

Pyrolysis of Scrap Tires and Conversion of Chars to Activated Carbon

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The primary objective of this work was to demonstrate the conversion of scrap tires to activated carbon. We have been successful in this endeavor, producing carbons with surface areas greater than 500 m²/g and significant micropore volumes. Tire shreds were pyrolyzed in batch reactors, and the pyrolysis chars activated by reaction with superheated steam. Solid products of pyrolysis and activation were studied with nitrogen adsorption techniques. We find that the porosity development during steam activation of tire pyrolysis char is similar to that reported for various other chars. A maximum in micropore volume is observed as a function of conversion, but the total surface area increases monotonically with conversion. We suggest that the activation process consists of micropore formation, followed by pore enlargement. The process conditions used in this study are a good starting point from which to optimize a process to convert tires to activated carbon.

Introduction

Scrap tires are a major environmental problem. An estimated 2.5×10^9 kg of scrap tires are generated each year in North America (Williams et al., 1990). The conventional method of reusing waste rubber is to convert it into rubber reclaim, which is suitable for mixing with virgin rubber compounding materials. However, rubber reclaim generated from scrap tires does not have suitable properties for use in tire manufacture and must be used for low-value rubber goods (Makarov and Drozdovski, 1991). Moreover, production with rubber reclaim can be more costly than production with virgin raw materials (Crane and Kay, 1975). As a result, the majority of scrap tires accumulate in dumps, posing hazards such as disease and accidental fires.

Tires contain carbon-black-reinforced rubber, and both inorganic and organic belt materials. The rubber component may be natural rubber, but styrene-butadiene (about 25% styrene) copolymer rubber (SBR) is more common. A typical tire compounding composition contains 62 wt. % SBR, 31 wt. % carbon black, and small amounts of other materials including extender oils, sulfur, zinc oxide, and stearic acid. Carbon black is used to reinforce the rubber. The rubber is cross-linked by vulcanization, which involves reactions with sulfur. Small amounts of zinc oxide and stearic acid are added to control

the vulcanization process and enhance the properties of the final products (Studebaker and Beatty, 1978).

The potential value of reusing the polymeric base of old tires has received considerable attention. Alternatives include production of goods with reclaim, use of ground rubber as construction filler, and degradation to basic raw materials by pyrolysis (Makarov and Drozdovski, 1991). Filler and reclaim applications have relatively small economic potential. Incineration of tires may be an effective means of waste volume reduction, but incineration does not recover much of the intrinsic value of the materials in the tire (Williams et al., 1990). The hydrocarbon base of tire rubber makes used tires as a potential source of liquid fuels and chemical feedstocks. Pyrolysis of tires to produce liquid hydrocarbons, gases, and solid products is an appealing resource recovery alternative.

In most tire pyrolysis studies, the quantity of char produced exceeds the amount of carbon black present in the scrap tires. Thus, the solid product may be regarded as a mixture of carbon black and char formed by tire rubber degradation. The economic feasibility of tire pyrolysis is strongly affected by the value of this solid pyrolysis residue. A similar situation exists for fossil fuel pyrolysis (NRC, 1990). The simultaneous production of valuable solid products and liquid fuels from what is presumably a waste material could make tire pyrolysis very profitable.

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conversion of scrap tires to activated carbon. We have been successful in this endeavor, producing carbons with surface areas greater than 500 m²/g and with significant micropore volumes. A related objective was to observe the development of porosity during activation. In this article, we report the results of a laboratory study of tire pyrolysis and activation. We have identified process conditions that are a good starting point for the optimization of activated carbon production from scrap tires and have characterized changes in the carbon pore structure as a function of carbon conversion during steam activation. We expect that these results will be useful in related studies on other polymeric scrap materials.

Background

Research on tire pyrolysis has proceeded on a laboratory and manufacturing scale for many years. Pilot-scale systems for the recovery of oils and carbon black from tires have been described in the literature (Schulman and White, 1979; Kaminsky and Sinn, 1980; Kawakami et al., 1980), and at least one of these research groups still has an active program in pyrolysis of polymeric wastes (Kaminsky and Rossler, 1992). The reactors in these studies range from rotary kilns to fluidized beds. While operating conditions are typically near ambient pressure, at least one extensive study of tire pyrolysis under subatmospheric conditions has been reported (Roy et al., 1990).

