

COPROCESSING OF COAL AND WASTE RUBBER

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ABSTRACT

The disposal of used tires, the main source of waste rubber, is an important environmental problem. We describe a method to transform used rubber tires into useful liquid products by coprocessing them with coal. Carbon black, an important constituent in rubber tires, provides a good hydrocracking catalyst during coprocessing. Due to the presence of carbon black in the rubber tires, the yields of liquids obtained by coal-rubber tires coprocessing are superior to those that could be obtained by coprocessing rubber with coal in the absence of carbon black.

INTRODUCTION

Over 200 million used rubber tires are discarded each year in the United States¹. When not indiscriminately dumped, they are usually either stockpiled or landfilled. Neither of these methods of disposal is likely to be accepted in the future, and major efforts are under way to find more environmentally acceptable solutions for the disposal of used rubber tires. Recently, Gillen² and D. J. Stopek, et al.³ reported successful coal-used rubber tires cofiring tests in power plants in Ohio and Illinois, respectively.

A different possible approach for the use of rubber tires is their coprocessing with coal to obtain liquids⁴. In this approach, we can take advantage of both the high hydrogen content of the organic material in rubber tires and of the good solvent properties of the depolymerized rubber to aid coal liquefaction. Also, the carbon black, a major constituent of rubber tires, can act as a catalyst in the process⁵⁻⁷. The liquids produced in coprocessing coal and tires could be a source of transportation fuels, or could be used in the production of new tires by replacing the petroleum-based aromatic oil. The unreacted coal and the carbon black remaining from tires can then be burned.

EXPERIMENTAL

The materials used in these experiments were: Illinois #6 coal, 20 mesh; tread material from a highway-collected rubber tire; vulcanized tread material; styrene-butadiene rubber; cis-polybutadiene rubber; aromatic oil provided by Dr. E. T. McDonell, Michelin America Small Tire Co. Akron, Ohio; elemental sulfur (Fisher Scientific Co.); and carbon black Mogul L (138 m²/g) provided by Cabot Corp. The elemental analyses of tires and of the coal used in these experiments are given in Table 1. The composition of the tread material as provided by E. T. McDonell is given in Table 2.

Liquefaction Experiments. The liquefaction experiments using shredded rubber tire materials and coal were performed in a laboratory shaker autoclave. In all experiments described, the reaction temperature was 425°C, the reaction time was 60 minutes, and the initial hydrogen pressure (at room temperature) was 1000 psi. The relative amounts of materials are given in Tables 3 and 4. In a typical liquefaction experiment the total amount of materials was 6-7 g.

After liquefaction, the liquid and solid products were separated by methylene chloride extraction followed by filtration. After the removal of methylene chloride by evaporation in a rotary evaporator, the residue was extracted with heptane, the soluble part separated again by filtration, and the heptane removed by evaporation in a rotary evaporator.

The conversion was calculated as the percent of the methylene chloride soluble materials vs. the initial organic materials in the reactants. For convenience of discussion, the heptane-soluble fraction will be defined as "oils" and the heptane-insoluble, methylene chloride-soluble fraction of the products as "asphaltenes." The insoluble solids are: unreacted coal, mineral matter from coal, and carbon black and zinc oxide from rubber tires.

The elemental analyses were performed by Huffmann Laboratories, Golden, CO and by PETC.

RESULTS AND DISCUSSION

Several tests were performed to test the concept of coal-rubber tire coprocessing and to assess the properties of the liquids obtained. The organic material from both highway-collected rubber

tire material and the tread material provided by Michelin are converted completely to liquid, heptane-soluble materials when processed alone under the above described conditions. In both cases the gas formation was under 1%. When shredded rubber tire material and Illinois #6 coal were coprocessed, coal conversions to methylene chloride soluble materials were ~51% and ~56% respectively, when the ratio of organic materials from tread and coal was 0.74 : 1 and 1.4 : 1. For comparison, when Illinois #6 was liquefied under the same experimental conditions in the presence of tetralin⁸ (ratio tetralin : coal, 2 : 1, by weight) the coal conversion was 57 %. The percent of heptane-soluble material obtained from coal was 31 % when the liquefaction was performed in the presence of tetralin⁸, and 37 - 41 %, when the liquefaction was performed in the presence of rubber-tread material⁴. The heptane-soluble oils that constitute the majority (~87 %) of the liquefied material are rich in hydrogen (Table 3).

As can be seen from the data in Table 2, carbon black is an important constituent of rubber tire material. From the information received from Dr. McDonnell¹, the usual surface area of the carbon black used in rubber tires is around 100 m²/g. We have found carbon blacks to be good catalysts in hydrocracking reactions⁵⁻⁷. We hypothesized that the carbon black present in rubber tires could exhibit catalytic activity during coal-rubber tire coprocessing. To check this assumption, coprocessing experiments were performed in the presence and in the absence of carbon black. When coal and a mixture of all the components of the tread material described in Table 2 were coprocessed, the conversions were very similar (~71%) to those obtained with the vulcanized tread material, and the gas production was under 1%. However, when the coal was coprocessed with the same components of tread material except carbon black the conversion decreased to 60% and the gas production increased to 6% (Table 4). Elemental analyses of the heptane soluble liquid products obtained in the experiments described in Table 4 are given in Table 5.

Comparative data for conversion to liquids (71% vs. 60%) when the coprocessing is performed in the presence and in the absence of carbon black indicate its role during coprocessing. The reduction in the quantity of gas formed when coprocessing is performed in the presence of carbon black (1% gases) versus in the absence of carbon black (6% gases) suggests the possibility that the aromatic fragments from coal products or rubber are alkylated with aliphatic fragments formed during rubber depolymerization. We have not yet succeeded in the unequivocal identification of such reactions, but

work with model compounds will soon be started.

