



# Utilization of Waste Tire Char and its Applications in Liquid Phase Adsorption: A review

<sup>1</sup>A.V.S.L.Sai Bharadwaj, <sup>2</sup>R.K Singh

M.Tech (Research) <sup>1</sup>, Professor<sup>2</sup>

National Institute of Technology- Rourkela

Email: <sup>1</sup>bharadwaj801@gmail.com, <sup>2</sup>rksingh@nitrkl.ac.in

**Abstract:-** A review of production of activated carbon from waste tire char is presented. This review compiles the work done by various researchers on the characterisation of activated carbon from tire char and its applications in liquid-phase adsorption. Effect of various process parameters particularly activation temperature, burn-off, surface area on the activation stage are reviewed. Influence of activation conditions physical and chemical of activating chemicals, on the active carbon properties is discussed. Under certain process conditions several active carbons with BET surface area over 1000m<sup>2</sup>/g has been produced with extensive micropore volume, over 40% of total pore volume. Adsorption characteristics of activated carbon were discussed.

**Keywords:** A: Activated Carbon, B: Activation, C: Pyrolysis.

## I. INTRODUCTION

The disposal of tires represents a major environmental issue throughout the world. Major aspects of tire problems are listed below:

- Tire stock piles provide breeding ground for mosquitoes, this in turn causing serious disease and affecting human health.
- Fire hazards in large stockpiles that could consequently cause uncontrollable burning and air pollution.
- The current “conservation of natural resource concept”, i.e. the reuse (retard) first, then reuse of rubber prior to disposal, does not accommodate the ever increased dumping of tires.
- Due to high cost of legal disposal of tires, illegal dumping may increase.
- Tires take up landfill space.

Production of char from waste tire pyrolysis has generated considerable interest. During past 10-15 years, several fundamental studies have reported that carefully controlled tire pyrolysis can produce a number of

products. Most of the literature refers to production of activated carbons from waste tire char. These activated carbons have been used to adsorb phenols, basic dyes. Present paper reviews the characterisation and applications of activated carbons prepared from waste tires.

## II. EXPERIMENTAL METHODS FOR CARBON PRODUCTION FROM TIRES:

Physical activation using CO<sub>2</sub>/Steam as oxidising agents are the most commonly used production of tyre carbons; overall process usually consists of two steps, carbonisation of raw material followed by activation at elevated temperatures. Carbonisation temperature ranges between 400°C-800°C, and activation temperature ranges between 700°C-1100°C. Carbon characteristics are generally increased by degree of activation but also by nature of activating agent. TABLE-I represents the summary of tire carbons activated by different conditions. For the purpose of elevating the degree of burn-off, the activation temperature is usually higher than 900°C to maintain a sufficiently high reaction rate.

When steam is used as activating gas apparent activation energy of gasification has been measured as 201 KJ/mol [1]. Pyrolysis and activation of tire were carried out in helium environment at 900°C with steam for 1hour, product obtained has a BET surface area upto 1260m<sup>2</sup>/gm, although the final mass yield product is as low as 9% of initial tire mass [14]. Experimental results show that a sharp increase in surface area has been observed when activation took place at a temperature of 900°C or above. It is also observed that burn-off (wt %) also increases at the same activation temperature of 900°C [16]. In one of the studies, tire rubber was pyrolysed at 600°C under nitrogen for a period of 45minutes, followed by activation conducted at 850°C-900°C, with a flowing steam-nitrogen mixture for 0.5-0.3hour. The resulting carbons exhibited high specific surface area upto 1031m<sup>2</sup>/gm with a decreasing trend in pore diameter with activation [10]. Waste tire char was employed as a precursor for the production of activated

carbons with steam activation in a fixed bed reactor at 900°C, carbons with different porosities were obtained by activating the char to different extents of burn-off. Experimental results show that the surface area and pore volume of the carbons increase with the extent of activation and pass through a maximum at a burn-off of 43%, above which the porosity decreases with further activation [25].

Some metallic components in ash are considered to have a significant influence on the rate of activation as well as the formation of pores in the presence of oxides on the surface [10]. To investigate the effect of ash on the reactivity of tire derived char, acid demineralisation was attempted to remove species such as calcium compounds prior to activation stage. It has been shown that the reactivity of char treated by 5M HCL was around 22% less than those samples without acid treatment in steam activation [1], in which calcium ions in the char catalysed the gasification reaction, which as a consequence decreases the importance of water-gas shift reaction. Acid treatment was also found effective in the removal of inert mineral matter, which blocked the pore

structure of pyrolysed char, leading to an increase of micropore and mesopore volumes. The tire derived carbon had a specific surface area of 1119m<sup>2</sup>/gm and 1.62cm<sup>3</sup>/gm mesopore volume, when the pyrolysed char was treated with 1M HCL at room temperature for one day prior to steam activation in which a mixture of steam/nitrogen was used [2].

