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THE ADSORPTION CHARACTERISTICS OF TIRE-DERIVED ACTIVATED CARBONS

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ABSTRACT:
The effects of heating temperature of pyrolysis and activation processes are essential to develop pore structures in the chars and activated carbons. Too high temperature causes pore narrowing and pore enlargement during pyrolysis and activation. The proper activation is essential for high aqueous adsorption of raw char, especially for small molecular adsorbates. Both raw chars and activated chars have relatively good adsorption capacity comparable with that of commercial carbons. Tire-derived activated carbons can be used as an excellent mesoporous adsorbent for larger molecular species.
KEYWORDS:
pyrolysis, activation, char, heating temperature, tire-derived activated carbon, porosity.

1. INTRODUCTION

The large amounts of used tires in dumps or landfills are environmental and fire hazards. Environmentally safe and feasible new tire recycling technologies are needed.

Used tires are a potential source of energy, fuels, and raw chemicals, because of the hydrocarbon base of tire rubber. Pyrolysis of scrap tires, with recovery of chars, oils, and gases, is generally considered to be an economically promising and environmentally acceptable disposal procedure. Tire rubber consists primarily of styrene-butadiene rubber (approx. 62%) and carbon black (31%) [1], [7]. When tire rubber is pyrolyzed, the rubber polymer matrix breaks down, yielding 33-38% solid char, 38-55% liquid oil, and 10-30% gasses by mass. The characterization and potential application of pyrolytic gases and oils has been the subject of a number of publications. Pyrolytic oils, a mixture of paraffins, olefins, and aromatics, possess a high calorific value and can be used directly as fuel or can be added to petroleum refinery feedstocks. [2] Oils can be properly cut according to desired temperatures, then they can either be solely used as a source of valuable chemical feedstocks or have some of the chemicals extracted and the residue used as a fuel [3]. Pyrolytic gas contains high concentrations of methane, butadiene, and other hydrocarbons with high calorific values [4]. Generally, the gas is used as a process heat resource instead of a commercial product because of its low yield in the pyrolysis process.

The pyrolytic char, consisting of recovered raw carbon black, inorganic rubber additives (e.g., zinc, clays, and silica), carbonaceous deposits, and nonvolatile hydrocarbons, has been formed during tire pyrolysis. The economic viability of a tire pyrolysis process depends on the quality of the pyrolytic char. However, its potential use is restricted to low-quality applications because of the presence of high carbonaceous deposits, high ash content (>10%), and large particle size [5]. Producing activated carbons from waste tire rubber enables recycling of this material and potentially provides a low cost adsorbent for air pollution control applications.

2. PHYSICAL CHARACTERISTICS OF ACTIVATED CARBON

Activated carbon is characterized by bulk density, total ash content, abrasion number and particle size which affect its sorption properties.

Bulk density is usually measured in $g.ml^{-1}$, and is used to determine the weight of a fixed volume of activated carbon. For granular activated carbons (GAC) used to determine an accurate value for the weight of GAC necessary to fill a fixed bed volume.

Total ash content is the measure of the amount of mineral matter (Ca, Mg, Si, Fe) in activated carbon. This parameter can be misleading by itself because the soluble ash content is a more important parameter than total ash content for liquid phase applications. For some applications higher ash content may be beneficial due to the ability of certain ash constituents to chemisorb specific types of adsorbates such as metals, inorganic species and some synthetic organics.

Abrasion/hardness number is the relative measure of the ability of granular carbon to resist attrition during handling and operation. The higher the value, the more resistant to physical degradation.

Particle size affects the rate of contaminant adsorption or catalytic activity. It determines the pressure drop across a granular carbon bed or a powdered carbon filter cake.

3. ACTIVATION PROCESS

Carbon is usually activated by steam or chemical treatment, with steam being more common. Steam activation involves two steps: pyrolysis and activation. Pyrolysis involves the conversion of the raw material into a disordered carbon structure with a very low volatile content. Carbonization is done at elevated temperatures in an oxygen-lean environment which keeps it from burning. In activation, some carbon atoms are vaporized, leaving behind the highly porous structure.

Steam activation is carried out in rotary kiln at temperatures of approximately 900°C. At these conditions, carbon reacts with steam to form carbon monoxide and hydrogen, which exit as gases. The result: a highly porous carbon material (Fig. 1) [6].

FIGURE 1. Electron microscope photograph of activated carbon pores

The adsorption characteristics of tire-derived activated chars are influenced by activation process parameters -.the activation temperature, time, agent flow rate, and agent kind on the tire char activation.

Raw tire shreds have to be heated in ultra-high purity nitrogen to activation temperatures in the reactor furnace, and subsequently activated. The activation gas is a mixture of a steam and ultra-high purity nitrogen. Tire shreds are activated at temperatures between 700 and 900°C for minimum half an hour.

