

## A MULTIPLE-PRODUCT APPROACH TO THE PROCESSING OF USED TIRES

M. A. Serio, M. A. Wójtowicz, H. Teng, D. S. Pines and P. R. Solomon  
Advanced Fuel Research, Inc.  
87 Church Street, East Hartford, CT 06108

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### ABSTRACT

The disposal of used tires by landfilling is becoming an increasingly serious problem in the U.S. From an environmental and economic standpoint, a better solution is to reprocess tires into valuable products such as activated carbon, other solid carbon forms (e.g., carbon black), and liquid and gaseous fuels. A process design is proposed which involves pyrolysis of tires, activation of the solid residue, partial combustion of liquids to produce carbon black, and the use of the high-BTU gas for process heat. The activation of the solid residue is done using CO<sub>2</sub>, which produces CO and activated carbon. The CO<sub>2</sub> is regenerated and the lost carbon is recovered using the Boudouard reaction to produce CO<sub>2</sub> and finely divided carbon. The latter material may be used as a substitute for carbon black. A preliminary assessment of the process is presented.

### INTRODUCTION

Scrap tires present formidable disposal problems. The very same properties that make them desirable as tires, notably their durability, also make their disposal and reprocessing difficult. Tires are well known to be virtually immune to biological degradation. The disposal of 280 million tires generated each year in the U.S. by landfill is increasingly becoming an unacceptable solution [1]. The tires take up large amounts of valuable landfill space and also present fire and health hazards. Recently, a large mountain of tires caught on fire in Canada with widespread environmental consequences due to the oils and gases generated from the decomposing tires. A better solution from an environmental and economic standpoint is to thermally reprocess the tires into valuable products [2]. Large-scale efforts employ tires either as a fuel (Oxford Energy Corporation, Modesto, CA) or as a filler for asphalt (Rubber Asphalt producers, Phoenix, AZ). These two technologies annually consume about 5-6 million tires. However, tire burning has had repeated problems with feeding the tires and slagging, while the rubber asphalt costs 40% more than conventional material. RW Technology, Cheshire, CT, has also tried to convert tires into other plastic products, but the market niche is small and the process is unreliable.

Three features underlie the problem of converting used tires and other waste polymers into useful, marketable products. The first problem is the low level of understanding of the chemistry and physics of tires during thermal degradation. Secondly, even if the thermal degradation processes were well understood, they would have to be monitored carefully to maintain product quality. The tire feedstock varies with time, and the process engineer must be able to monitor reactions and respond to changing conditions as necessary. Finally, the technology must produce a high yield of a product with a viable market. The best solution to disposing of waste tires is to develop a chemical process to convert the tires into another commodity material.

The proposed solution is to thermally reprocess the used tires into activated carbon, other solid carbon forms (e.g., carbon black, graphite, or carbon fibers) and/or liquid and gaseous fuels. The process is based on pyrolysis of tires and the key to its successful development is understanding and controlling the chemistry of low temperature carbonization so that the yield and physical properties of the products can be optimized.

Pyrolysis has been widely used for converting solid fossil fuels, e.g., coal, into liquid and gaseous hydrocarbons, a process which results in a solid char residue. Used automotive tires contain polymeric aromatic structures which are similar to those of coal in some respects. Not surprisingly, typical elemental compositions of both materials are also similar (rubber -- 88% C, 8% H, 2% O, 0.5% N, 1.5% S; and coal -- 82% C, 5.5% H, 8% O, 1.7% N, 2.4% S). Coal pyrolysis has been extensively studied [3-5] but investigations of tire pyrolysis are rarely reported in the open literature.

The most commonly used vulcanized tire rubber is a styrene-butadiene-copolymer (SBR) containing about 25 wt.% styrene [6]. A typical composition of tire rubber is: 60-65% SBR, 29-31% carbon black, 1.9-3.3% zinc oxide, 1.1-2.1 sulfur, ~ 2% extender oil, and ~ 0.7% additives (wt.%, as received) [6, 7]. In most cases, tire pyrolysis studies were performed under inert conditions [6, 8, 9]. Pyrolysis may also be carried out in mildly oxidizing atmospheres, such as steam and carbon dioxide, to improve the quality of pyrolytic products [9-11].

Tire pyrolysis experiments have usually been conducted in the 773-1173 K temperature range [6-8]. Similar to coal pyrolysis, the principal products from thermal degradation of tires are gases, liquid oils and solid carbon residues. The following yields of tire pyrolysis are typical (on an as-received basis): 33-38 wt.% char, 38-55 wt.% oil, and 10-30 wt.% gas. The product yields are affected by the pyrolysis conditions, such as pyrolysis temperature and heating rate. The literature on the analysis of products from tire pyrolysis is summarized below.

**Gas Analysis** -- Gases produced from tire pyrolysis are mainly hydrogen, carbon dioxide, carbon monoxide, methane, ethane and butadiene, with lower concentrations of propane, propene, butane and other hydrocarbon gases [6].

**Oil Analysis** -- The yield of oil from tire pyrolysis is high (~50 wt % of initial tire rubber), reflecting the potential of tire rubber to act as a substitute for fossil fuel and chemical feedstocks. The oils have high aromaticity, low sulfur content, and are considered relatively good fuels [11]. The molecular weight range for the oils is up to 1600, with an average molecular weight between 300 and 400 [6]. Infrared analysis of the oils indicates the presence of alkanes, alkenes, ketones or aldehydes, aromatic, polyaromatic and substituted aromatic groups [6]. The derived oils may also be an important source of refined chemicals, because it has been reported that they contain high concentrations of valuable chemical feedstocks, such as benzene, toluene and xylene [6].

