

Pyrolysis of scrap tires: Can it be profitable?

Processing them into higher value-added, marketable products—activated carbon and carbon black—may be the answer to the question of what to do with all of our used tires.

Marek A. Wójtowicz
Michael A. Serio

Scrap tires present formidable disposal problems. The same properties that make them desirable as tires—most notably, durability—also make their disposal and reprocessing difficult. Tires are almost immune to biological degradation. Dumping the 280 million tires that are generated each year in the United States into landfills is becoming an unacceptable solution (1). In addition to the continuous flow of waste tires, approximately 2–3 billion tires are already stored in piles throughout the United States; illegal dumping is also becoming a serious problem. Tires take up large amounts of valuable landfill space, provide breeding sites for mosquitoes and rodents, and present fire and health hazards. Recently, a large mountain of tires in Canada caught fire, and widespread environmental consequences resulted because of the oils and gases generated from the decomposing rubber. Such fires are difficult to contain because of the tires' high flammability and because of the pockets of air present in the piles. One fire in Huntington, VA, burned for nine months.

Large-scale efforts use tires either as a fuel (Oxford Energy Corp.) or as a filler for asphalt (Rubber Asphalt Producers). These two technologies consume about 28 million tires annually (2). However, feeding the tires and slagging are problems when the tires are burned, and the rubber asphalt filler costs 40% more than conventional material. RW Technology has also tried to convert tires into

other plastic products, but the market niche seems to be small.

Pyrolysis—the thermal degradation in the absence of oxygen—is another way to reprocess scrap tires. The products are fuel gas, oils, and a solid residue (char), which contains appreciable quantities of mineral matter and low-grade carbon black. The three products have comparable yields by weight.

More than 30 major pyrolysis projects have been proposed, designed, patented, licensed, or built over the past decade, but none has been commercially successful (3). The success of any tire-processing technology depends on environmental performance (emissions) and process economics. Almost no emissions are produced by tire pyrolysis except for minor fugitive sources and equipment leaks (3, 4).

The two most important factors affecting process economics are the tipping fees charged for tire disposal and the selling prices of the products (4). Tipping fees have been steadily increasing over years, and this trend is expected to continue. Depending on the region, fees vary from \$35 to \$108 per ton of whole tires delivered in mass quantities (3). Selling prices of the products yield low returns because of the low market value of the fuels and the low quality of the recovered char or carbon black (carbon black extracted from the pyrolysis char is of very low purity and cannot be used in tire manufacturing). Therefore, to obtain a positive cash flow, it would be desirable to develop a process based on the recovery of value-added products such as high-grade carbon black, activated carbon, or valuable chemicals (e.g., benzene, toluene, and xylene). We believe that significant improvement in the economics can be accomplished by upgrading the primary pyrolysis products to secondary products of higher value.

ene, and xylene). We believe that significant improvement in the economics can be accomplished by upgrading the primary pyrolysis products to secondary products of higher value.

Process description

The concept of pyrolytic reprocessing of waste tires into value-added products is presented in Figure 1. Characteristics of the reactants and products, the process conditions, and the yields of pyrolytic products are based on an extensive literature review and on the data collected in our laboratory (5, 6). The primary products of tire pyrolysis are pyrolytic gas (also known as pyro-gas), oils, and char. This process yields substantial quantities of oils and char, which can undergo additional processing to secondary, value-added products. According to the proposed scheme, char upgrading is implemented in a closed-loop activation step that yields an activated carbon and eliminates undesirable byproducts and emissions. A stream of CO₂ is used for high-temperature char activation, which is followed by CO₂ recovery through the reverse Boudouard reaction. The latter step is an optional feature of the proposed process. Upgrading the char produces high-surface-area activated carbon and finely divided carbon, which we refer to as the Boudouard carbon. Ash-free oils are turned into high-quality carbon black by using the furnace process. As an alternative, oils can be separated into valuable chemical feedstocks by distillation. Product upgrading is expected to greatly

The authors are with Advanced Fuel Research Inc.

