SOME IMPORTANT REACTION SEQUENCES IN THE WOMBAT PROCESS FOR CONVERTING SCRAP TIRES TO A HIGH CARBON GEL.

Richard C. Cummings and David L.Wertz
Department of Chemistry & Biochemistry
University of Southern Mississippi
Hattiesburg, MS 39406 USA

INTRODUCTION

The WOMBAT (Wertz Oxidative Molecular Bombardment at Ambient Temperature) process has been developed and refined in this laboratory over the past several years. The objective of this project is to convert scrap tires into a low polluting fuel via technology which is environmentally friendly and economically useful. The process has a high chemical oxygen demand but no external energy requirements.

RESULTS AND DISCUSSION

The WOMBAT process is initiated by introducing both the whole scrap tires and concentrated nitric acid into a closed reactor (see Figure One). Although the scrap tires are chemically inert to normal solvation processes and other types of chemical reactions using mild conditions, in the WOMBAT reactor the tires react to form a gel which is characterized by very low ash and sulfur contents. The production of greenhouse gases from combustion of the WOMBAT solid is slightly lower than that produced from typical bituminous coals.

The thermodynamic products of the WOMBAT process include steel belts (with surface corrosion), polymeric fibers, a solvent-swelled gel which may be processed into the high carbon WOMBAT solid partially described above, a solution containing several inorganic species extracted from the tires, and large quantities of $NO_x(g)$. The WOMBAT reactions appear to take place in the liquid phase, where at least three specific reaction processes occur. However, it is unclear at this time which liquid phase species present in concentrated nitric acid participate in these reactions. Consequently, in the reaction schemes presented below, HNO_3 represents a generic description of the reactants from the solution-phase nitric acid present at very high concentrations. Several of the more important reaction schemes are presented below. Although presented in a sequence, it appears that each of these (and perhaps other) reactions is occurring simultaneously in the reactor. In each of these reaction sequences, the thermodynamic products include $NO_x(g)$, and both $NO(g)$ and $NO_2(g)$ have been identified in the vapor phase within the WOMBAT reactor by FTIR. Of these, however, $NO_2(g)$ is the dominant species, while $NO(g)$ appears to occur only in trace amounts. In the discussions presented below, $NO_2(g)$ is used generically to represent the various NO_x species present in the vapor phase in the WOMBAT reactor.

The processes which occur in our reactor have a high chemical oxygen demand, as shown in Figure Two. The presence of high abundances of $NO_2(g)$ and $H^+(aq)$ in the reactor indicates that the very concentrated nitric acid, which serves as the source of the reactant(s) and also represents the principal continuing operational expense, is being comsumed in the WOMBAT process. Its escape into the atmosphere is not an environmentally acceptable process. For these two important reasons, the $NO_2(g)$ generated within the reactor, which approximates a closed adiabatic system, is catalytically recycled into reactant, as shown in the following reaction:

$$O_2(g) + 2\,NO_2(g) + 2\,H^+(aq) = 2\,HNO_3(g). \qquad (1)$$

Evidence of this reaction is provided by the gas chromatographic measurements $O_2(g)$ in the WOMBAT reactor. The disappearance of the atmospheric $O_2(g)$ within the WOMBAT reactor parallels the reduction in efficiency in the WOMBAT reaction processes within the reactor. Adding either $O_2(g)$ or air to the WOMBAT reactor causes the reaction to "froth"; suggesting that the addition of $O_2(g)$, even in small amounts, invigorates the reaction by causing an *in situ* increase in the abundance of the reactant $HNO_3(g)$. Thus, the environmentally unacceptable $NO_2(g)$ is converted via an equilibrium reaction to the economically important reactant, $HNO_3(g)$.

There is no evidence of nitration reactions or of any separation of the organic species (i.e., the separation of carbon black from the styrene-butadiene co-polymer, etc.) in the gelatinous solid material which is produced by our process.

The large abundances of $NO_2(g)$ produced in the reactor are thought to be due to several distinct reaction processes which occur, at least to some extent, similtaneously. These processes include the cleavage of the metal-rubber adhesion between the brass-coated steel belts and the vulcanized styrene-butadience (**SBR**) co-polymer portion of the tire, the extensive oxidation of the vulcanized **SBR**, the extraction of the organo-sulfur from the rubbery polymer, and the acid hydrolysis of the zinc and calcium salts from the **SBR** during its conversion to a gel

$$2\ NO_2(g) + 2\ H^+(aq). \qquad (2)$$

The presence of the oxidized (corroded) surfaces of the steel belts has been identified by environmental electron microscopy.

While step one is occurring, the vulcanized styrene-butadiene rubber (**SBR**) is further oxidized by a reaction scheme which may be represented as:

$$\mathbf{SBR}(s) + n\ HNO_3(aq) \rightarrow O_n\text{--}\mathbf{SBR}(s) + n\ NO_2(g) + n\ H^+(aq). \qquad (3)$$

In this process, the high carbon **SBR** material (~85%) is converted from a rigidly shaped solid to a gel which has a significant oxygen content (*ca.* 13.5%) with a concomitant reduction in the carbon abundance to *ca* 73%. Mass spectral studies indicate that much of the added oxygen is in the form of carboxylates.

Accompanying the oxidation of the **SBR** is the removal of the organo-sulfur from the **SBR** the vulcanized sulfur (from 1.5% in the original styrene-butadiene impregnated rubber to *ca.* 0.7% -- or less -- in the gel). The decrease in the organo-sulfur abundance has been verified both by x-ray spectroscopy and by gas chromatography. The sulfur from the impregnated tire is converted to aqueous sulfate in the WOMBAT reactor,i.e.,

$$S\text{-}R + 4\ HNO_3(aq) \rightarrow R + SO_4^{-2}(aq) + 4\ NO_2(g) + 4\ H^+(aq). \qquad (4)$$

The aqueous sulfate has been precipitated from the reactor solution and then identified by x-ray diffraction and x-ray spectroscopy.

