CARBON BLACK DERIVED FROM WASTE TIRE PYROLYSIS OIL

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Introduction

The disposal of 280 million tires generated each year in the U.S. is a great environmental problem. The tires take up large amounts of valuable landfill space and also present fire and health hazards. Tire-pyrolysis plants have been in operation for years, but the economics are poor, and most of these facilities have been shut down. This is mainly due to the low value of the end products, which are usually fuels (oil, pyrolysis gas, char). It is believed that reprocessing of waste tires into value-added products would improve the economic leverage.

This study addresses reprocessing of oils derived from waste-tire pyrolysis into carbon black – a valuable feedstock for the manufacture of tires, other rubber products, paints, pigments, ink, powder coating, toner, etc. Such a process would form a recycling loop for the carbon black recovered from waste tires. The objective of this work was to demonstrate the feasibility of the proposed approach in a laboratory scale. More specifically, the goal was to show that carbon black produced in the furnace process [1] using waste-tire oil as a feedstock could possess similar characteristics as the carbon black made from a traditional petroleum-based feedstock.

Materials and Experimental Techniques

Four oil samples were used in this study: (a) tire-pyrolysis oil prepared at Advanced Fuel Research, Inc. (AFR) in a two-inch diameter packed-bed reactor; (b) tire-pyrolysis oil obtained from a large-scale tire pyrolysis plant operated by Conrad Industries in Chehalis, Washington; (c) tire-pyrolysis oil obtained from a pilot-scale tire pyrolysis facility operated by Metso Minerals (formerly Svedala) in Danville, Pennsylvania; and (d) Exxon bunker oil provided by Caleb Brett. The highly aromatic Exxon oil is a typical high-grade feedstock that carbon-black manufacturers use in their normal operations. This oil was used as a reference for the tire-derived feedstocks.

In addition, a sample of the AFR tire oil (a) that had been aged for two years was examined to determine oil stability during extended storage at ambient temperature and pressure. The elemental composition of the above oil samples is given in Table 1.

Table 1. Elemental composition of the oils used in this study (wt%, dry ash-free basis). The analyses were performed by Huffman Laboratories of Golden, Colorado.

Element	AFR Tire Oil (aged)	AFR Tire Oil (fresh)	Conrad Tire Oil	Metso Tire Oil	Exxon Bunker Oil
Carbon	84.5	86.73	88.44	90.56	89.56
Hydrogen	11.1	10.77	9.55	7.01	7.42
Oxygen	3.0	1.55	1.31	2.17	0.29
Nitrogen	0.29	0.31	0.62	0.55	0.17
Sulfur	0.86	0.87	1.06	1.02	3.13

Since it is impractical to design, construct, and operate under realistic conditions a small-scale carbon black furnace, a laboratory entrained-flow reactor shown in Figure 1 was used in this study. The system consisted of an externally heated quartz reactor, two inches in diameter, equipped with a spray-nozzle assembly and a gas preheater. An ultrasonic atomizing nozzle (Sono-Tek, Milton, NY, model 8700-120MS) was connected to the reactor by means of a one-inch Cajon fitting.

Referring to Figure 1, a gas mixture to be used in an experiment was introduced into the preheater through a gas manifold and mass-flow controllers *MFC1* and *MFC2*. Oxygen concentration at the inlet could be adjusted by mixing streams of oxygen and nitrogen. Mass-flow controllers and rotameter *R* were calibrated, and temperature profiles inside the reactor were found to be quite uniform. The preheater was filled with crushed quartz pieces to facilitate heat transfer to the gas phase. The gas leaving the preheater came into contact with a spray of fine oil droplets ($d \leq 20\ \mu m$) produced by the atomizing nozzle. The oil was conveyed to the nozzle assembly by means of a syringe pump. A small stream of nitrogen, or nitrogen-oxygen mixture, flowed coaxially around the nozzle and prevented excessive droplet deposition on the walls near the reactor inlet. Fine particles formed in the upper part of the reactor had a residence time that was controlled by the gas flow rate. Residence times of up to 20 seconds could be achieved. The temperature within the gas preheater and the reactor was independently controlled, and thermocouples monitored temperatures at several points in the system (see Figure 1). Carbon-black particles were collected at the bottom of the reactor and on the filter. Temperatures in excess of 1100 °C could be reached without overheating the temperature-sensitive nozzle. This was accomplished partly thanks to the cooling of the nozzle assembly with a fan.