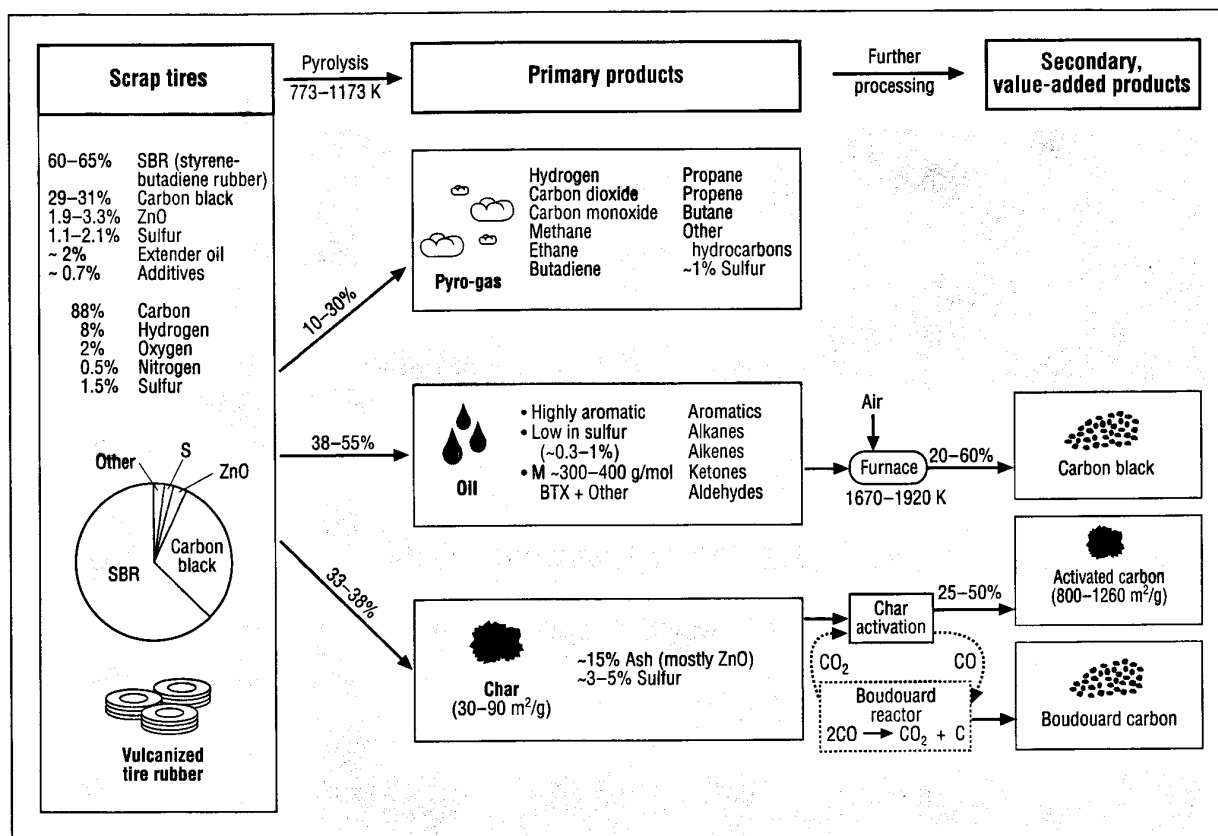


Figure 1. The pyrolytic reprocessing of scrap tires yields substantial quantities of oils and char, which can undergo further processing to secondary, value-added products. Char upgrading results in producing high-surface-area activated carbon and Boudouard carbon. Ash-free oils are turned into high-quality carbon black, or the oils can be separated into valuable chemical feedstocks by distillation.

improve the economics of scrap tire pyrolysis.

Our proposed process is shown in Figure 2 (p. 50). A stream of scrap tires enters the pyrolyzer, where it comes into contact with a recycle stream of product gas, which acts as a carrier gas for pyrolysis. Mixing used tires with other waste material and solid-waste pretreatment are optional features of the process. Another option is to recycle part of the pyrolysis oil from the condenser into the pyrolyzer; this option is represented by a dotted line in Figure 2. It is expected that the recycled oil will undergo partial cracking, leading to an altered gas composition at the reactor outlet. System flexibility allows for wide variations in the ratio of gas to oil recycling, depending on product characteristics and requirements. The pyrolyzer operates at ~1173 K, and the product streams are fuel gas (which also contains pyrolysis liquids) and char. The pyrolysis liquids are separated from the volatiles in a condenser and then subjected to partial combustion in an oil furnace to produce carbon black. The latter step is almost identical to the commercial

carbon black manufacturing, except that the feedstock is pyrolysis oil rather than a petroleum product. The high-BTU gas is combusted to supply the process heat requirements. The solid product does not have sufficient surface area to make it commercially attractive, and thus, an activation step is needed. Char activation uses CO_2 at the same temperature as the pyrolyzer (~1173 K), which reduces the CO_2 to CO . The consumed CO_2 is regenerated in a Boudouard reactor with simultaneous formation of finely divided carbon.

