCTURAL CHARACTERISTICS OF TYRE PYROLYSIS CHAR

The physical and chemical characteristics of the waste tyre char have been reported in many research articles [15,16]. It is of great interest to understand the structural characteristics of tyre char for its further application. The modification scheme of tyre char could be determined by its structural characteristics.

2.1 Physical Structure Characteristics

The primary physical properties of tyre char are its composition, specific surface area, pore volume, and pore diameter. Elemental analysis, proximate analysis, SEM, EDS, TGA, XRF, BET, and Raman spectroscopy are examples of common physical characteristic detection procedures [17]. The fixed carbon content, ash content, element analysis, and proximate analysis are used to further characterize tyre char. TGA in an air atmosphere could potentially be used to determine the ash concentration [18]. Tyre char is a high-carbon substance, typically more than 85%, that is mostly derived from the carbon black that is injected during the tyre formulation process. In addition, during the pyrolysis process, subsequent condensation and depolymerization events generated by the pyrolysis volatiles result in the production of carbonaceous deposits across the tyre char surface. Process circumstances have a major impact on the amount of these reactions [19,20].

The heating value of tyre char is associated with high carbon content. The HHV of tyre char is reported in the literature to range between 25 and 32 $MJ \cdot kg^{-1}$, [21-23]. However, the interest in tyre char as a solid fuel is hindered by the high sulfur content.

Tyre char's stability could be examined using TGA analysis in an environment with inert gas. The low-temperature tyre char's qualities are more erratic than those of the high-temperature tyre char because the discarded tyre doesn't undergo complete thermal degradation. The breakdown of inorganic chemicals on the tyre char's surface at high temperatures could be the cause of this [24]. The presence of disorder in carbon and graphene 2D hexagonal lattice in the tyre char with Raman spectra has been reported [24]. In the meantime, the char generated from the pyrolysis of the tyre tread and the char created from the pyrolysis of the tyre side wall have completely distinct elemental and proximate analysis results. Compared to the tread rubber char, the side wall rubber char has less ash in it [2]. At -196^{0}C, N_2 adsorption-desorption (BET) analysis might be used to measure the specific surface area and pore diameter. Numerous reports have demonstrated that tyre char has a specific surface area of less than 140 $m^2 \cdot g^{-1}$ [22,25], in addition, there are more mesopores and few micropores in tyre char [2,24]. Various tyres produce tyre char with highly varied physical structures. It should be highlighted that these characteristics are very dependent on the type of carbon black utilized in tyre formulation as well as the pyrolysis conditions, particularly pressure, temperature, and residence time. The char formed during the pyrolysis of the tyre tread rubber and side wall rubber differs significantly [19].

2.2 Chemical structure characteristics.

Tyre char's chemical properties mostly consist of its calorific value and surface functional groups. Tyre char's chemical properties could be ascertained using FT-IR, XRD, and HHV [26]. FT-IR provides a good picture of the kind and strength of the surface functional groups associated with tyre char. The surface functional groups of tyre char often consist of alcohols, carboxylic acids, phenols, and C-O/C-O-C chemical structures, according to published research [27]. Additionally, it has been reported that tyre char surface sulfur retention is higher at low temperatures than at high ones, this is thought to be caused by some stable metallic sulfides that persist in the tyre char as well as the relatively high sulfur volatility at high temperatures [28]. The surface nature of activated char from the waste tyre was reported to be hydrophobic [29].

3 COMPARISON OF PROPERTIES OF TYRE CHAR WITH COMMERCIAL CARBON BLACK

Tyre char's primary ingredient, carbon, makes up more than 80% of the material. Tyre char has a particular surface area of about 90 $m^2 \cdot g^{-1}$ and contains a certain amount of ash [21, 30]. Zn, Si, Al, Na, Ca, and Fe are among the inorganic components in ash, according to EDS and XRF examinations of tyre char. Ash has a comparatively greater Si concentration than other elements—up to 3.47% [24]. In tyre char, certain nanoparticles combine to form microparticles. The tyre char has fewer pores, a rough surface, an uneven form, and an uneven size distribution. However, tyre char has fewer particles than commercial carbon black [31]. Commercial carbon's main particles typically have a mean size in the nanometer range (8–100 nm), and they frequently aggregate into grape-like clusters up to 500 nm in size. Tyre char has a well-developed porous structure, with more mesopores than micropores and an average pore diameter of 25–30 nm [31].

4. UPGRADING OF TYRE PYRO CHAR

According to some researcher, untreated tyre char has the potential to be useful for recycling and could replace commercial carbon black in rubber additives [32]. The ash content in tyre char can limit the end-use application of tyre char [19]. The high sulfur content of tyre char also represents a major drawback for its utilization [15]. The possibility for ash and volatile oily materials to adhere to tyre char's surface during the pyrolysis process, clogging pores and acting as agglomerating particles, is another disadvantage of tyre char. Because tyre char's quality has been demonstrated to be lower than that of commercial carbon black, it must be treated and filtered before to use [19]. It is important to remember that the minerals added during the tyre manufacturing process are primarily responsible for the high ash concentration of tyre char [33,34].