The process of tire activation yields carbon with adsorptive characteristic similar to those of commercially available activated carbons. Adsorptive capacities for toluene, phenol, polychlorinated biphenyls (PCBs) and aniline are comparable to those obtained with commercial carbons.

The significant parameter for sorption characteritic of activated carbon is the pyrolysis temperature. Table 1 presents the analysis of pyrolytic chars obtained from process at temperature range from 450 to 550°C [5].

Table 1. The content of pyrolytic products in tire-derived chars obtained under the variable pyrolysis temperature

Char composition (wt %)	Pyrolysis temperature		
	450°C	500°C	550°C
Moisture	3,40	2,35	1,28
Ash	12,51	12,32	14,58
Volatile matter	16,61	16,14	6,92
Fixed carbon	67,47	69,19	77,22
Calorfic value (MJ/kg)	31,2	31,5	30,0

With increasing temperature, the content of volatile matter decreases, on the other hand, the content of fixed carbon increases. The content of volatile matter drops sharply between 500 and 550°C. The temperature in excess of 550°C favors the evaporation of volatile matters.

The chars contain approximately 81-82,17% carbon (on dry basis) and contributes >90% to the organic matters of char. The hydrogen content is decreasing slightly with increasing temperature, indicating that the lower formation of hydrocarbon deposits at a higher pyrolytic temperature.

The nitrogen and sulfur contents of chars is approx. 0,45-0,61% and 2,28-2,53%, respectively. They both seem not to be influenced by pyrolysis temperature.

The calorific value of pyrolytic char is 30 to 31,5 MJ/kg, and the value is decreasing with increasing pyrolysis temperature. The calorific value is in relation to the content of volatile matter. The char has enough calorific value to be used as fuel.

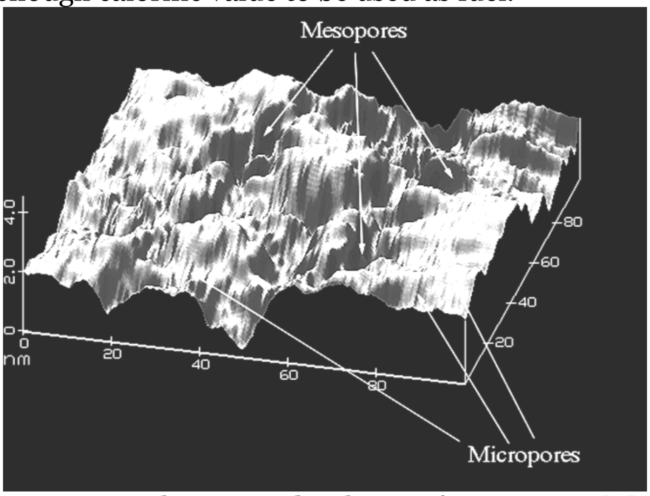

FIGURE2. The activated carbon surface scanning [8]

The good material mixing due to the kiln rotation promotes the quality of char products.

Pore Characteristics and Surface Area of Pyrolytic Char. It is known that the pore volumes of char or carbon include the macropore (>50 nm), mesopore (~2-50 nm), and micropore volumes (<2 nm) (Fig. 2) [8].

In general, the tire carbons have more meso- and macropores in comparison to carbons prepared from coals, and increased mass loss increases the surface area.

4. APPLICATIONS OF TIRE-DERIVED ACTIVATED CARBON SORBENTS

Activated carbon with the pore size distribution in powdered, granular and extruded forms can be used as a cost effective adsorbent for water, gas phase and industrial process applications.

In water applications, the activated carbon may be used for drinking water treatment, dechlorination, for process water treatment, swimming pools and aquaria water treatment, wastewater treatment, groundwater and landfill leachates treatment, for soil and water remediation and last but not lest for beverage water treatment.

In gas phase applications, activated carbon can be effectively used for solvent recovery and VOC removal, flue gas treatment applications, in gas masks, for pressure swing adsorption, solvent and vapor recovery, air and gas purification and desulfurization.

In industrial process applications, activated carbon (AC) is used as catalyst, for amine glycol and fine chemicals production, AC is also used in electroplating and dry cleaning, further for cane sugar, corn sweeteners, scrap candy, lactose, edible oils and fatty acids production, wine and fruit juice production, in spirits distillation process, and medicinal, pharmaceutical, agriculture and mining processes [6], [7].

5. THE CONCLUSIONS

Sorbents made from scrap vehicle tires provide a two-fold environmental benefit: waste vehicle tires are recycled, and new sorbents are produced that may be more economical and beneficial to the environmental quality industry.

The steam activation process significantly affects the surface characteristics of the carbon black derived from the pyrolysis of waste tires. The temperature of the pyrolysis and activation process influences significantly the sorption capacity of activated carbon for certain contaminants, and on the other hand, the economical feasibility of waste tires recycling.

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