The net result of this process is the conversion of used tires into three marketable products: activated carbon, carbon black, and Boudouard carbon. The production of carbon black and Boudouard carbon is a novelty in the proposed scheme, yet it may be integrated into the process by adapting existing technologies. The elements of the process are described here.

Feed stream preparation. The tires are shredded and possibly combined with another waste stream. The use of mixed wastes would improve the appeal and the number of sites where a plant could be installed. This feature,

however, increases the complexity of the design as well as the operating costs. The size reduction required for scrap tires does not appear to be excessive. In fact, higher char activation efficiencies were reported for coarse waste material (~170 mg) than for fine particles (<50 mesh) (5). The optimal size of scrap tire material for the process has not been determined. Because the cost of shredding increases with decreasing particle size, there is an economic incentive to make the tire pieces as large as possible. For smaller particles, pretreatment with O_2 increases char yields and surface areas (5). It is not clear, however, whether these benefits justify the added cost of oxygen pretreatment.

Pyrolysis and char activation units. Although a rotary kiln reactor has been successfully used for pyrolysis of tires, it is not necessarily the best solution for a high-throughput system (7). A kinetic analysis of tire pyrolysis indicates that the process is relatively fast and can be completed in <1 s at 873 K. This speed allows the use of an entrained-flow reactor, which is appropriate for high-throughput applications. Unfortunately, only relatively

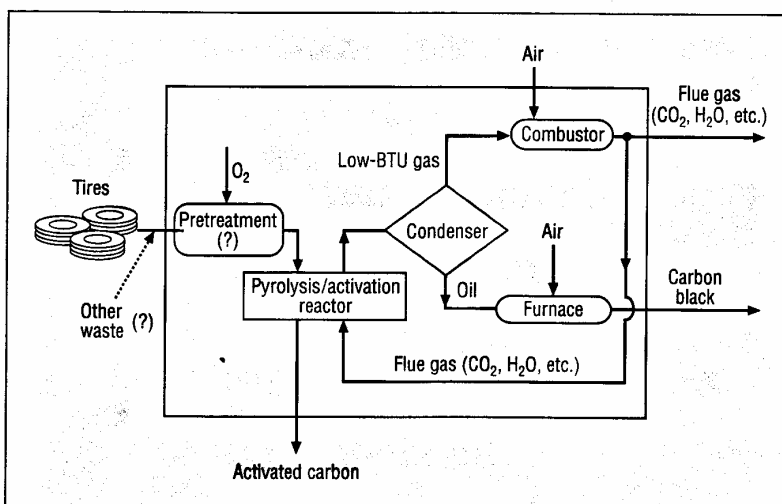


Figure 3. A single countercurrent moving-bed reactor. This scheme combines tire pyrolysis and char activation in a single unit.

