USING XRF ANALYSIS TO DEVELOP A HIGH-TECH BUSINESS

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ABSTRACT

Using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry coupled with microprocessor controlled chemical reactions, new high-tech products, each with commercial potential, have been developed from scrap tires. Each of the products is produced from WOMBAT tire-derived powder, whose production is monitored by WDXRF on a day-to-day basis. Currently, the most important product is a low polluting fuel which is co-blended from tire-derived powder and biomass. The abundances of zinc and sulfur in these fuel blends have been monitored prior to and after combustion by WDXRF. The abundance of impurities in the products made from processed WOMBAT reactor fluids has also been measured by WDXRF.

INTRODUCTION

The very high carbon content of scrap tires means they have the potential to be a renewable energy source. Currently, the commercial value of carbon-based fuels is governed by the sulfur content of the fuel; i.e., the cost of scrubbing the sulfur oxide effluents from its combustion products. Tires contain \textit{ca.} 2.0\% sulfur by mass as well as 2.0-2.3\% zinc, and each of these elements is environmentally regulated. In addition, tires typically contain 20-25\% steel as well as CaCO\textsubscript{3}(s) and/or SiO\textsubscript{2}(s) in the range of 0.2 – 1.0\%. Emissions from combusting whole scrap tires frequently exceed the allowable values for zinc and/or sulfur dioxide, and combustion of whole tires also causes the buildup of large amounts of steel in the boilers. At numerous sites in the United States, scrap tires are shredded into two components—rubber chips and high metal tire chips (HMTC’s), which have irregular shapes and compositions. WOMBAT Technologies International, Inc. is a high-tech business focused on converting scrap tires and/or HMTC’s into useful materials. The purpose of the WOMBAT technology is to recover the fuel value from the rubber in tires in an environmentally friendly manner by separating the tire rubber from the steel belts and then reducing the abundances of the environmentally unacceptable inorganic moieties to acceptable levels. A schematic of the microprocessor controlled, continuous WOMBAT tire-processing technology is presented in Figure 1.
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Figure 1. Schematic of the WOMBAT process and the array of process products

The initial step in our technology is the catalytic oxidation, under conditions of acid hydrolysis, of the carbon-sulfur-metal(s) bonding networks in the tire’s tread; i.e., $R-S-M + O^* \rightarrow SO_4^{2-} + M^{n+} + R$; where R represents the tire’s bulk rubber. During this reaction sequence, the steel from the tire is successfully separated from the rubber matrix of the tire. In subsequent oxidation steps, the three inorganic moieties—zinc, calcium, and sulfur—are attacked by the oxidizing species and at least partially removed from the rubber. The result of the secondary reactions is the production of tire-derived powder (TDP). This TDP contains irregularly shaped particles with diameters in the range of 10-50 microns. WDXRF spectrometry has been used to measure the abundances of sulfur, zinc, calcium, (and other inorganics) in the tire-derived powder, in the reactor fluids, and in the secondary reaction products such as fertilizer and WOMBAT Hybrid Fuels.

WDXRF has also been used to relate the efficiency in the removal of sulfur, calcium, and of zinc from the rubber matrix and to various chemical and mechanical variables (i.e., temperature, pressure, catalyst, etc.) within our reactor. In addition, the consistency in removal of zinc, sulfur and calcium from the rubber matrix has been evaluated by WDXRF.

**EXPERIMENTAL**

*WDXRF Methodology.* All of the spectra discussed in this presentation were obtained using a modified Rigaku S-MAX spectrometer with a rhodium X-ray tube operated at 40 kV and 30 ma. Each sample was mounted onto a conventional sample holder using a pre-cut #3518 mylar (0.25 mil x 2.5") window. Each sample was analyzed at reduced pressure. The secondary X-rays emitted by each sample were focused onto a PET crystal ($d = 4.375$ Å) for dispersion. A gas proportional counter using P-10 gas in its chamber was used as the detector. Intensities were measured for each sample over the range from
θ = 8.00° to 149.00° at increments of Δ2θ = 0.02°, with a counting time of 1 second at each angular setting. This angular range allows for measurement of secondary X-rays of wavelength from 1 – 8.5 Å, a range that includes all the inorganic moieties typically added to tires during their production and inorganic moieties which could be introduced from our processing. All spectra are presented as intensity vs. wavelength of the secondary X-rays. Reported intensities are peak areas (after corrections for background and polarization), which have been graphically integrated using computer software. The “spectrum” due to the mylar-covered sample holder was also measured and found to be unimportant in the analysis of the analytes discussed below.

Samples. A piece of tire tread was machined into a disk, 2.5 cm in diameter and 2 mm thick. This disk was mounted onto the metal surface of a SPEX sample holder and then subjected to WDXRF analysis. The tire-derived powder was ground in order to pass through a -100 mesh screen. A 1.0 gram sample of each loose powder was mounted onto the SPEX sample holder, sealed with the mylar film, and then analyzed by WDXRF. The solutions, taken from the process reactor, were contained in a 43 mm disposable closed X-ray sample cell, covered with the mylar film, and then mounted onto a conventional sample holder for WDXRF analysis.