Various methods have been suggested to demineralize tyre char and increase its market value. Ash leaching, for instance, can be done either before or after tyre pyrolysis. The chemical pathway and selectivity of the pyrolysis reactions can be altered by the ashes found in tyre rubber. Furthermore, pyrolysis can result in the generation of harmful species and less corrosion on process equipment when the feedstock is demineralized [35].

The main constituent of waste tyres ashes is ZnO, moreover, other metallic species commonly present are Fe, Al, Ca, and Mg [16, 36, 37]. Leaching is the method of choice for demineralizing tyres. A number of variables affect how well this liquid-solid extraction process works, most notably the feedstock's characteristics (particle size or starting porosity) and the operating environment (temperature, contact time, leaching rate, or agitation). The solubility and composition of the ashes [38].

Various leaching reagents have been utilized in tyre or tyre char demineralization; solvents are categorized into three classes based on pH: alkaline, acidic, and water. Of them, acid leaching—using HCl, H_2SO_4, or HNO_3 is employed more frequently in earlier literature reports [27, 39, 40]. Since tyre char is porous, leaching is easier than it would be with original rubber; in fact, effective ash removal only happens on the rubber's surface [41].

Tyre char demineralization is an intriguing pre-activation process; hence, the removal of minerals encourages the formation of new mesopores and micropores, which serve as active sites in the activation stage that follows [42,43]. Additionally, this technique is intriguing because it prevents the substantial burn-off carbon losses during activation from leading to a rise in ash content [19,44]. Additionally, acid treatment has been shown to have a good impact on tyre char's sulfur concentration. For instance, Gao *et al*., [19] leached tyre char using a mixture of HCl and HNO3, which produced extremely efficient desulfurization of tyre char (95.3%). Nevertheless, the demineralization of tyre char using H_2SO_4 may encourage the addition of further residual sulfur. Certain types of sulfur in carbonaceous materials can also be removed more effectively by applying alkaline reagents [28].

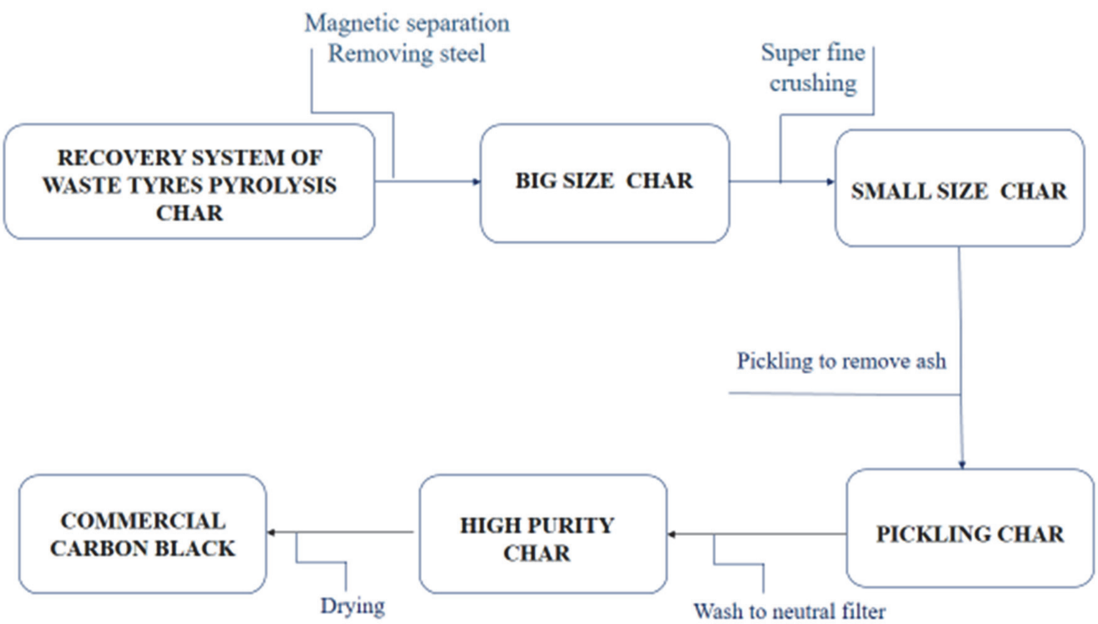

Fig.3: Flow chart of char from waste tyre via pyrolysis modified to carbon black

Tyre char is partially gasified during the physical activation process utilizing a variety of oxidizing chemicals, primarily carbon dioxide and steam. Particle size, temperature, activation agent, and activation time are the typical operational variables that are taken into account [19]. Different alteration procedures are required based on the purposes. Fig. 3 depicts the typical tyre char alteration procedures. After being ultra-finely ground, the tyre char's particle size dramatically shrank in comparison to the original, and the powdered result was tightly packed. Particle agglomeration is easier with finer particle sizes. The process of creating activated carbon from used tyres usually consists of two stages: (i) Waste tyres are pyrolyzed in an inert gas atmosphere to create gas, pyrolysis oil, and carbon compounds that can be used as fuel. (ii) Chemical or physical means are used to activate the tyre char [19]. However, the drawbacks of conventional activation techniques are their intricate procedures and poor effectiveness. The procedure of modifying tyre char must be altered in accordance with the application requirement in order to meet the standard criteria needed for commercial carbon black [19].

