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AN EVALUATION OF DISCARDED TIRES AS A POTENTIAL SOURCE OF FUEL

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ABSTRACT

The destructive distillation of rubber tire samples was studied by thermogravimetry, differential scanning calorimetry, combustion calorimetry, and mass spectroscopy. The decomposition reaction was found to be exothermic and produced a mass loss of sixty-five percent. The products from the distillation process were a solid residue with a heating value of about -3×10^7 J kg^{-1}, a liquid with a heating value of about -4×10^7 J kg^{-1}, and a combustible gas of undetermined heating value. The gas evolution curves which were obtained indicate that a variety of organic materials are evolved simultaneously during decomposition of the rubber polymer.

INTRODUCTION

The search for an alternative to petroleum energy has encompassed the investigation of a wide range of materials to determine their suitability as a fuel. While some materials, such as oil shale and coal deposits, are obvious energy resources which are being studied and exploited at an accelerated rate, other materials with smaller energy yields are also being considered to a lesser degree. One such material is the distillates obtained from the destructive distillation of scrap tires which has been studied by the Firestone Tire and Rubber Company in cooperation with the Bureau of Mines[1]. The Pittsburgh Energy Research Center of the Bureau of Mines has also studied the distillation of tires[2] and the National Aeronautics and Space Administration is interested in this process.

Substantial quantities of chemical energy remain locked in the rubber structure of discarded automobile tires; this energy can be recovered through distillation in the absence of oxygen. In addition to the ecological advantages inherent in the destruction

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of discarded tires, a combustible oil and gas is obtained which contains a variety of organic compounds[1]. The composition of the distillate depends on the type of rubber and the compounding procedures used in the manufacture of the tires. Four types of rubber—natural, styrene–butadiene rubber (SBR), polyisoprene, and polybutadiene—account for the major portion of rubber in tire manufacture[3]. These rubbers are compounded with other materials in varying proportions according to the requirements of the finished product. A representative compounding formula for the rubber used in passenger tire treads[3] is given in Table 1.

TABLE 1

TYPICAL COMPOUNDING FORMULAE FOR PASSENGER TIRE TREADS[3]

	Natural rubber	*SBR cis-polybutadiene*
Smoked sheet	57.6%	—
SBR 1712	—	46.8%
cis-Polybutadiene	—	11.3
Reogen	1.2	—
K-Stay G	—	2.3
Stearic acid	1.4	0.9
Zinc oxide	2	1.4
Agerite resin D	0.9	0.7
Agerite HP	0.3	0.2
Antozite 67S	2.3	1.8
Microcrystalline wax	0.6	0.5
Philrich 5	2.9	3.2
HAF	28.8	—
ISAF	—	29.5
Sulfur	1.4	0.8
Amax No. 1	0.3	—
Amax	—	0.7
Redax	0.3	—

In this investigation, preliminary data on the magnitude of the energy recoverable from discarded tires is presented as well as data relating to the nature of the decomposition process and recovered distillates.

EXPERIMENTAL

Samples

The tire samples used in this experiment were obtained by cutting 6 by 6 cm squares from the tread and sidewall portions (blackwall only) of eight passenger and two truck tires which were selected in a random manner. These squares were then cut to pass through a 2 mm sieve and were thoroughly mixed. Samples were taken from the mixture with multiple runs made with each analytical technique to insure reproducibility.

INSTRUMENTAL

Thermogravimetric and differential scanning calorimetry curves were obtained with a DuPont Mode 900 Thermal Analyzer equipped with the Model 950 thermogravimetry accessory. Heating rates of 5, 10, 20, and 100 °C min^{-1} were used for runs made in nitrogen as well as in vacuo. The temperature axis in the DSC curve refers to the sample temperature.

The computer controlled thermogravimetry–mass spectroscopy system used in this study has been previously described[4].

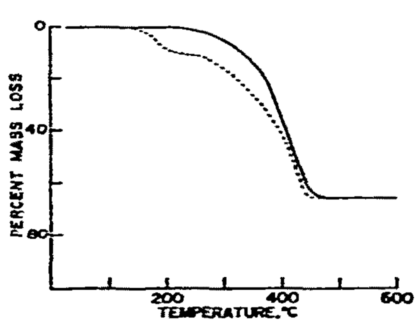
The combustion calorimeter used in this study was manufactured by Parr Instruments and used according to standard procedures[5].

RESULTS AND DISCUSSION

Thermogravimetry

Thermogravimetric curves for tire samples in a nitrogen atmosphere and in vacuo are presented in Fig. 1. Decomposition began at about 225 °C in nitrogen and appears to have occurred in a single step, while decomposition in vacuo appears to be a two-step process beginning at about 150 °C. The initial mass loss in vacuo appears to be about ten percent of the original mass and partially overlaps the second step which begins at about 275 °C. The decomposition process was complete for both sets of conditions by about 450 °C after a total mass loss of 65 percent. The residue which remained, appeared to be primarily carbon and was stable when the analysis was terminated at 1000 °C. The residue also retained the original shape of the sample which indicates that the sample did not melt during decomposition.