The particle size of tire rubber was found to have influence on the porosity of resultant carbon generated from steam activation. Both surface area and micropore volume of carbons produced from powdered tire rubber (particle size < 0.42mm) were 5% and 40% higher than those carbons prepared from particles in larger size (particle size < 2.0mm) [17]. It is believed that smaller particles allowed better diffusion of steam molecules into the structure, leading to a more homogenous activation of carbonised precursor. For the process in which tire rubber was heated at 700°C, followed by activation under steam-nitrogen mixture at 925°C for 640 minutes, the BET surface area and micropore volume was found to be 1070m<sup>2</sup>/gm and 0.5cm<sup>3</sup>/gm respectively [17].

Table-I: Pore and Surface Characteristics of Tire Carbons Activated Under Different Conditions

S. NO	Reference	Particle size of tire rubber (mm)	Charring conditions (oC,hr)	Activation conditions (oC, hr)	Char, burn-off (%ash - content)	Chemical treatment	Activating gas flow rate (ml/min)	Bet surface area (m <sup>2</sup> /gm)	Volume (micropor) (cm <sup>3</sup> /gm)
1	Adrian M. Cunliffe et.al(1999)	30	450,1.5	935,-	64	Steam	146	640	-
2	Ariyadejwanich et.al(2003)	<0.595	500,1	850,4	77.5	Steam	680	1119	0.57
3	Allen JL et.al (1999)	50	800,-	877,-	41	Steam	-	528	-
4	Brady TA et.al(1996)	2.5	600,0.75	850,-	-	Steam	542	1031	0.28
5	Guillermo San Miguel et.al(1998)	<0.42	500,-	(300-1000),-	42	N <sub>2</sub>	500	85	-
6	Lehmann CMB et.al(1998)	2-3	-	850,3	-	Steam	500	1000	.44
7	Ogasawara S et.al(1987)	2	-	900,3	-	Steam	61	1260	-
8	R. Helleur et.al(2001)	1cm	550,-	875,7	25.5	Co <sub>2</sub>	342	270	-
9	S.-E. Wen et.al(2005)	2.5-7	450,-	950,4	20	Co <sub>2</sub>	300	140	.053
10	San GM et.al(2001)	<150µm	700,-	925,10.5	15-25	Steam	500	1070	0.498
11	San Miguel G et.al(2003)	<150µm	700,-	925,-	40.5	Co <sub>2</sub>	-	1070	0.554
12	Sun J et.al	3	600,0.75	900,1	-	Steam	500	1031	0.28
13	Streat M et.al(1995)	-	-	800,24	-	Steam	200	346	-
14	Teng H et.al(1995)	<0.3	900,-	900,-	-	Co <sub>2</sub>	-	813	-
15	Teng H et.al(2000)	0.2-0.3	-	700,0	-	KOH,N <sub>2</sub>	100	474	0.23

Carbon dioxide is considered as one of the potential activating agents in production of activated carbon, from tire. Product prepared in 1atm carbon dioxide at 900°C with surface area of 370m<sup>2</sup>/gm at 50% burn-off was reported in literature [22], revealing that surface area of tire carbons were increased by performing activation under a higher partial pressure of activating agent. The surface area achieved by carbon dioxide activation

exhibits a linear increase with increase in burn-off due to relatively low level of carbon monoxide and hydrogen at initial stage of activation [16]. Another study reported a mass loss of 25.5% and carbon dioxide activated carbon was found to have a surface area of 270m<sup>2</sup>/gm, while the carbon prepared via steam activation at similar burn-off(25-9%) was 302m<sup>2</sup>/gm [18]. The effect of activation temperature in the carbon dioxide activation process was investigated in a case where tyre rubber was heated to