Work with model compounds⁵⁻⁶ has shown that carbon blacks are good catalysts at temperatures lower than those described in this paper, and that their catalytic activity at constant concentration is dependent on the surface area. Two logical developments of rubber tire-coal coprocessing studies would be 1. Coprocessing at lower temperatures (350-400°C), and 2. Coprocessing in the presence of high surface carbon blacks. The carbon blacks currently used in the rubber industry have surface areas in the range of 100 m²/g, but carbon blacks with surface areas over 1400 m²/g are commercially available⁶.

Data in Table 2 indicate that a heavy petroleum fraction ("aromatic oil") is used in a rather large concentration (20% by wt. in the tread material) in rubber tires. Since an automobile tire contains about 15 pounds of organic materials (i.e., 3 lb aromatic oil), a production of about 200 million rubber tires per year will require about 600 million pounds (273,000 tons) per year of aromatic oils. Preliminary results (Table 6) indicate that at least a part of this oil could be generated from coprocessing coal with used rubber tires, so that a valuable, hydrogen-rich material can be recycled.

From a process viewpoint, it may be advantageous to recycle a part of the liquid product, so that a feed slurry of coal and shredded rubber tires can be manipulated more easily. Also, our data with model compounds^{5,7} indicate that high pressure is not necessary for reactions in the presence of carbon black. Both lines of research deserve further study.

CONCLUSIONS

Our experimental results show that the coprocessing of used rubber tire and coal can provide an alternative use for waste rubber materials. The liquids formed in this coprocessing are hydrogen rich and are a potential source for the aromatic oil component in new tires. Also, these liquids can be a source of transportation fuels.

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DISCLAIMER

Reference in the paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. McDonell, E. T.; Michelin America Small Tire Co., personal communication.
2. Gillen, J. E.; Proceedings Eighth Annual International Pittsburgh Coal Conference. The University of Pittsburgh School of Engineering, Center for Energy Research, October 14-18, 1991, p. 859.
3. Stopek, D. J.; Millis, A. K.; Licklider, P. L.; Proceedings Eighth Annual International Pittsburgh Coal Conference. The University of Pittsburgh School of Engineering, Center for Energy Research, October 14-18, 1991, p. 865.
4. Farcasiu, M.; Smith, C. M.; U.S. Patent 5,061,363, October 29, 1991.
5. Farcasiu, M.; Smith, C. M.; Energy and Fuels 1991, 5, 83.
6. Farcasiu, M.; Smith, C. M.; Ladner, E. P.; Sylwester, A. P.; Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem. 1991, 36, 1869.
7. Farcasiu, M.; Smith, C. M.; Hunter, E. A.; 1991 Proceedings of Conference on Coal Science, ed. IEA Coal Research Ltd., Butterworth, Heinemann Ltd. 1991, p. 166.
8. Cugini, A. V., PETC; personal communication.

TABLE 1. Elemental analyses: rubber tires and Illinois #6 coal

Sample	Elemental composition Organic components, wt%			Inorganics wt. %
	C	H	S	
Illinois #6 coal	80.4	5.4	2.1	11
Rubber tire*	82.6	11.0	2.9	34**
Tread material*	85.3	11.0	2.9	34**

* Calculated elemental composition of the organic material after correction for the 34% of inorganic material present in tread material.

** The inorganics present as 34% of the tread consist of carbon black (33) and zinc oxide (1).

TABLE 2. Rubber tire (tread material) composition.

Composition	%
styrene-butadiene rubber	35
cis-polybutadiene rubber	8.5
aromatic oil (from petroleum)	20
carbon black	33
zinc oxide	1
sulfur	1

TABLE 3. Elemental analyses of heptane-soluble products obtained from liquefaction of used rubber tires and tread material.

Sample	Heptane-Soluble Products Elemental Analysis, wt.%		
	C	H	S
Used rubber tire	86.5	10.9	0.4
Illinois #6 / used rubber tire (1/1.4 by wt. organics)	84.5	10.5	0.5
tread material (Michelin)	88.9	10.1	0.1
Illinois #6/tread material (1/0.74 by wt. organics)	87.8	9.7	0.5

TABLE 4. Coprocessing of coal and rubber materials in the presence and absence of carbon black.^a

Sample		#Conversion (wt. %)			Liquids Composition	
Rubber	Coal	All	rubber	coal	Oils	Asphaltenes
1. Tread mat.	none	100	100	-	100	0
2. Tread mat.	yes	71	43	28	89	11
3. Tread comp*	yes	73	43	30	84	16
4. Tread.mod**	yes	60	-	-	87	13

^aReaction conditions: 60 min, 425°C. Weight ratio organic materials in rubber/coal 0.74:1.

1 and 2. Vulcanized tread material (Table 2).

3. Tread material compounds (mixed in the proportion described in Table 2).

4. As 3, but without carbon black.

Based on methylene chloride soluble material.

* <1% gas.

** 6% gas.

TABLE 5. Elemental analyses of heptane-soluble fractions (Expt. identified in Table 4).

Exp.#	Elemental Analysis (wt. %)				
	C	H	N	S	O
1	88.9	10.1	0.25	0.13	1.2
2	87.8	9.7	0.36	0.47	1.7
3	87.5	9.5	0.56	0.47	2.0
4	87.5	9.4	0.36	0.57	2.2

TABLE 6. Comparative elemental analyses of petroleum based "aromatic oil" and heptane-soluble coprocessing products.

Sample	Elemental Analysis (wt.%)			
	C	H	N	S
"Aromatic oil"	86.8	10.2	-	2.28
Heptane-soluble (Table 5, Expt. 2)	87.8	9.7	0.36	0.47