Tire pyrolysis

Tire pyrolysis yields gaseous, liquid and solid products. Most research work has emphasized the search for pyrolysis conditions that maximize the yield and market value of the liquid products (Williams et al., 1990). Typical pyrolysis yields (by weight) reported in the literature are 25–60% condensable liquids (oil), 30–50% char, and the balance noncondensable gases consisting of hydrogen, carbon monoxide and dioxide, and small hydrocarbons. It is important to note that a substantial amount of solid product is recovered in virtually all laboratory- and pilot-scale tire pyrolysis processes.

The inorganic constituents of scrap tires may become impurities or "ash" in the pyrolysis chars, or the inorganics may volatilize and become part of the liquid or gas product streams. The fate of sulfur during tire pyrolysis is particularly important for fuel applications of the products. Electron microscopy with elemental X-ray analysis shows that the positions of zinc deposits within tire char particles coincide with the positions of sulfur deposits, suggesting that the ZnO and sulfur present in the tires react during pyrolysis to form ZnS (Ogasawara et al., 1987; Teng et al., 1992). Because sulfur is retained as an ash constituent of the char, the liquid and gaseous products have relatively low sulfur contents and are suitable for low-sulfur-emission fuel applications. In a typical pyrolysis experiment, approximately 78% (by weight) of the original sulfur is retained in the pyrolysis char, with 13% emitted in the gas-phase (predominantly as SO₂) and 9% in the liquid-phase product (Teng et al., 1992).

Tire char may find use as a solid fuel, although this may be precluded for environmental reasons by the sulfur content. Collins et al. (1974) reported an ignition temperature of approximately 510°C and a heat of combustion of order -3×10^4 kJ/kg (about -360 kJ/mol if char is considered to be carbon only) for tire pyrolysis chars.

Tire char can be used as a reinforcing filler for low-value rubber goods and perhaps as a printing ink pigment after appropriate treatment (Petrich, 1991). Several studies have been conducted on using tire char, instead of carbon black, for filling polymers and vulcanizates (Crane and Kay, 1975; Kawakami et al., 1980; Makarov and Drozdovski, 1991). The quality of vulcanizates filled with tire char tends to lie between the qualities of vulcanizates produced with high-activity and low-activity commercial carbon blacks. It is important to note that carbons used in these applications have a relatively low selling price. A higher value use for the tire char would make pyrolysis processing of scrap tires much more attractive.

Activated carbon

Activated carbons are used as adsorbents in applications like wastewater treatment and solvent vapor recovery. The high adsorption activity of these carbons results from the high surface areas in the interior of the particles. Commercial activated carbons have surface areas greater than 400 m²/g and many have areas over 1,000 m²/g. Complete characterization also requires a description of the pore-size distribution. Pores are typically divided into three classes: macropores ($d > 50$ nm), mesopores ($2 \text{ nm} < d < 50 \text{ nm}$), and micropores ($d < 2 \text{ nm}$). Most of the internal area lies in micropores (de Vooys, 1983). Microporosity is usually characterized by a micropore volume, since there is no generally accepted method of determining micropore size distribution. Kinetic effects may render smaller micropores inaccessible on the time scale of many adsorption applications. The adsorption activity of the internal surface also depends on surface functionality (de Vooys, 1983; Jagiello et al., 1992; Murrell et al., 1988).