700°C in nitrogen, when this temperature was reached gas was substituted by carbon dioxide at a flow rate of 500ml/min and further heated to 950°C-1100°C for 60-640 minutes [18]. The results showed that increasing temperature had little effect on the characteristics of carbons in the temperature range between 950°C-1100°C. Thermo chemical degradation of waste tires in a carbon dioxide atmosphere without treatment of devolatilization (pyrolysis) in order to obtain activated carbons with good textural properties such as surface area and porosity was studied, in this case operating variables studied are carbon dioxide flow rate (50 and 150ml/min), temperature (800°C and 900°C) and reaction time (1-3hour). Kinetic measurements show that the reactions involved in the thermo chemical degradation of waste tire with carbon dioxide, are similar to those developed in the pyrolysis process carried out under nitrogen atmosphere and temperature below 760°C, for particular sizes of 500µm and 5°C/min. Activated carbon with surface area of 414 m<sup>2</sup>/gm at temperature of 900°C, carbon dioxide volumetric flow rate of 150ml/min and 180minutes of reaction time was obtained [12]. Scrap tires were first pyrolysed under nitrogen or carbon dioxide gas under various temperatures to produce char, and then activated by the post-pyrolysis oxygenation at different temperature ranges as soon as the pyrolysis process was completed. Batch mode removal of aqueous copper using the chars revealed that, for nitrogen and carbon dioxide the optimum conditions for pyrolysis was at 550°C and for activation was from 250°C-550°C [25].

Chemical activation is an alternative process of production of activated carbon from tyres. Preparation of activated carbon by chemical activation is a single step process in which carbonisation and activation is carried out simultaneously. Initially the precursor is mixed with chemical activating agent, which acts as dehydrating agent and oxidant. Chemical activation offers several advantages over physical activation which mainly includes, (i) lower activation temperature (<800°C) compared to physical activation physical activation temperature (800°C-1100°C), (ii) single activation step, (iii) higher yields, (iv) better porous characteristics, and (v) shorter activation time. The most commonly used chemical activating agents are H<sub>3</sub>PO<sub>4</sub>, ZNCl<sub>2</sub>, and KOH. Although a wide variety of activating agents are used, using KOH in making carbons has become popular in recent studies. Tire rubber is mixed with KOH pellets in the mass ratio of 1:1, and activated at 850°C in nitrogen for 0.5-1.5hour. In this case a higher activation temperature was chosen for treating samples so that a shorter activation period could be applied [19]. The activation period was set at 1.5hour, giving the resultant carbon a specific area of 820m<sup>2</sup>/gm and a micropore volume upto 0.274cm<sup>3</sup>/gm. The authors also reported that a smaller particle size (0.4mm) of tire was used and was favourable as it would allow good surface contact with KOH. The effect of mass ratio between KOH and tire proved to be an influencing factor to the pore development of carbon derived from

tire [23]. The experimental results shows that the BET surface area increased as the KOH/tire mass ratio increased and reached the maximum. When the ratio is 4 beyond that point the BET surface area declined significantly in parallel with yield. It was shown that at the activation temperature of 700°C and zero holding period, the carbon produced had a maximum BET surface area of 474m<sup>2</sup>/gm with a micropore volume of 0.23cm<sup>3</sup>/gm. Increasing the holding period to 2hours would result in a increase of mesopore volume. But in return, micropore volume would go down as the consequence of the collapse of micropore walls in an extended heating process due to hydrophobic nature of the tyre surface that prevented penetration of KOH into the interior of rubber matrix. Higher surface areas would be possible if the contact between KOH and tyre particles could be improved. In one of the study tire rubber is pyrolysed (at a flow rate of 170ml/min) in a horizontal furnace under a steam of argon heated at 10°C/min from room temperature to final pyrolysis temperature of 550°C or 800°C. In this case chemical activation with KOH is performed at 550°C or 800°C, with waste tires weight ratio of 4:1 for 60minutes in argon temperature (flow rate of 330ml/min), giving resultant carbon a specific area and pore volume of 210m<sup>2</sup>/gm, 0.213cm<sup>3</sup>/gm (at 550°C) and 574m<sup>2</sup>/gm, 0.519cm<sup>3</sup>/gm (at 800°C) [20]. Waste tires were pyrolysed at 450°C in a batch reactor under atmospheric pressure for 2hours recovered carbon black residues were studied to investigate their characteristics for use of possible adsorbent. Due to various inorganic additives of the original tire that contaminated the carbon black obtained, it was treated with acid for demineralization. In this case the demineralised carbon black was activated at 900°C in a furnace and observed that acid treatment and activation increased the surface areas and decreased the concentration of contaminants [8]. Waste tire rubber is used for the removal of pesticides from waste water by adsorption phenomenon. In this case by applying successive chemical and thermal treatment, a basically carbonaceous adsorbents is prepared which has "not only a higher mesopore, micropore content but also has a favourable surface chemistry" [24].