Previous investigators[1] have reported that the highest yields of liquid products were obtained from tires at a carbonization temperature of 500 °C while highest yields



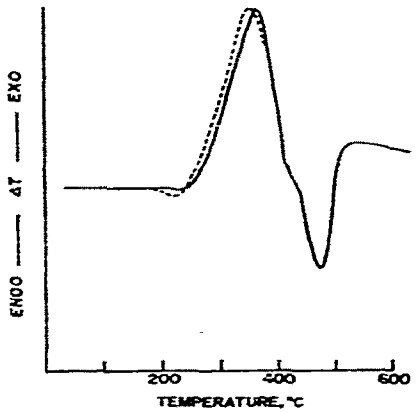


Fig. 1. Thermogravimetric curves for tire samples at a heating rate of 10 °C min^{-1}. (a) ———, In a nitrogen atmosphere; (b) – – –, in vacuo.

Fig. 2. Differential scanning calorimetry curves for tire samples at a heating rate of 10 °C min^{-1}. (a) ———, In a nitrogen atmosphere; (b) – – –, in vacuo.

of solid and gaseous products were obtained at 900 °C. This suggests that the heating rate might influence the mass loss observed by thermogravimetry. However, this effect was not observed for heating rates in the range from 5 to 100 °C min^{-1} since all curves showed the same mass loss of 65 percent.

The effluents from the thermobalance were trapped in a preweighed liquid nitrogen cold trap. As each analysis was terminated, the trap was brought to room temperature, dried, and weighed. An average of about 85 to 90% of the evolved gases remained in the trap at room temperature. The effluent separated into two layers with the bottom layer, constituting about 5 to 10% by volume, being a colorless liquid which was probably water. The top layer was a dark brownish yellow liquid which had a pungent odor.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) curves for the tire samples in nitrogen and in vacuo are presented in Fig. 2. These curves show that the decomposition process is exothermic with the maximum temperature difference between sample and reference occurring at about 375 °C. An average decomposition energy of -3×10^5 J kg^{-1} (negative indicating exothermic) was obtained from quantitative measurements of twenty different curves. However, this value can be considered accurate only to within an order of magnitude because of the difficulty in determining the baseline and the problems associated with reproducibility of sample packing. This first DSC peak coincides with the mass loss region of the TG curves.

A second peak was observed in the DSC curve beginning at 440 °C with the maximum temperature differential occurring at about 475 °C. This peak was endothermic and may have partially overlapped the decomposition peak. Since the TG curves show that no mass is lost during the temperature interval of this second peak, structural changes are assumed to occur within the carbon residue. This absorption of energy is probably due to the breaking of carbon–carbon bonds in the remaining carbon skeleton. An alternative explanation is that the peak is due to phase transitions of one or more of the compounding materials. However, this seems unlikely since no peak was recorded as the residue was cooled or was reheated, which indicates that the original peak resulted from an irreversible process.

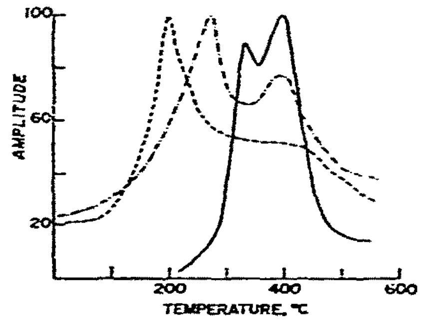
The heat of combustion of the tire residue remaining at 1000 °C was determined by obtaining the DSC curve of this substance in an oxygen atmosphere. The combustion process was strongly exothermic beginning with ignition (observed visually) at 510 °C. Samples larger than 1 mg produced a temperature jump from 510 °C to in excess of 660 °C within an interval of a few seconds, and the aluminum pans were completely melted. Quantitative measurements of the heat of combustion were hampered by the small sample size which had to be used in order to record a DSC curve and included a small contribution from the partial oxidation of the aluminum pans. However, all measurements were of the order of magnitude of the heat of combustion of carbon to carbon dioxide which is reported[6] as -3.267×10^7 J kg^{-1}. The combustion process appeared to be clean with no apparent residue remaining in the pan.

Combustion calorimetry

Samples of the liquid collected in the nitrogen cold trap from the distillation of the tire samples were ignited in a combustion calorimeter at a pressure of 25 atm of oxygen. The liquid samples were taken from the top layer of the distillates in the cold trap to minimize the water content. The average heat of combustion of the liquid was calculated to be -4×10^7 J kg^{-1} which is slightly less than the heating value of fuel oil. For distillates from different samples this value varied by about 5 percent.