A typical experiment involved an initial heat-up of the system to the desired temperature, followed by continuous injection of tire oil at a specified rate. Particles of carbon black formed in the process of spray drying were collected after each run. The following process parameters were used: (1) reactor temperature: T = 1100 °C; (2) oxygen concentration: C_{O2} = 0% and 50% of stoichiometric requirement; (3) carrier gas flow rate: V = 2000 and 500 ml/min (STP), which corresponded to residence times in the reactor, $\tau \approx 5$ and 20 seconds.

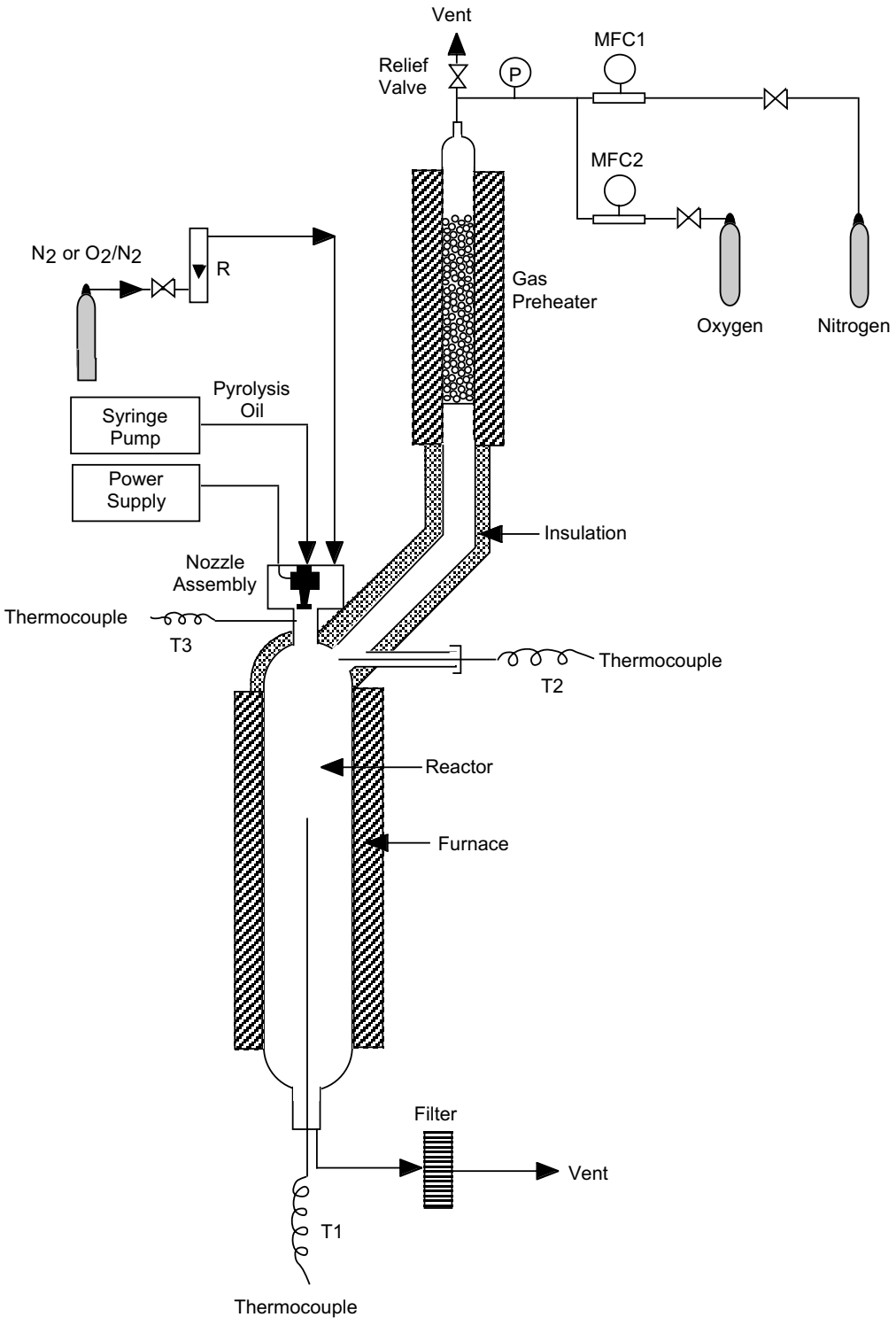

Figure 1. Experimental set-up used to produce carbon black. *MFC1* and *MFC2* are mass-flow controllers, *T1*, *T2*, and *T3* are thermocouples, *R* is a rotameter and *P* is a pressure gauge.