Carbon gasification

The rate of carbon gasification is proportional to the surface concentration of carbon atoms. At first glance, one would expect that this concentration could be expressed in terms of the total surface area of the carbon sample (TSA) or in terms of the specific surface area (A_g). However, it has been clearly demonstrated in gasification studies of carbons ranging from highly graphitized carbon blacks (Laine et al., 1963) to coal chars (Radovic et al., 1983; Lizzio and Radovic, 1991) that the parameter governing the rate is not the total surface area, but the reactive surface area (RSA). Furthermore, the reactive surface area is different from the often measured active surface area (ASA) in that the active surface area provides adsorption capacity, but the adsorption sites are not necessarily reactive. Following Lizzio and Radovic (1991), defining the units of TSA, ASA and RSA as (grams of total, active, or reactive surface carbon/gram of total carbon), the overall rate of gasification is:

$$R = \eta k C_{cs} = \eta k (TSA) \left(\frac{ASA}{TSA} \right) \left(\frac{RSA}{ASA} \right) = \eta k (RSA) \quad (1)$$

The effectiveness factor, η , is the ratio of the overall rate of reaction to the rate that would occur if the entire surface were exposed to the same conditions as the particle exterior (Satterfield, 1991). For optimal preparation of porous solids, η should be unity.

The concept of reactive surface area is of great importance

in tire char gasification, since the char is a heterogeneous mixture of carbon black and pyrolyzed SBR. The heterogeneity of reactivity in this material is similar to, but perhaps simpler than, the heterogeneity of reactivity in coal chars. With a typical tire composition having 30 wt. % carbon black, and a typical pyrolysis char yield of 35–40 wt. %, between 75 and 85% of the char is the original carbon black, and the balance is charred rubber. It seems likely that the rubber char is more reactive than the carbon black because of the general understanding that disordered carbons gasify more rapidly than well structured materials (Marsh and Kuo, 1989; Radovic et al., 1983). Activated carbon precursors typically contain carbon which is organized into graphite-like clusters and carbon which is disorganized. The disorganized carbon is gasified in the early stages of activation (Wigmans, 1989).

Our previous work (Merchant and Petrich, 1992) showed that the gasification kinetics of tire char were much slower than those of chars derived from coal or almond shells. These observations support the expectation that chars from different raw materials vary in degree of graphite-like organization, which affects gasification kinetics.

Experimental Studies

Raw materials

The truck tire shreds used in our experiments were about 1 cm in size, while the automobile tire pieces were about 0.5 cm. The tire samples contained no metallic belt materials, but did contain synthetic cords.

Pyrolysis reactors

Two pyrolysis systems with different heating rates were used in this study. Both operate at a pressure of approximately 1 atm. One of the reactors is a 75-mL, stainless steel U tube (2.54-cm-OD) heated by a muffle furnace. This system has a maximum heating rate of 25°C/min. A second system consists of a straight Inconel tube (1.3-cm-OD, 10-cm-long) heated in a fluidized sand bath. Although this system has a much smaller capacity, it provides much faster heating rates, since the reactor is immersed in a preheated sand bath. Heating rates up to 150°C/min can be achieved. Cooling rates are comparable to the heating rate. In both systems, liquid products are collected in cold water test-tube traps. Nitrogen purge flow rate through the reactor is typically 1.5 L/min (referenced to 1 atm and 273 K) (Merchant, 1992).

Activation reactor

Chars are activated by gasification with steam in a quartz tube reactor. The tube is wrapped with a ceramic-beaded resistor wire heater. Temperature is controlled by adjusting the voltage applied to the heater. The system includes a syringe for periodic injection of water into a heated stream of nitrogen. The heat input is adjusted so that the quantity of water injected is boiled away in the interval between injections. Char particles in each sample range from a few millimeters in diameter to relatively fine powder.

About 0.5 mL of water was injected into the system every 2 min (0.014 mol/min). The nitrogen flow rate was 0.59 g/min (0.021 mol/min). Based on these values, the average concentration of steam was 40 mol % during these experiments. Total pressure was slightly above atmospheric pressure. The

water feed rate was chosen to prevent axial concentration gradients in the reactor tube [that is, water conversion below the differential reactor criterion of about 5% (Satterfield, 1991)]. Based on the data given below, for example, 0.7 g carbon gasified in 60 min at 850°C, our reactor operates at about 7% H₂O conversion. Thus, we are not in serious violation of the differential reactor condition.