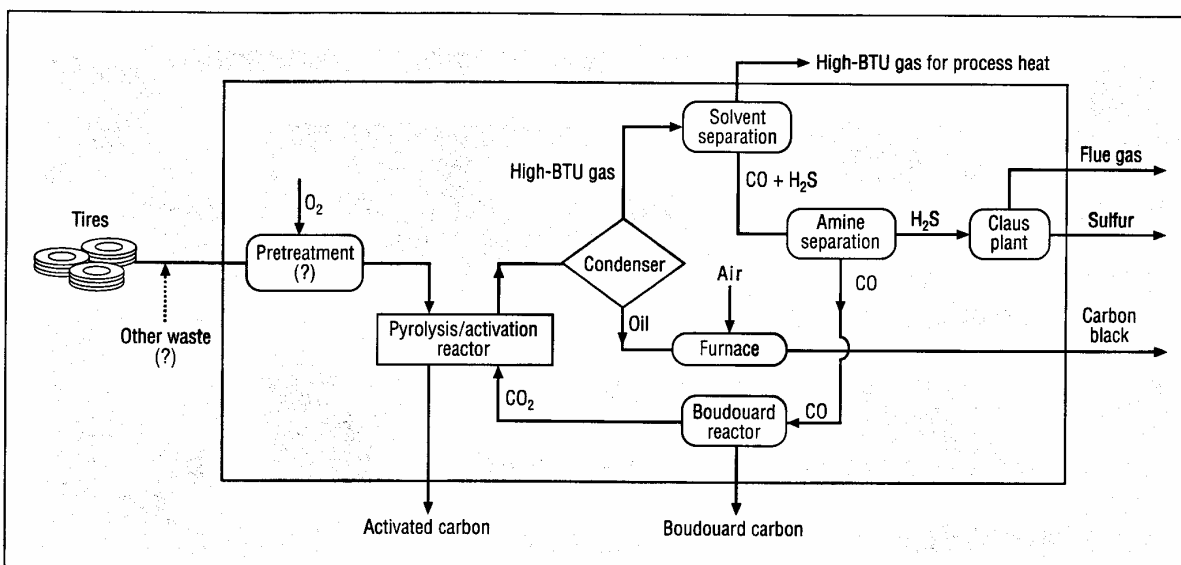


Figure 4. Co-separation process. One disadvantage of the single-reactor scheme is that, if Boudouard carbon is produced, a fairly complex separation step is required to recover pure CO from the pyrolysis gas.

is required.

- Use as transportation fuel would require upgrading because of the relatively high aromatic content of the oil.

- Because carbon black is required to make tires, the production of carbon black from the oil is a form of tire recycling and seems to be more practical than trying to recover the original carbon black from the char.

Boudouard carbon production from CO. This process step was discussed by Walker (9) as part of his coal-processing scheme. The temperature of the Boudouard reactor is maintained at 773–800 K, and the carbon product is ash free and has a particle size significantly smaller than can be obtained by grinding (15). In fact, the particle size of Boudouard carbon is small enough to burn completely in a

diesel engine (16). Boudouard carbon is similar to carbon black (except for having a zero-hydrogen content), and in some cases can be substituted for carbon black. The potential applications of this product include the manufacture of colorants and lubricants.

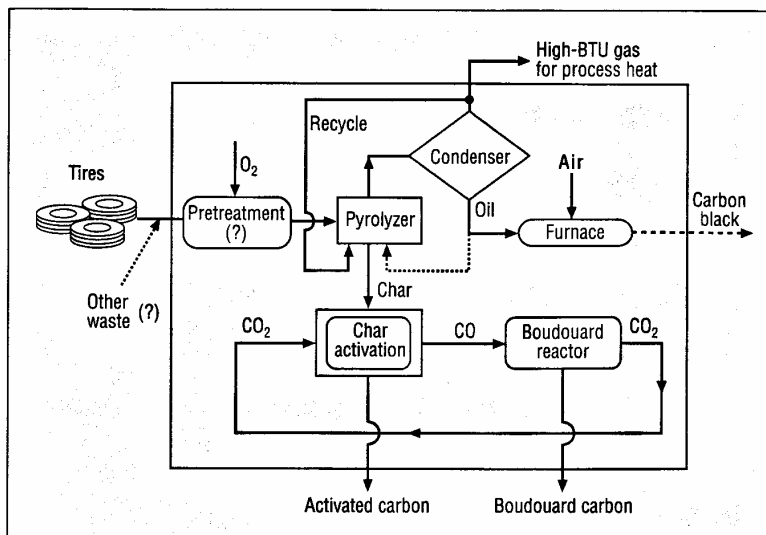
The production of finely divided carbon from CO has never been commercialized, presumably because of the relatively high value of CO and uncertainties associated with marketing Boudouard carbon. During World War II, however, the reaction was used in Germany to produce a substitute for carbon black (17). Although some information on the reaction kinetics and product characteristics has been available for a long time (18, 19), more research and development are needed to make the process

commercially viable. In particular, the following topics must be addressed: product quality, the determination of reaction rates at various CO-to-CO₂ ratios in the feed gas, reactor-type selection and design, separation of Boudouard carbon from the iron catalyst, and exploration of noncatalytic reaction pathways.