It should be noted that, due to reactor limitations, the temperature used in this study (1100 °C) was substantially lower than 1400–1650 °C, which is the range used by large-scale commercial facilities. Furthermore, the entrained-flow reactor shown in Figure 1 operated in a laminar-flow régime, whereas turbulent flows are typical for large-scale facilities. For these reasons, it was expected that, if carbon-black particles could at all be produced in the laboratory reactor, their particle sizes would be rather large. This would translate to relatively low BET surface areas and low iodine numbers. This was not considered a problem in this study as the objective was to demonstrate the feasibility of using tire-derived oils, and not to optimize reactor performance or product properties.

Results and Discussion

Data shown in Table 1 indicate very little variation in elemental composition of oils produced from different tire feedstocks and under different pyrolysis conditions. It is interesting to note that good agreement was found between the data obtained for the freshly prepared tire-oil sample and for the oil stored in the laboratory for over two years. The extent of oil oxidation that occurred during storage is deemed low to moderate, as judged from the difference in oxygen content of the fresh and aged samples. This is indicative of the good stability of the tire oil, and, thus, little or no difficulty is expected with the transportation, storage, and handling of this feedstock.

The good chemical stability was demonstrated using Fourier transform infrared (FT-IR) spectroscopy. Samples of the fresh and aged tire oil were placed on KBr pellets and characterized using the technique described by Solomon *et al.* [2–4]. The collected FT-IR spectra of the fresh and the aged samples were found to be very similar.

Seven runs were performed in the entrained-flow reactor, and the conditions used in these experiments are shown in Table 2. The collected carbon black samples were characterized, as discussed below, and a summary of results is presented in Figure 2.

Table 2. Process conditions used in entrained-flow reactor runs.

Run No.	Feedstock	Residence Time (s)	Gas	Oil Flow Rate (cm^3/min)
001	AFR Tire Oil (fresh)	5	N_2	0.10
002	Conrad Tire Oil	5	N_2	0.10
003	Conrad Tire Oil	20	N_2	0.10
004	Metso Tire Oil	20	N_2	0.11
005B	Conrad Tire Oil	20	25 vol% O_2 / 75 vol% N_2	0.11
006	Conrad Tire Oil	20	N_2	0.11
007	Exxon Bunker Oil	20	N_2	0.16

Surface Area – The surface area measurements were performed using two techniques: iodine adsorption and BET surface area determination (nitrogen at 77 K). In the latter

method, a Micromeritics Digisorb 2600 instrument and standard ASTM procedures were employed. Iodine adsorption measurements were carried out by Akron Rubber Development Laboratory, a company that specializes in carbon black testing for the rubber and carbon-black industries.