Analytical methods

Nitrogen adsorption experiments are conducted at liquid nitrogen temperature (77 K) in an Omnisorp 360 continuous sorption apparatus (Omicron Technology Corporation). We outgas chars under vacuum at 110°C prior to helium calibration and nitrogen adsorption. The ultimate pressure is on the order of 10⁻² Pa. Chamber dead volume is measured by continuous introduction of nonadsorbing gas (helium) into the chamber prior to nitrogen adsorption (McEnaney and Mays, 1989).

The surface area of unactivated tire chars can be determined from nitrogen adsorption at 77 K by the Brunauer-Emmett-Teller (BET) isotherm (Brunauer et al., 1938). The BET theory applies because tire chars have little microporosity prior to activation. Development of microporosity during char activation leads to deviations from the BET isotherm. Alternative methods such as pore filling models and the t-plot approach are preferred for microporous carbon characterization (Stoeckli, 1990; Murrell et al., 1988; Lippens and de Boer, 1965; Gregg and Sing, 1982), but BET surface areas continue to be reported. We report both the BET areas and the characterization information provided by the t-plot method so that our results may be compared easily to other published work.

Studies have suggested that the area occupied by the nitrogen molecule on a graphitic basal plane is 0.20 nm², rather than the usual 0.162 nm² used in characterizing most adsorbents (Gregg and Sing, 1982). Since we do not know that a graphitic model applies to many of our chars, we have used the conventional value (0.162 nm²) to calculate surface areas. Thus, our reported values of surface area are probably lower than the actual values. Because porous adsorbents also have external surface areas, it is a common practice to compare the surface area to that of a similar nonporous material (Gregg and Sing, 1982). We have not resorted to reference materials since we used fairly large particle sizes (> 10 μm) for adsorption experiments and do not expect much of a contribution to the total surface area from external area. As an example, a commercial carbon black with particle diameters between 0.2 and 0.5 μm has a BET surface area of only 6–9 m²/g (Lahaye and Prado, 1981).

Analysis of the adsorption isotherms with the t-plot method (Satterfield, 1991; Lippens and de Boer, 1965) provides the surface area of meso- and macropores, and micropore volume. The t-plot (volume of gas adsorbed vs. adsorbed film thickness) is generated from the adsorption isotherm by using a standard curve for nonporous materials which relates adsorbed film thickness to the partial pressure of adsorbing nitrogen gas. The y-intercept obtained by extrapolating the linear portion of the t-plot yields the micropore volume (volume in pores of less than 2 nm diameter). The slope of the linear region extending through the origin provides the surface area represented by meso- and macropores (2–50 nm and greater than 50 nm diameter).

Table 1. Pyrolysis Conditions and Characterization of Chars from Scrap Tires

Char	Pyrolysis Conditions and Char Yield					Nitrogen Adsorption Tests		
	Apparatus	T (°C)*	t_R (min)	Yield (wt. %)	Ash (wt. %)	S_{BET} (m ² /g)	$S_{m/m}$ (m ² /g)	W_o (mL/g)
TT-A	Furnace	560	60	35	11.1	48	27	0.01
TT-B	Furnace	520	60	35	11.6	67	61	0.002
AT-A	Sand Bath	510 (550)	63	33	11.2	74	70	<0.001
AT-B	Sand Bath	527 (570)	90	33	not tested	72	66	0.002
AT-C	Sand Bath	416 (445)	90	34	not tested	77	85	0.00
AT-D**	Sand Bath	530	60	35	not tested	83	129	0.00

*Values in parentheses are the temperature of the sand bath rather than the sample.

**Char AT-D was prepared using the U-tube reactor from the muffle furnace apparatus in the rapid-heating sand bath apparatus. The liquid product yield in this run was 44 wt. %, which is typical for our experiments on tire pyrolysis.

Results and Discussion

Pyrolysis results

Tire pyrolysis experiments show that the polymer structure is effectively degraded (about 33 wt. % char yield) in less than 60 min at pyrolysis temperatures above 500°C and within 90 min, when the temperature is approximately 420°C. The tire chars are very porous, with internal surface areas around 70 m²/g. Carbon-13 nuclear magnetic resonance spectra for tires have two absorptions corresponding to aromatic and aliphatic carbons. Spectra of the chars have a single peak in the aromatic range. These results are similar to those observed for a variety of pyrolysis chars (Merchant and Petrich, 1992).