Gas evolution–mass spectroscopy

The gases evolved from the thermal decomposition of the tire samples were leaked directly into a mass spectrometer to obtain the gas evolution curves presented in Fig. 3. These curves represent the intensity of specific mass peaks as a function of sample temperature and therefore may represent contributions from molecular fragments and product gases in proportions which cannot be determined. This condition arises since a mixture of gases rather than a pure product is introduced into the mass spectrometer ionization chamber. However, with some knowledge of the possible and probable constituency of the evolved gases, reasonable assignments can be made for some of the peaks to yield conclusions of a general nature.



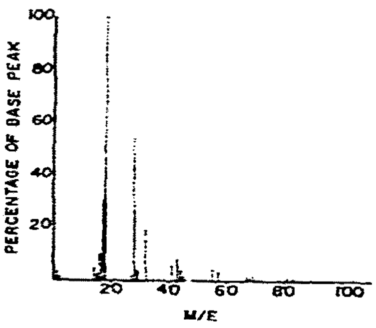


Fig. 3. Mass spectrometric measurement of gas evolution curves for (a) — — —, water; (b) —·—·—, nitrogen; and (c) ———, rubber decomposition products resulting from the thermal decomposition of tire samples at a heating rate of 6 °C min^{-1} in vacuo with data reduction performed according to the procedure described by Gibson[4].

Fig. 4. Mass spectrum of gases evolved from the thermal decomposition of rubber tires at 150 °C.

The gas evolution curves in Fig. 3 show that the initial mass loss from the tire sample in vacuo is due primarily to water. The gas evolution curve for water, $m/e = 18$ versus temperature, indicates that the major portion of the water vapor is evolved prior to the decomposition of the rubber constituents. This initial water loss probably results from the thermal degassing of adsorbed atmospheric moisture and gases. A typical mass spectrum from this temperature range, such as the spectrum at 150 °C shown in Fig. 4, shows a large water peak with additional peaks which correspond to atmospheric gases such as nitrogen, oxygen, and carbon dioxide. The gas evolution curves in Fig. 3 show that nitrogen is also evolved prior to the destruction of the rubber polymer.

The decomposition of the rubber compounds produces a mixture of organic compounds and fragments. However, plots of all significant mass numbers up to $m/e = 100$ versus temperature produce a series of gas evolution curves which are identical in shape and will superimpose on each other. These curves are therefore represented by the single gas evolution curve in Fig. 3. This curve indicates that the rubber decomposes in a manner such that a variety of products are evolved simultaneously rather than different products at different temperatures. The complexity of the distillate mixture is suggested by a typical mass spectrum from this temperature interval such as the spectrum at 425°C in Fig. 5. Due to calibration considerations, only that portion of the spectrum from $m/e = 1$ to 100 was recorded in this study. However, previous studies[1] have shown that well over a hundred constituents, some with molecular weights in excess of 300 g mol^{-1}, are contained in the effluent from the distillation of tires.

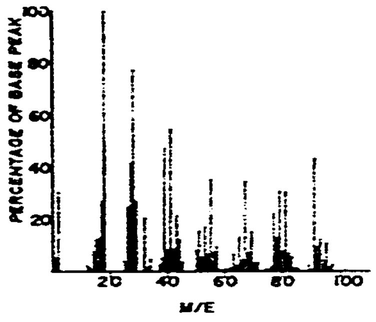


Fig. 5. Mass spectrum of gases evolved from the thermal decomposition of rubber tires at 425°C.

CONCLUSIONS

The calorimetric data obtained in this study indicate that a significant quantity of fuel with a heating value approaching that of fuel oil is recoverable through the destructive distillation of rubber tires. Distillation processes utilizing dynamic heating conditions of 100°C or less per minute yield products in three phases. These phases consist of a solid residue with a heating value of about -3×10^7 J kg^{-1}, an organic liquid phase with a fuel value of about -4×10^7 J kg^{-1}, and a gas which was observed to burn but for which no quantitative measurements of heating values were made Water was also observed as a liquid phase. Decomposition of the tire rubber seems to occur through a mechanism which generates a large variety of organic compounds simultaneously.

A realistic estimate of the quantity of energy recoverable from scrap tires through a large scale operation would have to include such energy expenditures as transportation, sample grinding and preparation, separation of impurities such as the metal in the tire bead, pollution abatement, and any additional refining required before the fuel is burned. However, since a net energy gain appears feasible, and since the process is compatible with existing technology and is ecologically beneficial, the destructive distillation of discarded tires is probably a logical means of energy conservation.

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