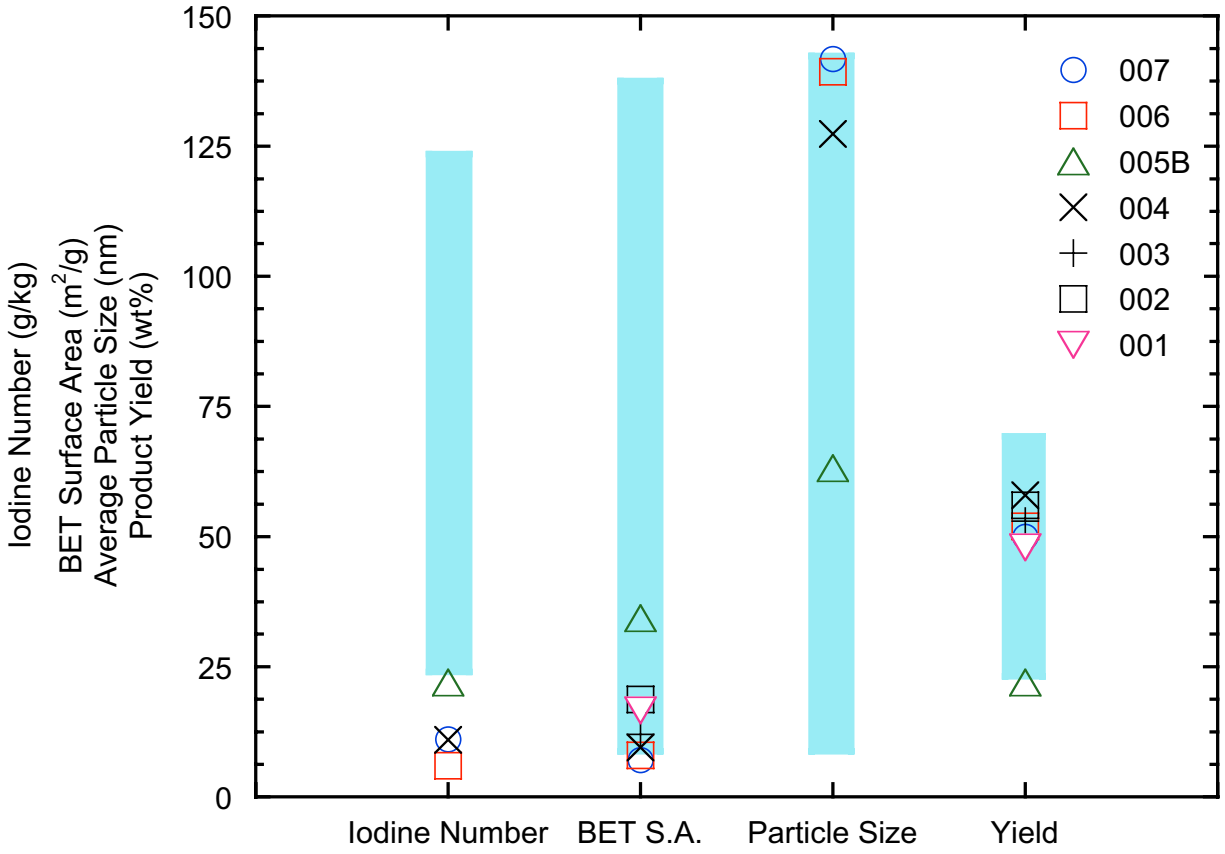

Figure 2. Carbon-black characterization. The key to the run numbers shown in the legend is given in Table 2.

BET surface areas and iodine numbers shown in Figure 2 are close to the lower end of the range of values that are typical for industrial grade carbon blacks. This is not surprising as the low temperature used in this study was expected to result in the relatively large particle sizes characteristic of the low-temperature carbon blacks. In addition, the non-oxidizing conditions used in most runs might have led to the condensation of hydrocarbon vapors on the carbon black particles during the particle collection process. Therefore, access of iodine to particle surface might have been limited, which was manifested in lower iodine adsorption. The problem was less severe with nitrogen in the BET surface-area measurement due to the lower molecule size of nitrogen, as compared with iodine, and a sample-outgassing step prior to surface-area determination.

Particle Size – The transmission electron microscopy (TEM) analysis produced high quality micrographs for carbon black particle size analysis. The carbon black samples

generated in this project were analyzed for particle size distribution at Akron Rubber Development Laboratory, Inc. Their technique involved dispersing carbon blacks in chloroform, dilution, and placing 2–3 drops of the dispersed black onto carbon coated 200 mesh copper grids for analysis. The TEM employed was Philips model EM400T interfaced with a Gatan model 637 Wide Angle TV Camera and Scion AG-5 frame-grabber. Individual particles were identified and the sizes of only these particles that had at least half a diameter visible were measured using Jandel Scientific software. A well developed grape-like structure characteristic of carbon black was found in the products obtained from all types of oil studied.

The measured particle sizes were in the range of carbon black materials, although at the high end of what is typical. The large particle sizes were expected given the maximum reactor temperature limitation of 1100°C. The particle size of the carbon black generated from the Exxon oil also fell into the high end of the typical particle range. The particle size was markedly smaller, however, in the case of the carbon black generated in the presence of oxygen (sample 007). This is believed to be due to the higher particle temperatures in the combustion environment.

Product Yield – Carbon-black yields were determined as the ratio of the mass of the carbon black collected to the mass of the feedstock oil delivered to the reactor system. Because of the inherent difficulties in collecting 100% of the carbon black formed in the system, it is believed that the yield values presented in Figure 2 are rather conservative. The yield data clearly fall in the range of values typical for the industry. It is also interesting to note that the yields of the carbon black produced from the tire oils are essentially the same as the yield of the carbon black obtained from the Exxon oil.

Conclusions

1. Despite the experimental limitations (low temperature and laminar flow), the data for carbon blacks produced from tire oils generally fall into the range of values characteristic of ASTM carbon blacks. TEM micrographs revealed the well defined grape-like structures that are so characteristic of carbon black. No contamination from char residue was observed.

2. The properties of a carbon-black sample produced from the reference Exxon oil are similar to the characteristics of the samples derived from tire-pyrolysis oil. Thus, any deviations from the typical product characteristics are probably the artifacts associated with non-standard and non-optimum reactor design (laminar flow) and process conditions (low temperature).

3. Four tire-derived oils used in this study were found to have similar elemental composition. FT-IR spectra collected on samples of fresh and aged tire oils (two years of storage) were shown to be similar, which indicates high chemical stability of this feedstock.

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