Our primary concern has been with the solid char products, since we are interested in producing activated carbons. A list of chars from pyrolysis at various conditions is presented in Table 1. Because we suspect that good contact is not established between the thermocouple and the rubber samples in the pyrolysis reactor, we report the sand bath temperature in addition to the measured sample temperature. Our experience with coal pyrolysis in this system (Merchant and Petrich, 1991) has shown that the bed temperature is about 20°C less than the sand bath temperature. Char yields from pyrolysis of truck tires and auto tires are in the 33–35 wt. % range. This “char” consists of the carbon black originally in the tire embedded in carbon produced by decomposition of the rubber. Based on typical carbon black loadings, the “char” is roughly 75% carbon black particles. Ash content, defined as the percentage of char mass remaining after combustion at 600°C for 2 h, is about 11 wt. % for all tire chars. The ash content of one of the truck tire chars (TT-A) has been reduced to 2.6 wt. % by leaching in hydrochloric acid.

Nitrogen adsorption experiments were conducted on most of the pyrolysis chars. Our tests showed that varying the sieve fraction used for these tests had only a slight effect (about 5%) on the measured BET surface area, S_{BET} . We analyzed the adsorption isotherms by the BET and t-plot methods to determine the BET surface area (S_{BET}), micropore volume (W_o), and the surface area of the meso- and macropores ($S_{m/m}$) reported in Table 1.

All three automobile tire chars and one of the truck tire chars have BET surface areas around 70 m²/g and virtually no microporosity. One of the truck tire chars (TT-A) has a smaller surface area, but shows some microporosity. The difference between TT-A and TT-B surface areas cannot be attributed to the difference in pyrolysis temperature, since higher pyrolysis temperatures have been shown to generate higher

surface area chars (Williams et al., 1990). The only significant difference in these two samples is that the TT-A tire shreds had been cut to about a third of their original size, and most of the synthetic cord material was removed. The tire shreds were used as received for the TT-B experiment. We can tentatively attribute the difference in surface area between TT-A and TT-B to a particle size effect. Although faster heating has been reported to result in increased char surface area (Williams et al., 1990), it does not appear to follow that pyrolysis of smaller particles—which should heat up faster—will result in higher surface area.

Char AT-D has a BET surface area of 83 m²/g and no measurable microporosity prior to activation. The linear region of the t-plot for this char extrapolates to negative values of micropore volume, so the value of $S_{m/m}$, which is considerably greater than S_{BET} , is not meaningful. The t-plot behavior may reflect unusual pores in tire char caused by the presence of carbon black particles.

Activation results

Table 2 presents the experimental parameters and results for our tire char activation study. The conditions listed are temperature (T), residence time (t_R), average steam feed rate (F_{H_2O}), and nitrogen feed rate (F_{N_2}). Carbon conversion (X_C) is defined as the fraction of char mass gasified on an ash-free basis. The pyrolysis conditions and adsorption characterization parameters of the tire chars prior to activation are listed in Table 1. All measurements on automobile tire char D (AT-D) were made on char from a single pyrolysis run.

The conversions obtained after activation at 850°C are plotted as a function of reaction time in Figure 1. There is some scatter in the data, but there is strong evidence for a linear burnoff curve up to about 50% conversion. This result is similar to that reported for steam activation of coal reject derived char (Lu and Do, 1992).

Char reactivity studies are usually performed with equipment that allows continuous monitoring of mass loss. The slope of the conversion-time profile at any time is the instantaneous overall rate of reaction (dX_C/dt). Since our equipment is designed to generate reasonable quantities of activated char for adsorption characterization, we do not have the luxury of continuous burnoff curves at various temperatures. Single points at different temperatures must suffice. If we assume that these data points fall in the linear portions of the corresponding burnoff curves, then X_C/t_R approximates dX_C/dt .

