

# Kinetics of tire derived fuel (TDF) char oxidation and accompanying changes in surface area

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## ABSTRACT

The oxidation behavior of tire-derived fuel (TDF) char has recently been studied by several groups. In the present study, TDF char oxidation has been examined between 670 and 825 K, at oxygen partial pressures ranging from 2 to 19.8 kPa. The order of reaction with respect to oxygen varied with burnoff, and was in the range 0.72–0.86. The activation energy of reaction ranged with burnoff from 138 to 150 kJ/mol. The reaction rate does not correlate well with BET surface area, but did correlate well with the surface area in pores ranging in size from 1.2 to roughly 7 nm in width. Pores smaller than 1.2 nm exist in the char, but appear not to be used or developed by the oxidation reaction. Results for chars that have been acid washed to remove some inorganic matter show lowered reactivity, and a distinctly different pattern of pore development with burnoff. This is, in turn, reflected in a very different pattern of reactivity change with burnoff for such materials.

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## 1. Introduction

Tire derived fuel (TDF) is of value in a number of different combustion applications ranging from cement clinker production to electrical power generation. For this reason, the kinetics of tire char reactivity have been studied by a number of groups in recent years, e.g. [1–6]. The present study is concerned with the temperature and oxygen partial pressure dependence of tire char combustion processes. It also considers the role that development of porosity can play in determining the course of reactivity. Finally, the potential role that inorganic catalysts might play in determining that reactivity is briefly considered. Throughout this work, there is an assumption that reactive sites, whether catalyzed or not, are uniformly distributed over the available physical surface area. This seems to be the simplest initial assumption that is physically plausible, particularly for the larger pores that are believed to play the main role in offering reactive sites.

The yields of char from tire pyrolysis appear to be generally quite similar to, but higher than, the original content of carbon black in the tire. Carbon black is added (typically about 30 wt.% [7]) as a reinforcing agent to the styrene butadiene rubber (SBR) and natural rubber of the tire. The carbon blacks are themselves not pure carbon, since they must contain functional groups that will bind with the rubber. Nevertheless, because of their low hydrogen to carbon ratios, the carbon black particles can be ex-

pected to be fairly non-volatile, unless they receive hydrogen donated by the rubber components or extending oils (which are plasticizers and inexpensive fillers, present to about 5 wt.%). Thus the carbons derived by pyrolysis will contain much of the original carbon black, but they are quite different in form and composition.

The yields of carbon from pyrolysis can be affected by the temperature history of the material [4,6,8–13] and by exposure to oxygen before pyrolysis [12]. In one study [8], a yield of approximately 39% by mass was achieved, in experiments in which the tires were heated slowly (5 °C/min) to 720 °C. The yield dropped to 26% when the rate was increased to 80 °C/min. Another study did not, however, support this trend, obtaining a relatively constant yield of 35–38% over a heating rate range from 3 to 20,000 °C/min [12]. Oxygen pretreatment in this case significantly increased the yield to 45%.

Hence, when considering the results of any study of tire char oxidation kinetics, it must be recalled that the material that is being examined is a product of a complicated pyrolysis process, all aspects of which are not yet fully understood. Subtle influences of char preparation conditions may influence the results obtained in a kinetic study.

## 2. Experimental

### 2.1. Materials studied

The char used in this work was prepared from a sample of ground tire kindly provided by Advanced Fuel Research, Inc. of East Hartford, Connecticut (these samples, had, in turn, been received

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from Oxford Tire of Plainfield, Connecticut). The tire material contains 5% inorganics that report to ash and has a particle size of roughly 1 cm, as received. Samples were pyrolyzed in a tube furnace at 1273 K for 2 h, in a flow of high purity helium. Generally, 35–60 mesh (250–500  $\mu\text{m}$ ) particles were used for this study.

In some experiments, a char with reduced inorganic content was examined. This char was prepared by washing 35–60 mesh particles of the pyrolyzed char in a 12 M HCl solution. The washing was carried out at room temperature in four cycles, with fresh acid being used in each cycle. The first cycle involved contacting the char with acid for a period of 2 h, and was followed by a second cycle with fresh acid for 90 min, followed by two more cycles of 1/2 h each, again each with fresh acid. The wash liquid was generally colorless, except for a slight yellow tinge to the liquid from the first wash. The acid washes were followed by a water wash to neutral pH. The inorganic content of the raw char was roughly 15%, on the basis of ash residue following combustion at 700 °C. On the same basis, the ash content of the acid-washed char was 5.6%. The analyses of the ashes left after complete combustion of both the raw and acid-washed chars are shown in Table 1.

## 2.2. Surface area and porosity characterization

Adsorption isotherms were determined in an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Co.). Adsorption of  $\text{N}_2$  was performed at 77 K. The nominal surface areas of chars were estimated using a standard BET approach, based upon the nitrogen adsorption isotherms [14,15]. In some cases, other theories were applied to examining the same isotherms, and these will be described below. Before measurements, samples were outgassed at a minimum temperature of 573 K for at least 4 h in vacuum. Trends in development of surface area and porosity in tire chars from the same starting materials have been recently reported elsewhere [16].