Standard Mixtures. In order to correlate measured intensities for analytes of importance, (i.e., zinc, sulfur, and several divalent metals), binary and tertiary mixtures containing the analytes of interest dispersed into activated carbon were prepared. Each standard mixture set included samples of 1%, 2%, 3%, 4%, and 5% analyte. A 1.0 g sample of each mixture, as a loose powder, was subjected to the WDXRF protocol noted above. The area under the Kα peak characteristic of each analyte was measured in each spectrum. The peak area for each sample was correlated to analyte abundance for each set to a linear correlation of R² > 0.996. From the linear equations, the abundances of the analytes in our samples were determined by: % analyte = (peak areax – bx)/mx, where bx is the intercept and mx is the slope of the linear relationship relating the peak area for the Kα peak for analyte x to its abundance in the sample.

RESULTS AND DISCUSSION

Shown in Figure 2 are the WDXRF spectra of a section of scrap tire tread and WOMBAT tire-derived powder produced from processing the tire tread in our chemical processor. The WDXRF spectrum of the tire tread disk is dominated by the zinc Kα peak (1.44 Å). Smaller Kα peaks due to calcium (3.36 Å) and to sulfur (5.37 Å) are also discernible, along with the rhodium peak (4.60 Å). From comparison to our standard curves for zinc, for calcium, and for sulfur, their abundances were determined to be 2.12%, 0.98%, and 1.97%, respectively. In the tire-derived powder (TDP), the zinc abundance was lowered to 0.11%, the sulfur abundance was lowered to 1.31%, and the calcium abundance was lowered to < its lower limit of detection. Independent analysis by Galbraith Laboratories and by Southern Company has confirmed our WDXRF results.
Reaction conditions within the WOMBAT reactor have been varied, and the reduction in abundance of zinc and of sulfur has been measured by WDXRF in order to determine optimum relationships between reaction time, temperature, pressure, relative reactant/tire material ratios and the extraction efficiencies of the inorganic moieties.

Process consistency has been judged by evaluation of the WDXRF spectra of several batches of TDP prepared under similar operation conditions. Satisfactory reproducibility of the tire-derived powder has been judged to be statistically indistinguishable WDXRF spectra of the several batches produced under similar reaction conditions.

The iron K$_\alpha$ peak (1.94 Å) in the WDXRF of the tire-derived powder is caused by the unwanted dissolution of iron metal from the tire tread. WDXRF analysis has been used to determine the reactor conditions which minimize the intensity of the iron peak; i.e., the dissolution of iron from the tire tread.

A combination of WDXRF and x-ray diffraction analysis has shown that the high temperature ash (HTA), produced from combusting the WOMBAT tire-derived powder in an oxygen-rich environment, is principally composed of iron oxides with a small amount of zinc oxide present as well. Comparison of the zinc peak in the HTA to the zinc peak in the tire-derived powder may be used to determine the retention of zinc (as ZnO) in the HTA.

Co-Blended Fuels. The WOMBAT tire-derived powder is being combined with various biomass components to produce co-blended (hybrid) solid state fuels. These low
polluting, high-energy fuels have economic potential. Shown in Figure 3 is the WDXRF spectrum of such a fuel.

![Comparison of WDXRF spectra](image)

Figure 3. WDXRF of a WOMBAT Hybrid Fuel pellet composed of 33% tire-derived powder (by mass) and 67% sawdust

Analysis of this spectrum indicates that this WOMBAT Hybrid Fuel has a sulfur content which satisfies the “low sulfur” criterion. In addition, this WDXRF spectrum indicates that the zinc and iron abundances are also reduced significantly. The new peak, due to silicon ($\lambda = 7.13$ Å) is due to silicate moieties in the sawdust. From this WDXRF spectrum, the following may be calculated:

a. The amount of $SO_x(g)$ that must be scrubbed from the flue gas of the combustion products of the hybrid fuel,
b. The amount of HTA, which now includes the silicon dioxide as well as iron oxide(s) and zinc oxide.

Correlation of the silicon peak intensity with the heat value of the sawdust and a similar correlation of the sulfur peak area with the heat value of the tire-derived powder makes it possible to calculate the heat value of the WOMBAT Hybrid Fuels with reasonable accuracy.

The WOMBAT technology produces a considerable amount of NO$_x$ in both the gas phase and in solution. The NO$_x$ products have been neutralized to a solid product by reaction with KOH. The WDXRF spectrum of the solid product is presented below.
Zinc is a growth retardant for many plants. To realize the economic potential of this solid state product, its zinc abundance must be kept quite low. The WDXRF spectrum of this solid product (Figure 4) indicates that the intensity of the zinc peak (1.44 Å) < its lower limit of detection, which indicates that the zinc abundance in this solid sample is quite low. This low zinc abundance indicates that our solid product has economic potential.

CONCLUSIONS

Every step of the development of the WOMBAT tire-derived powder and the corresponding Hybrid Fuels utilizes WDXRF spectral analysis. Included are: the relationship between reactor conditions (both chemical and mechanical) and uniformity of the tire-derived powder, correlation of analyte peak areas to abundances of those analytes, and predictors for both heat value and environmental clean-ups due to combusting both the tire-derived powder and combusting the WOMBAT Hybrid fuels under high temperature, oxygen rich conditions. The commercial value of solid nitrate product(s) may also be inferred from the WDXRF spectra of the product(s).

REFERENCES