Arrhenius-type plots of X_C/t_R vs. $1/T$ provide estimates of

Table 2. Activation of Scrap Tire Pyrolysis Chars

Char	T (°C)	t_R (min)	Activation		X_C (%)	Nitrogen Adsorption		
			F_{H_2O} (mol/min)	F_{N_2} (mol/min)		S_{BET} (m ² /g)	$S_{m/m}$ (m ² /g)	W_o (mL/g)
AT-B	850	30	0.057	0.021	9	121	77	0.02
AT-C	850	30	0.052	0.021	15	164	88	0.04
AT-D	780	60	0.016	0.021	9.54	not measured	—	—
AT-D	850	20	0.014	0.021	16.1	166	78	0.044
AT-D	850	30	0.014	0.021	30.5	308	108	0.097
AT-D	850	45	0.014	0.021	28.1	307	102	0.099
AT-D	850	50	0.014	0.021	35.3	not measured	—	—
AT-D	850	60	0.013	0.021	47.9	485	196	0.139
AT-D	850	80	0.014	0.021	59	553	382	0.074
AT-D	850	100	0.014	0.021	51.6	519	390	0.055
AT-D	920	60	0.015	0.021	73.0	607	560	0.011

the gasification activation energy ranging from 226 kJ/mol (low conversion data points only) to 153 kJ/mol (high conversion data points included). The high value is much higher than the value of 170 kJ/mol reported for the kinetically controlled steam gasification of coal reject char (Lu and Do, 1992), but does lie in the 164–270 kJ/mol range reported for steam gasification of a variety of chars (Li and van Heiningen, 1991). The lower value suggests that mass-transfer effects begin to intrude at high conversions (high porosities). Both estimates are high enough to convince us that we are gasifying in the chemically controlled regime (small mass-transfer resistance, $\eta \sim 1$), as required for good porosity development.

Development of surface area and porosity

Figure 2 shows how surface area and microporosity (S_{BET} , $S_{m/m}$, and W_o) develop during 850°C activation of automobile tire char AT-D. There is a very good linear correlation between S_{BET} and conversion. This result is consistent with the finding that surface area increased linearly with decreasing char yield during “wet pyrolysis” (Ogasawara et al., 1987). The surface area of meso- and macropores ($S_{m/m}$) does not increase during the early stages of activation, but microporosity does increase, reaching a maximum near 50% conversion. This differs from an earlier finding that tire char microporosity increased very slowly after 30% burnoff, but did not have a maximum in the

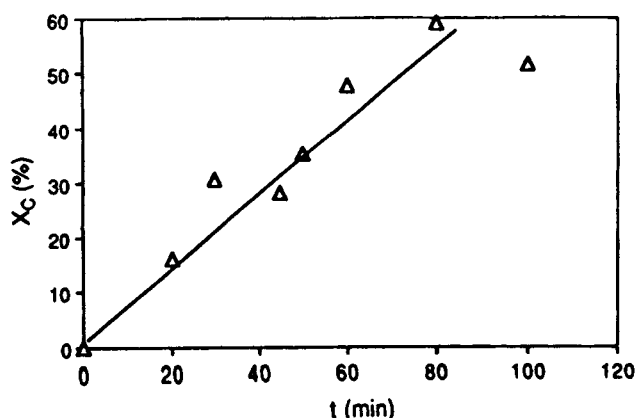


Figure 1. Carbon conversion as a function of reaction time during steam gasification of tire pyrolysis char AT-D.