Energy and mass balances. The fuel gases produced during pyrolysis can be used to provide process heat for the pyrolysis and activation stages. Some heat can also be recovered from the manufacturing of carbon black by partial combustion of the oil and from the production of Boudouard carbon. Preliminary estimates show that the process outlined in Figure 2 will be self-sufficient from an energy standpoint. Existing

Figure 2. Tire pyrolysis process proposal.

The net result is three marketable products: activated carbon, carbon black, and Boudouard carbon. The production of carbon black and Boudouard carbon is very much a novelty, although it may be integrated into the process by adapting existing technologies.



small particles can be fed into such a reactor, mainly because of heat-transfer limitations. For the larger pieces of tire material, a fluidized-bed reactor could be used. In either case, a hot cyclone is desirable to separate char particles from the volatiles. In this scheme, char activation by CO₂ takes place in a separate reactor, allowing the oxides of carbon to be cycled between the activation step (producing CO) and a disproportionation step (producing CO₂ and carbon). In this way, CO₂ is periodically consumed (activation) and regenerated (disproportionation), and CO and CO₂ stay relatively pure.

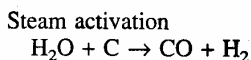
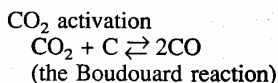
Another possibility is to use a moving-bed countercurrent system. Although the solids throughput would necessarily be lower, this disadvantage would be offset by combining the pyrolysis and char activation stages in a single reactor. In this scheme, tire pieces would be fed into the reactor at the top and CO₂ at the bottom (Figure 3). A temperature of ~1173 K would prevail at the bottom of the reactor so that the char would be progressively pyrolyzed and then activated as it moves through the reactor. This design simplifies the process of feeding the tire pieces and eliminates the need for a hot cyclone because the volatiles and char come out of opposite ends of the reactor. The moving-bed concept has been used in a large-scale coal gasification plant in Beulah, ND, that produces synthetic pipeline gas (8).

There are some differences between the two processes, however. The tire-processing unit would operate under atmospheric pressure because there is

little or no advantage in producing activated carbon at an elevated pressure. The coal gasification system is internally heated by introducing O₂ at the bottom and partially combusting a portion of the coal. In the tire-processing reactor, the pyrolysis gases that come off the top of the unit would be combusted externally, and the hot exhaust gases (mostly CO₂ and H₂O) would be introduced into the bottom of the reactor for char activation. The reactor would be insulated to prevent heat losses.

The single-reactor scheme (Figure 3) for processing tires has two disadvantages: The pyrolysis gas has a lower heating value because it is diluted with the flue gas, and if Boudouard carbon is to be produced, a fairly complex separation step is required to recover pure CO from the pyrolysis gas (Figure 4). Previous work has shown that the final activated carbon product is not very sensitive to the conditions under which pyrolysis is carried out (5), thus allowing for greater design flexibility.

We have shown that activation using an 8% CO₂/He mixture at 1173 K for 3–10 h is sufficient to obtain chars with high surface area (5). The residence time can be reduced by raising the temperature, increasing the CO₂ partial pressure, or by using steam instead of CO₂. The char activation chemistry can be represented by the following two reactions:



Both reactions are endothermic, and the equilibrium reaction becomes more favorable as the temperature increases. The use of steam produces a higher reaction rate and a higher surface area product, and the use of CO₂ increases the production of CO from the activation step. The CO can then be subjected to the reverse Boudouard reaction for the production of finely divided carbon (9–12).

Carbon black production. The oils from tire pyrolysis can be used to produce carbon black because the properties of tire-derived oils are similar to those of the petroleum fraction used in carbon black manufacturing (13). In the oil furnace process, a highly aromatic feedstock is converted to carbon black by partial combustion and pyrolysis at 1673–1923 K in a refractory-lined steel reactor. The properties of carbon black that are important in reinforcement applications—in tires, for example—are particle size and structure (degree of agglomeration into three-dimensional networks). These properties are controlled by the nozzle design, reaction chamber geometry, temperature, residence time, and turbulence intensity (14). As an alternative to carbon black production, the oil from tire pyrolysis can be used for its fuel value, although it requires additional processing to remove aromatic components.