### III. PROPERTIES AND CHARACTERISTICS OF TIRE CARBON

#### 3.1 Surface area:

Surface area is one of the key indicators attributed to the adsorptive properties of porous materials. The most commonly used model in determination of surface area is well known as BET equation [5]. The development of surface area is shown to have a linear relationship with degree of burn-off, which is a function of different factors such as activation temperature and holding time [1], [14], [16], [6], [18]. Generally increase in activation temperature would result in rise of burn-off due to burn out of micropore walls. It appeared that most steam activated carbons exhibited higher BET surface area than those prepared from carbon dioxide activation. The

BET surface area of steam activated carbons are generally in excess of 1000 m<sup>2</sup>/gm [14, 10, 2, 18, 6] although carbon dioxide activation also gave products with good surface area ranging from 270 to 980 m<sup>2</sup>/gm [17], [23], [18], [13], [15]. This could be explained by molecular nature of steam because the water molecule is smaller than carbon dioxide, giving faster diffusion into the porous matrix and micropores [18].

### 3.2 Pore size and volume:

Pores in different sizes are important to the overall capacity of adsorbents in adsorption process. The presence of micro and mesopores in activated carbons enhance the adsorption of large adsorbates such as dye molecules [20]. When using steam as an activating agent, pores in tyre carbons would be broadened [19] and the adsorptive capacity of tyre carbons will increase with increase in micropore volume in certain gaseous adsorption process due to the enhanced adsorption potential of gas molecules in small pores [10], [3]. Experimental data suggested that tyre chars developed a very narrow micro porosity during the initial stages of steam activation process (up to 15-25% burn-off). When the holding period was extended continuous pore enlargement increased the porosity from a predominantly micro- to a mesoporous structure [17]. It should be noted that chemical treatment of tyre rubber before activation results in change of porosity. When the pyrolytic char was treated with 1M hydrochloric acid prior to steam activation, the increase in both micro and mesopore volumes from 0.26 and 1.09 cm<sup>3</sup>/gm to 0.57 and 1.62 cm<sup>3</sup>/gm, respectively were observed [2]. For a chemical activation process in which KOH was used as an activating agent, literature values reported that the total pore volume rose in parallel with the increasing amount of KOH impregnated. This phenomenon is due to enlargement of micropores developed at the initial stage of activation [22].

## IV. APPLICATIONS OF TYRE BASED ACTIVATED CARBON IN WASTE WATER TREATMENT:

Commercial activated carbons is a preferred adsorbent for the removal of micro pollutants from aqueous phase, however, its wide spread use is restricted due to high associated costs. Activated carbons prepared from conventional (from agriculture and wood industry) and non-conventional (from municipal and industrial waste) can be applied in various aqueous treatment process, namely to remove organic pollutants, dyes, volatile organic compounds and heavy metals [9]. There is a wide range of applications of tyre char and carbons in different areas. Similar to other adsorbents tyre carbons can be used in waste water treatment process. Activated carbons have long been used in the removal of organic and inorganic species in industrial production process. Owing to high surface area (ranging from 164 to 1260 m<sup>2</sup>/gm) and pore volume (up to 1.62 cm<sup>3</sup>/gm), tyre carbons are considered as potential adsorbents in waste

water treatment for the purpose of removing organic pollutants such as phenol and p-chlorophenol. Experimental results were found promising, as the amount of uptake was comparable to conventional carbons derived from coal and wood [21]. Other examples in using tyre derived activated carbons in water treatment include the removal of chromium [15], lead [10], dyes, and phenol [10], [2], [22], [7]. Tyre rubber carbonised at temperatures ranging from 450°C-750°C were tested for adsorption efficiency of methylene blue, phenol, iodine [16]. When the chars were further activated by carbon dioxide, the uptake of iodine was over 350 mg/gm, showing a high adsorption capacity for species of larger molecular weight [16]. Similar observations in which the steam activated tyre carbons showed better adsorption capacity for dye (black 5) and slightly lower phenol adsorption capacity in comparison with commercial carbons [2].

## V. CONCLUSION

This review presents the current status of research in production of activated carbon from environmental applications using waste tyres. Several active carbons have been produced with BET surface area over 1000 m<sup>2</sup>/gm using steam activation. Although several studies report the production of tyre derived activated carbons using carbon dioxide, these generally have surface areas in the range of 270-980 m<sup>2</sup>/gm. Wet chemical activation using KOH has achieved a surface area of 820 m<sup>2</sup>/gm at a activation temperature of 850°C. There is a wide range of applications of tyre char and carbons in waste water treatment process.

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