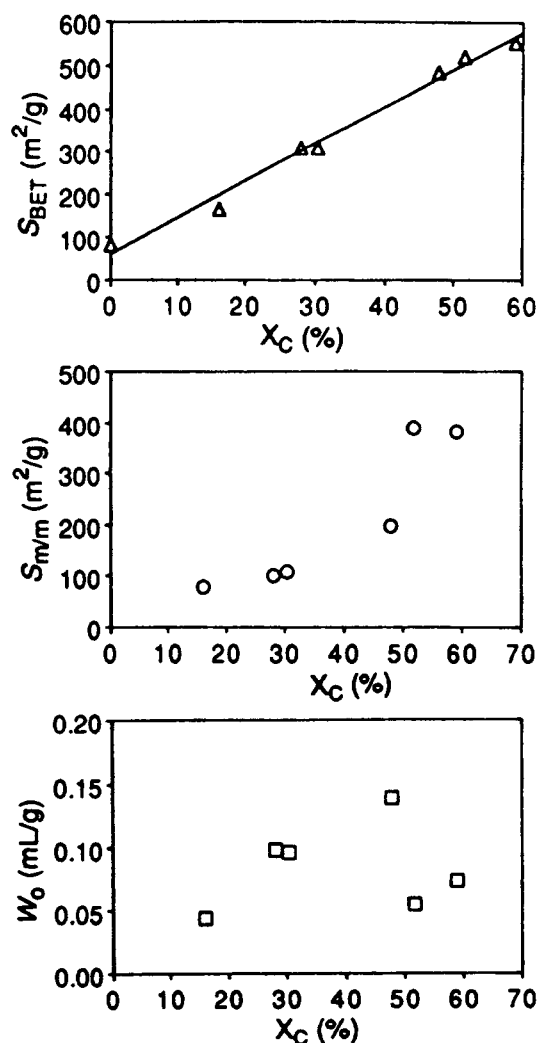


Figure 2. Development of surface area and microporosity during 850°C activation of tire pyrolysis char AT-D as a function of carbon conversion (ash free basis).

S_{BET} is the surface area determined by fitting the nitrogen adsorption data with the BET equation. $S_{m/m}$ and W_o are the surface area in meso- and macropores (pore diameter > 2 nm) and the micropore volume (volume in pores with diameters < 2 nm), respectively. These two parameters derive from an analysis of the adsorption data by the t-plot method.

20–70% burnoff range (Stoeckli and Ballerini, 1991). In addition, our microporosity maximum of about 0.15 mL/g of activated product is lower than the limiting value (about 0.25 mL/g) observed in that same study. The earlier study used activation conditions similar to those used here, but the authors did not report the inlet water concentration. Other possible reasons for the discrepancy in results include differences in char reactivity due to pyrolysis conditions and scrap tire composition, and different activation temperatures (Stoeckli and Ballerini report 800–900°C). It is interesting to note that our maximum micropore volumes (0.2–0.3 mL/g of starting material) are comparable to those reported for peat semicoke activation (Wigmans, 1989).

The fact that the surface area in the meso- and macropores ($S_{m/m}$) rises steeply at conversions close to the microporosity maximum suggests that activation of tire pyrolysis chars proceeds by creation (or opening) of micropores followed by pore growth. At low conversions, we suspect that micropores form as branches of the existing pores. These micropores continue to grow both in length and diameter until they exceed 2 nm. At this point, our characterization methods reflect any further increase in diameter as an increase in $S_{m/m}$ and a decrease in micropore volume (W_o). This type of pore development behavior will lead to a maximum in micropore volume with conversion (Hurt et al., 1991).

The trends discussed above for 850°C activation of one particular tire char seem to apply for tire char activation in general. Figure 3 contains plots of S_{BET} , $S_{m/m}$, and W_o vs. burnoff for the various activated tire chars we have tested. A linear trend is found between S_{BET} and burnoff. $S_{m/m}$ does not increase significantly until about 40% burnoff, which coincides with the micropore volume maximum. These trends are the same as in Figure 2. Differences in activation conditions and apparatus do not change the trends. As long as activation is carried out via chemically controlled gasification, differences in apparatus and conditions will not affect the pore development. They will, of course, affect the activation rate. It must also be noted that the tire chars were quite similar prior to activation. They resulted from essentially complete pyrolysis runs and had considerable porosity but no microporosity. It is not surprising that they show similar pore development during burnoff. This result does not mean that all tire chars activate at the same rate or can achieve the same level of internal porosity. Further studies are needed to determine the relationships among pyrolysis conditions, char reactivity, and the pore structure achieved during activation.