The conversion of the oil stream to carbon black is a more attractive option for several reasons:

- A solid product is easier to store and handle.
- The value of the solid product is higher than that of any possible fuel.
- Little or no upgrading of the material

tire pyrolysis units such as the one operated by Conrad Industries in Centralia, WA, usually generate more pyro-gas than is needed for process heat, and excess gas is often burnt in an outside flare. On-site energy savings could improve process economics.

The net yields of the products depend on the degree of activation required in the production of activated carbon. A high degree of activation would correspond to a larger amount of Boudouard carbon produced from the CO stream. Estimated relative yields are shown in Figure 1.

Economics

A preliminary cost analysis for the proposed tire reprocessing scheme shown in Figure 2 indicates that the process could be profitable. The following formula is used to evaluate process economics:

$$P = F + R - C - T - S - D$$

where P is the profit, F is the tipping fee collected for tire disposal, R is the revenue received from the sale of products, C is the processing cost for operating the facility, T is the cost of transportation of tires, S is the cost of tire shredding, and D is the cost of disposal of waste products. Furthermore, the revenue breaks down to

$$R = R_1 Y_1 + R_2 Y_2 + R_3 Y_3$$

where R_1 , R_2 , and R_3 are selling prices of activated carbon, carbon black, and Boudouard carbon, respectively; Y_1 , Y_2 , and Y_3 are net yields of these products with regard to the starting tire material. The value of fuel gas is neglected, although proper use of this source of energy can improve process economics. All the above terms are expressed in dollars per tire.

We assume pyrolysis yields of 35% char, 20% pyrolytic gas, and 45% oils as well as a 50% char burn-off during activation. Additional assumptions are listed in the box.

Simple calculations lead to the following figures (in dollars per tire): $F = 0.50$, $R_1 = 1.05$, $R_2 = 0.58$, $R_3 = 0.45$, $C = 0.50$, $T = 0.18$, $S = 0.40$, and $D = 0$. This is equivalent to the net profit of \$1.50/tire, an annual gross income of \$6 million, and a payback period on the capital investment of approximately 3.3 years.

More detailed economic analysis still needs to be done, but even this simplified and fairly conservative treatment demonstrates the high commercial potential of the proposed

Additional assumptions

- Average weight of a tire is 20 lb.
- Yield of carbon black in the furnace process is 40%.
- The most economical tire processing capacity is 100 tons/day (i.e., ~4 million tires per year) (20).
- Capital cost of such a plant is \$20 million—twice the capital investment estimated in Reference 20, because more equipment is required.
- Tipping fee charged by the plant is \$0.50/tire.
- Selling price of activated carbon is \$0.30/lb; activated carbon for wastewater treatment sells for about \$0.68/lb (private communication from William Petrich, Independent Environmental Services, Inc., August 1993).
- Selling price for carbon black is \$0.16/lb; high-quality carbon black sells for \$0.28/lb (3).
- Selling price of the Boudouard carbon is \$0.13/lb, comparable with the price of low-grade carbon black derived from scrap tire char (3).
- Cost of plant operation is \$0.50/tire, comparable to the cost of operating the tire incineration plant in Modesto, CA (3).
- Tire transportation cost is \$0.20/ton/mi. This cost usually ranges from \$0.15 to \$0.20 ton/mi for transportation of whole tires over a distance of 100 mi (3).
- Average distance over which tires need to be transported is 100 mi.
- Tire shredding cost is \$0.40/tire; the typical cost charged by shredding companies was \$0.19–\$0.75/tire in 1989 (3). Shredding costs vary depending on the fineness of the product.
- Cost of waste product disposal is negligible.

approach. The profitability of the process is expected to increase because of increasing tire disposal charges.

For the sake of comparison, the cost of scrap tire incineration without heat recovery is about \$0.02–\$0.03/lb (i.e., about \$0.40–\$0.60/tire) (21). The cost of power generation from waste tires is 1.5–5.1 times higher than the corresponding cost for coal, depending on whether whole or ground tires are used (21). Depolymerized scrap rubber can also be used as liquid fuel, but in general, depolymerization is difficult and involves extensive high-pressure treatment. Clearly, reprocessing waste tires into fuels does not seem to be an economically attractive option.