5. APPLICATIONS OF TYRE CHAR

The primary driver of the tyre char market's explosive growth is the annual increase in the global supply of discarded tyres, which has very low or even negative costs as a process feedstock. As a result, the cost of generating tyre char is reduced. Tyre char, with an ash level of roughly 7.0–15%, makes up 30-37 weight percent of the results of tyre pyrolysis, as a result of the various sources and pyrolysis processes of discarded tyres. The usage of tyre char has been proposed for numerous purposes. Tyre char, for instance, can be used as the pigment added to printing ink, which is a colloid dispersive system made up of filler, connecting material, pigment, and auxiliary agent [19,23,24]. For example, the performance of tyre char as a pigment in offset printing ink has been reported [28].

The application of tyre char as solid fuel has also been reported in the literature [24,26]. It was also suggested that tyre char could be used as filler in modifying asphalt [28,42]. The specific surface area, pore diameter, and surface properties of tyre char are also different when obtained under different tyre pyrolysis conditions [4,19].

Small pore widths and developed pores are features of tyre char. It cannot, however, match the application requirements of commercial carbon black due to its low specific surface area. Its economic worth is therefore minimal [23,24,26]. As a result, efforts are concentrated on finding efficient ways to raise tyre char's added value. Tyre char now has a wide range of applications; Fig. 4 illustrates these potential uses. The primary uses of activated carbon are as adsorbents made from modified tyre char [28], as well as asphalt additives, battery materials, commercial carbon black, rubber reinforcing materials, and catalyst support materials. Additional applications include gasification of fuel gas, adsorbent (activated carbon) as a catalyst and supporting material, reinforcement of tyre rubber as a material for batteries and capacitors, and materials for construction [19].

Fig. 4: The main high added value application of tyre char

6. CONCLUSION

Many different fields employ tyre char extensively. Tyre char that hasn't been altered can be utilized straight away as a solid fuel and tyre rubber reinforcement agent. Additionally, tyre char could be utilized directly as a catalyst material to lower operating costs and enhance the quality of the oil and gas produced during pyrolysis. To increase its economic value, the modified tyre char with its increased specific surface area and decreased ash content might be employed as a capacitor electrode, catalyst and catalytic support, and an adsorbent material for activated carbon.

The majority of tyre char applications are still in the early stages of laboratory research. Comprehensive technical and economic analyses of tyre char activation technology and waste tyre pyrolysis are lacking. However, as waste tyre pyrolysis technology develops and becomes more industrialized, the standards for pyrolysis product quality will rise. It is recommended that tyre char recycling applications be developed, since this might lead to a high degree of potential economic opportunities for the waste tyre pyrolysis business. Even with the advancements in waste tyre pyrolysis technology and the use of pyrolysis products, numerous problems still need to be fixed in order to satisfy various industrial demands.

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IZVOD

KARAKTERISTIKE PIROLIZE IZ OTPADNIH GUMA, NADOGRADNJA I PRIMENA

Piroliza otpadnih guma može da reciklira energiju i proizvede proizvode za višekratnu upotrebu (ulje, ugljen i gas). Iako u literaturi ima mnogo pregleda u vezi sa piroliznim karakteristikama otpadnih guma, ovaj rad je kritički pogledao kao pirolizni ugljen kao jedan od korisnih proizvoda. Njegove fizičke karakteristike uključuju prečnik pora, zapreminu pora, specifičnu površinu i sastav. Uobičajene tehnike detekcije fizičkih karakteristika uključuju elementarnu analizu, proksimnu analizu, SEM, EDS, TGA, KSRF, BET i Raman spektroskopiju. Hemijske karakteristike ugljenisane gume uglavnom uključuju kalorijsku vrednost, površinske funkcionalne grupe (tj. fenole, alkohole, karboksilnu kiselinu i hemijske strukture C-O/C-O-C) koje se mogu odrediti pomoću FT-IR, XRD. Veće zadržavanje sumpora na površini ugljenisane gume postiže se na niskoj temperaturi u poređenju sa onim dobijenim na visokoj temperaturi. Ugljenost guma se takođe može direktno koristiti kao katalizatorski materijal za smanjenje operativnih troškova i poboljšanje kvaliteta piroliznog ulja i gasa. Modifikovano ugljenisanje pneumatika sa visokom specifičnom površinom i nižim sadržajem pepela može se koristiti kao adsorbujući materijal sa aktivnim ugljem, nosač katalizatora i katalizatora, elektroda kondenzatora za stvaranje veće komercijalne vrednosti, kao adsorbent, u baterijama i tako dalje. Predlaže se da se razvijaju aplikacije za reciklažu ugljenih guma, što može stvoriti visok nivo potencijalnih ekonomskih izgleda za industriju pirolize otpadnih guma.

Ključne reči: *Piroliza, otpadne gume, ugljen, modifikacija, čađ.*

Naučni rad

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