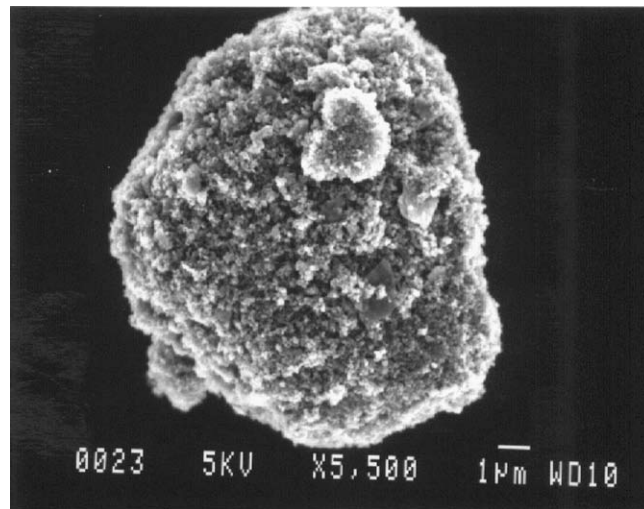
The choice of nitrogen as a preferred adsorptive for this material has been discussed elsewhere [16]. In that work, it was concluded that nitrogen was a superior choice to carbon dioxide, and the well-known problem of restricted diffusion of nitrogen does not play a role in this particular material that is characterized by relatively large porosity. In fact, what was observed is the well-known problem that carbon dioxide has in filling the large micropores and mesopores that are characteristic of these materials.

An electron micrograph image of the TDF char is shown in Fig. 1. It shows the characteristic “grape cluster” appearance of such materials, and this may be ascribed to the retention of carbon black particles as the backbone of the char particle. The micrograph supports earlier conclusions to the effect that the basic carbon black derived units that make up the char have diameters in the range

**Table 1**  
Composition of the ash from combustion of raw and acid-washed TDF chars

Element	Raw char	Acid-washed char
Aluminum (% as $\text{Al}_2\text{O}_3$ )	7.88	7.59
Calcium (% as $\text{CaO}$ )	5.04	1.33
Iron (% as $\text{Fe}_2\text{O}_3$ )	2.46	1.14
Magnesium (% as $\text{MgO}$ )	1.62	1.30
Manganese (% as $\text{MnO}$ )	0.02	<0.01
Phosphorous (% as $\text{P}_2\text{O}_5$ )	8.46	32.69
Potassium (% as $\text{K}_2\text{O}$ )	0.79	0.81
Silicon (% as $\text{SiO}_2$ )	19.8	30.0
Sodium (% as $\text{Na}_2\text{O}$ )	1.32	0.76
Sulfur (% as $\text{SO}_3$ )	4.68	0.09
Titanium (% as $\text{TiO}_2$ )	<0.01	<0.01
Cadmium (% as $\text{CdO}$ )	<0.01	<0.01
Zinc (% as $\text{ZnO}$ )	38.43	7.45

Analyses provided by Huffman Laboratories, Golden, CO.



**Fig. 1.** Electron micrograph of a raw TDF char particle.

10–100 nm [16]. The pictured char particle is smaller than those actually used in the reactivity and surface area experiments, but should be otherwise representative of the structures of those particles.

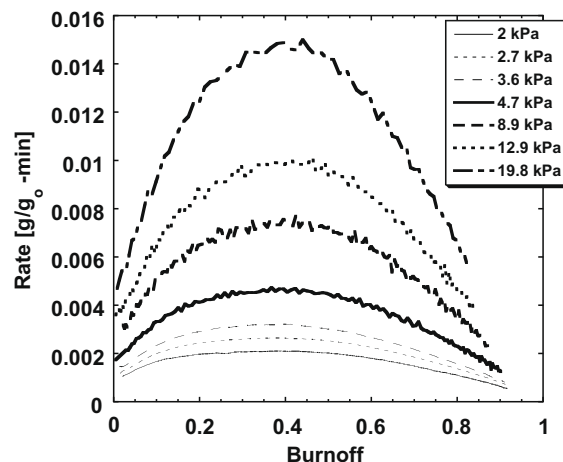
## 2.3. Reactivity measurements

The char reactivity measurements at atmospheric pressure and below were performed in an Online Instruments TG-plus thermogravimetric analyzer. The reactions were performed in a mixture of helium and reactant gas ( $\text{O}_2$  or air), flowing at a rate of about 220  $\text{cm}^3/\text{min}$ . Samples of 30–50 mg were dispersed on a circular platinum pan with a large flat surface and raised sides, resulting in a particle beds of about 1 mm thickness. Char samples were outgassed at 1173 K for 30 min prior to reactivity measurements.

## 3. Results and discussion

### 3.1. Variation in rate with burnoff

Fig. 2 displays the reactivity of tire char towards oxygen as a function of burnoff, at a temperature of 723 K. This is under intrinsic rate control conditions, as will be discussed further below. The



**Fig. 2.** Reactivity of tire char towards oxygen at indicated partial pressures, as a function of ash-free burnoff. All experiments performed at 723 K.

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