Pyrolysis processes with value-added products can be made profitable and competitive compared with incineration plants. In addition, despite its

reasonably good environmental record, tire incineration faces increasing opposition from communities concerned about potential emissions. This barrier is expected to be significantly lower in the case of scrap tire pyrolysis. Asphalt rubber is probably the most competitive tire-derived product currently on the market. Although almost twice as expensive as regular pavement, asphalt rubber has demonstrated superior performance and durability. According to legislation passed in 1991, the use of asphalt rubber may be required in 5% of new pavement as early as in 1994, with a projected increase to 20% by 1997 (3). Unfortunately, the estimated total demand for this product is still at about 2% of the amount of scrap tires available (21). Therefore, one can conclude that a large market exists for other technologies targeted at scrap tire reprocessing into useful products.

Tire-derived activated carbons could be used, for example, in wastewater treatment, stabilization of landfills, and recovery of organic solvents and vapors. Boudouard carbon may have a variety of uses that are yet to be explored, including the manufacture of colorants and lubricants. The liquid stream can be used in the production of carbon black, fuel oil, or valuable chemical feedstocks. Oil-derived carbon black can be reused in tire manufacturing, which forms a recycle loop for this material. Pyrolytic gas can be used for process heat generation.

Conclusions

Our preliminary process design uses scrap tires as the input; activated carbon, carbon black, Boudouard carbon, and fuel gas are produced. The technology has the potential to convert a waste stream of tires into marketable products. Because the typical feedstocks for activated carbon and carbon black are either coal or petroleum, the proposed technology would eliminate the need to deplete these resources. The process allows a high degree of flexibility in the relative amounts of each product to reflect changes in the feed stream and market conditions. Another advantage of the system is the production of activated carbon and carbon black from used tires, with inorganic material ending up in the product with a high tolerance for this component (activated carbon). After additional research is completed, the proposed technology should be applied in reprocessing other polymer wastes found in U.S. industry (e.g., end

cuttings from automobile hoses or products that do not pass quality control). Additional research and development of the process as well as the study of product uses are under way.

Acknowledgments

The financial support of the National Science Foundation (Grant III-9215045) is gratefully acknowledged; the project officer was Edward Bryan. The authors also acknowledge the contributions of Hsiheng Teng (now at Chung Yuan Christian University, Taiwan) and Rosemary Bassilakis (Advanced Fuel Research Inc.) to the experimental effort in this area as well as the helpful discussions with Mark A. Petrich (Merck & Co. Inc.), William Petrich (Independent Environmental Services Inc.), Eric M. Suuberg (Brown University), David G. Walker (Walker Chemists Inc.), and Peter R. Solomon (Advanced Fuel Research Inc.).