In addition, the zinc (*ca.* 2% is added in the construction of modern tires to improve their structural stability) is extracted by acid hydrolysis into the nitric acid solution during the reactor processes by an acid hydrolysis reaction such as:

$$Zn + HNO_3(aq) = ZnO_a(H_2O)_b + NO_2(g) + a\ H^+(aq). \qquad (5)$$

The absence of zinc in the resulting gel and its presence in the reactor solution have been verified by x-ray spectroscopy, although the specific coordination complex(es) containing the zinc have not been identified. The low ash content of the WOMBAT gel (~0.7%) is additional evidence of the successful extraction of the zinc (and other metals) from the tires. The zinc may be extracted from the WOMBAT reactor solution by chelation, as verified by x-ray spectroscopy and by x-ray diffraction, and recovered.

Some important characteristics of the WOMBAT solids are compared to several of the Argonne Premium Coals in Table I. Shown in Table II are some environmentally important fuel factors presented as ratio per million BTU's for these fuels.

CONCLUSIONS

Although the reaction schemes presented above are simplistic, taken together they account for the thermodynamic products involved in the conversion of scrap tires to useful materials.

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TABLE I. PROPERTIES OF SEVERAL SOLID STATE FUELS.

A. MEASURED FUEL VALUES

FUEL	BTU's/TON	C/TON	ASH/TON	SO_2/TON
Beulah Zap	14.9 M	1000 pds	132 pds	64 pds
Illinois # 6	22.0 M	1210 pds	285 pds	319 pds
Pittsburgh #8	26.8 M	1485 pds	182 pds	86 pds
WOMBAT	27.5 M	1083 pds	29 pds	28 pds

TABLE II. SOME IMPORTANT COMBUSTION PRODUCT RATIOS.

RATIO	FUEL			
	BZ	IL	PIT	WOMBAT
PDS CO_2/ 1 M BTU	246	201	203	196
PDS SO_2/ 1 M BTU	4.3	14.5	3.2	1.1
PDS ASH/ 1 M BTU	8.9	13.0	6.8	1.1

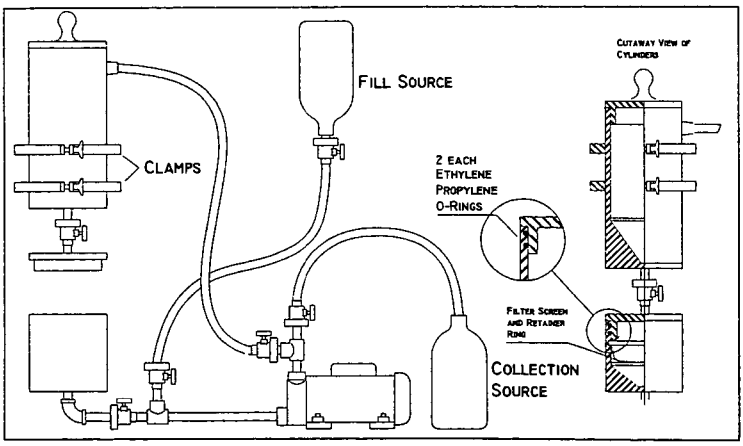

FIGURE ONE. SIMPLIFIED SCHEMATIC OF THE WOMBAT REACTOR.

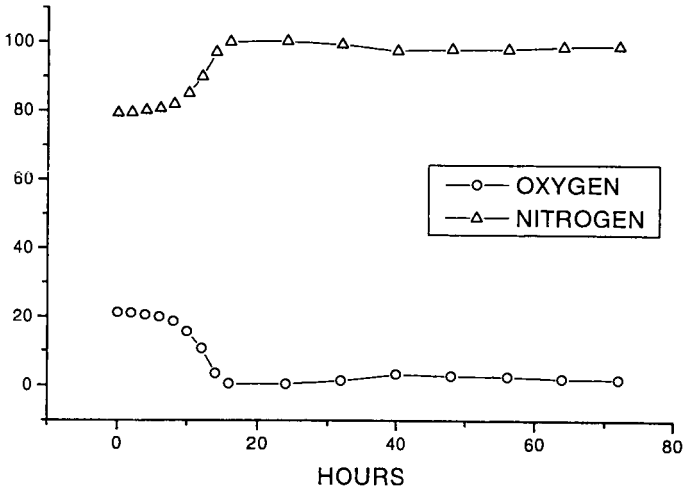

FIGURE TWO. GAS CHROMATOGRAPH OF THE OXYGEN ABUNDANCE IN THE WOMBAT REACTOR.

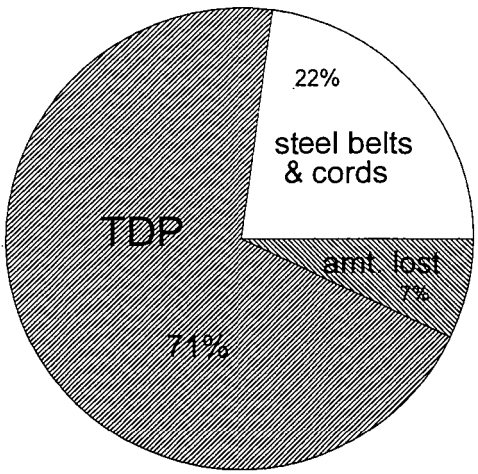

FIGURE THREE. COMPOSITION OF THE RECOVERED PARTS OF THE TIRE.

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