Conclusions

We have prepared activated carbons with surface areas in excess of 500 m²/g by activating tire pyrolysis chars at 850°C in an atmospheric pressure nitrogen stream containing 40 mol % H₂O. Gasification under these conditions appears to be chemically controlled because of the surface area enhancement and high apparent activation energy. The process conditions used in this study are a good starting point from which to optimize a process to convert tires to activated carbon.

We find that the porosity development during steam activation of tire pyrolysis char is similar to that reported for various other chars. A maximum in micropore volume is observed as a function of conversion, but the total surface area

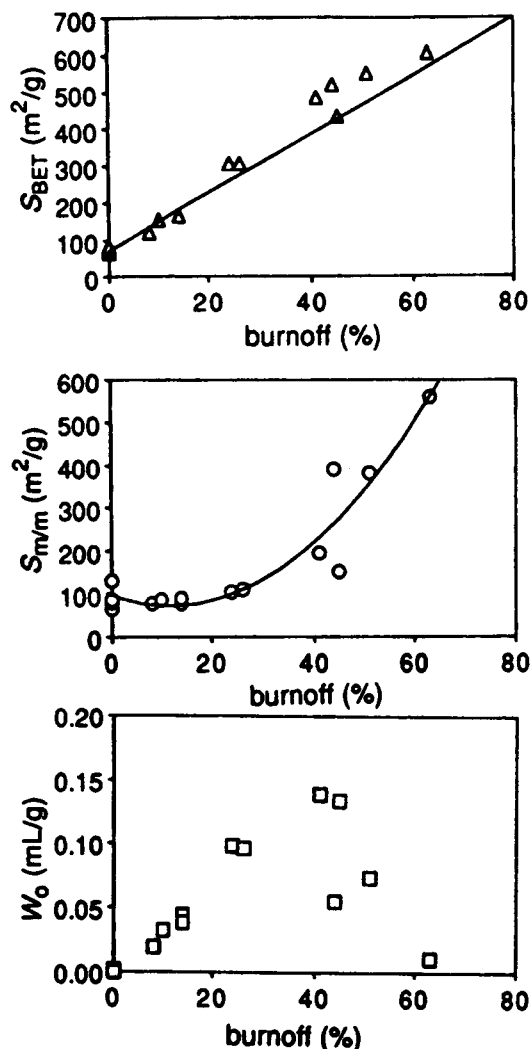


Figure 3. Development of surface area and microporosity during activation of various tire chars as a function of burnoff (char mass loss).

A range of activation conditions were used in these experiments. S_{BET} , $S_{m/m}$, and W_o are defined in the text.

increases monotonically with conversion. We suggest that the activation process consists of micropore formation, followed by pore enlargement.

The work presented here is of general interest in the resource recovery and carbon science fields. Because the porosity development in the tire chars is so similar to the reported data on porosity development in other chars, it seems likely that the activation behavior of chars from other polymeric scrap will be qualitatively similar to the tire char activation. We are investigating other scrap materials for their likelihood of successful conversion to activated carbon, including chlorinated polybutadiene, polyurethanes from automobile parts manufacture, and nylon carpet manufacturing waste.

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Notation

A_g = specific surface area, m^2/g
 ASA = active surface (g of active carbon/g of total carbon)
 C_{cs} = concentration of surface reactive carbon (g of reactive carbon/g of total carbon)
 d = pore diameter
 F_{N_2} = flow rate of nitrogen
 F_{H_2O} = flow rate of steam (water)
 OD = outside diameter
 R = overall rate of reaction, 1/time
 RSA = reactive surface (g of reactive carbon/g of total carbon)
 S_{BET} = surface area determined by the BET method (Brunauer, 1938)
 $S_{m/m}$ = surface area in meso- and macropores
 t = time
 t_R = reaction time
 T = temperature
 TSA = total surface (g of surface carbon/g of total carbon)
 W_0 = micropore volume, mL/g
 X_C = carbon conversion

Greek letter

η = effectiveness factor for reactions in porous particles

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