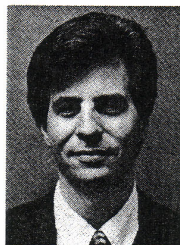
References

- (1) *New York Times*, 9 May 1990; p. D1.
- (2) U.S. Environmental Protection Agency, Office of Solid Waste. *Markets for Scrap Tires*; U.S. Government Printing Office: Washington, DC, 1991; EPA/530-SW-90-074B.
- (3) Clark, C.; Meardon, K.; Russell, D. *Scrap Tire Technology and Markets*; Noyes Data: Park Ridge, NJ, 1993.
- (4) Dodds, J.; Domenico, W. F.; Evans, D. R.; Fish, W.; Lassahn, P. L.; Toth, W. J. *Scrap Tires: A Resource and Technology Evaluation of Tire Pyrolysis and Other Selected Alternate Technologies*; U.S. Department of Energy: Washington, DC, 1983.
- (5) Teng, H.; Serio, M. A.; Wójtcowicz, M. A.; Bassilakis, R.; Solomon, P. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 3102-11.
- (6) Serio, M. A.; Wójtcowicz, M. A.; Teng, H.; Solomon, P. R. In *Conversion and Utilization of Waste Materials*; Khan, M. R., Ed.; Taylor & Francis: Washington, DC, 1996; pp. 105-22.
- (7) Petrich, M. A. *Conversion of Plastic Waste to Valuable Solid Carbons: Final Report of a Project in the Innovative Concepts Program*; U.S. Department of Energy: Washington, DC, 1991.
- (8) Penner, S. S. *Coal Gasification: Direct Application and Synthesis of Chemicals and Fuels*. U.S. Department of Energy: Washington, DC, 1987; DOE/ER-0326.
- (9) Walker, D. G. *Prepr. ACS Div. Fuel Chem.* **1991**, *36*(3), 1129.
- (10) Watanabe, T. *Bull. Inst. Phys. Chem. Res. (Tokyo)* **1929**, *8*, 288.
- (11) Donald, J. H. *Annotated Bibliography of the Literature and Patents Relating to the Production of Carbon by the Decomposition of Carbon Monoxide*; Mellon Institute of Industrial Research: Pittsburgh, PA, 1956.
- (12) Walker, D. G.; Hadley-Coates, L. *Int. J. Energy Res.* **1988**, *12*, 243.
- (13) Merchant, A.; Torkelson, J. M. "Pyrolysis of Scrap Tires"; Chemical Engineering Department, Northwestern University: Evanston, IL, 1990.
- (14) Austin, G. T. *Shreve's Chemical Process Industries*, 5th ed.; McGraw-Hill: New York, 1984.
- (15) Soehngen, E. E. *Development of the Coal-Burning Diesel in Germany*; U.S. Energy Research and Development Administration: Washington, DC, 1976; FE/WEPO 3387-1.
- (16) R. H. In *Coal Conversion Technology*; Yen, C. Y.; Lee, S., Eds.; Addison-Wesley: Reading, MA, 1979; p. 171.
- (17) B.I.O.S. Final Report 1399, Item 22, quoted in Reference 18.
- (18) Walker, P. L., Jr.; Rakaszowski, J. F.; Imperial, G. R. *J. Phys. Chem.*, **1959**, *63*, 133.
- (19) Walker, P. L., Jr.; Rakaszowski, J. F.; Imperial, G. R. *J. Phys. Chem.*, **1959**, *63*, 140.
- (20) Wolfson, D. E.; Beckman, J. G.; Walters, J. G.; Bennett, D. J. *Destructive Distillation of Scrap Tires*; U.S. Department of Interior, Bureau of Mines: Washington, DC, 1973; Report 7302.
- (21) Paul, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; John Wiley: New York, 1988; vol. 14, p. 787.

Adapted with permission from *Conversion and Utilization of Waste Materials*, edited by M. Rashid Khan. Copyright 1996 by Taylor & Francis. All rights reserved.



Marek A. Wójtcowicz is a senior chemical engineer in the hydrocarbons group at Advanced Fuel Research Inc. (PO Box 380379, East Hartford, CT 06138-0379; 860-528-9806). He is the coauthor of more than 30 research papers on coal combustion, gasification, pyrolysis, air pollution control, thermal annealing of carbons, chemical reaction kinetics, adsorption, chemisorption, and heterogeneous catalysis. He has a Ph.D. in chemical engineering from Brown University. Previously, he was a postdoctoral research associate at Delft University of Technology (the Netherlands), where he researched the evolution of nitrogen during coal combustion and pyrolysis.



Michael A. Serio is the vice president for R&D and the manager of the hydrocarbons group at Advanced Fuel Research Inc. He is the coauthor of more than 110 research papers on pyrolysis, gasification, combustion, and liquefaction of coal; jet fuel thermal stability; pyrolysis of biomass, tires, and synthetic polymers; and the formation of pollutants from the combustion of coal and other hydrocarbons. He has a B.S. degree in chemical engineering from Cornell University and a Ph.D. in chemical engineering from the Massachusetts Institute of Technology.

AMBIGUOUS SCIENCE

Science demands a tolerance for ambiguity. Where we are ignorant, we withhold belief. Whatever annoyance the uncertainty engenders serves a higher purpose: It drive us to accumulate better data. This attitude is the difference between science and so much else. Science offers little in the way of cheap thrills. The standards of evidence are strict. But when followed they allow us to see far, illuminating even a great darkness.

Carl Sagan, *Pale Blue Dot*

THEY HAVE EYES . . .

. . . [P]eople do not see; they only recognize. And what they do not recognize remains invisible to them.

Simon Leys, *N.Y. Review*



"Take two of these and call me in the morning."