**Carbon Residue Analysis** -- The carbon residue could become a marketable product if its properties were similar to those of manufactured carbons. The simultaneous production of valuable solid products and gaseous and/or liquid fuels from what is currently a waste material would make tire pyrolysis economical if a large supply is readily available. This situation exists in many regions of the U.S.

As mentioned before, tire pyrolysis performed in an inert environment can produce 33-38 wt. % of carbon residue. It has been reported that the char yield increases with decreasing pyrolysis temperature and decreasing heating rate [6]. The surface area of the tire char also depends on pyrolysis temperature and heating rate. The surface area of a tire char produced by pyrolysis in an inert gas usually ranges from 30 to 90 m<sup>2</sup>/g [6-8].

Basically, there are two uses of tire chars: as a reinforcing filler and as an adsorbent. Commercial carbon black is usually used for filling polymers and vulcanizates. Use of tire char as an end product for the tire and printing ink industries has been reported to be unsatisfactory [6, 8]. This is due to the high ash content of tire char. Chars from tire pyrolysis contain as much as 15 wt. % of ash, with the majority of this ash being zinc oxide [8]. A means of removing the ash from tire char is an important issue in the process of producing useful carbon black from the solid residue from waste tires. An alternative approach, which is advocated in the current study, is to use the solid residue to produce activated carbon for which the ash content is less critical. High-quality carbon black can be made from the liquid products, which are absolutely ash-free, and finely divided carbon can additionally be obtained from the CO produced during char activation.

Carbon as an adsorbent is usually evaluated by its surface area, and this is why an activation process is necessary to produce salable activated carbons from tire char. To develop a high internal surface area, char can be activated by mild oxidation with steam or carbon dioxide at high temperatures. The slow kinetics of carbon gasification in steam and CO<sub>2</sub> allow gas molecules to diffuse into the micropores and enlarge the existing surface area. The activation process usually follows hydrocarbon pyrolysis performed in an inert environment, but it is possible to accomplish pyrolysis and activation in one stage by pyrolyzing under mildly oxidizing conditions [7].

Ogasawara et al. [7] carried out the pyrolysis and activation of tires in one stage. The carbon residue from 1 hour of steam activation at 1173 K was found to have a surface area of 1260 m<sup>2</sup>/g,

while pyrolysis in helium yielded char with a surface area of 87 m<sup>2</sup>/g. The carbon residue produced from this "wet method" is as good as the commercial activated carbon in terms of surface area, but the carbon yield was only 9 wt. % of the starting tire material. Therefore, a method to increase char yield from tire pyrolysis is one of the most important issues in making activated carbon from waste tires. In a recent study [12], a high surface area activated carbon (> 800 m<sup>2</sup>/g) was produced in relatively high yields from pyrolysis of tires at temperatures up to 1173 K, followed by CO<sub>2</sub> activation at the same temperature. The surface area of this carbon is comparable with that of commercially available activated carbons.

The objective of the present study is to propose and carry out preliminary assessment of a process leading to the conversion of waste tires into marketable products such as activated carbon or carbon black. Some quantities of gaseous and liquid fuels can also be produced. Process flexibility, in terms of the type and amounts of particular products, is a desirable feature in view of high variability of markets. This work is based on the results of a recent laboratory study of scrap-tire reprocessing [12].

## PROCESS DESCRIPTION AND DISCUSSION

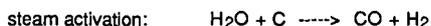
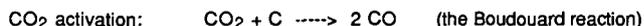
A schematic of the proposed process is shown in Figure 1. A stream of scrap tires enters the pyrolyzer where it is contacted with a recycle stream of pyrolysis gas. Mixing used tires with other waste material and solid-waste pretreatment are optional features of the process and they are discussed below. The pyrolyzer operates at approximately 1173 K, and the product streams are fuel gas, which also contains pyrolysis liquids, and char. The pyrolysis liquids are separated from the gas in a condenser, and they are subjected to partial combustion in an oil furnace to produce carbon black. 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 needs an activation step. Char activation is carried out using CO<sub>2</sub> at approximately 1173 K, which results in CO<sub>2</sub> reduction to form carbon monoxide. The consumed CO<sub>2</sub> is regenerated in a Boudouard reactor with simultaneous formation of finely dispersed carbon (Boudouard carbon). The net result of the process is the conversion of used tires into three marketable products: activated carbon, carbon black, and Boudouard carbon. The particular elements of the process scheme are described in more detail below. Pyrolysis and char-activation units constitute the heart of the process and their integration is very much a novelty in the proposed scheme. Carbon-black and Boudouard-carbon production will be integrated into the process by adapting existing technologies.

**Feed-Stream Preparation** -- The tires are first shredded and then 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 amount of size reduction required for scrap tires does not appear to be excessive. In fact, higher char activation efficiencies were reported when coarser waste material was used (~170 mg pieces versus -50 mesh particles) [12]. The size of scrap tire material that would be optimal for the process is still to be determined. Since shredding costs are high (at least \$0.20/kg), there is an economic incentive to make the tire pieces as large as possible. For smaller particle sizes, pretreatment with O<sub>2</sub> was found to increase char yields and surface areas [12]. Pretreatment with chlorine would probably have a similar effect but would also likely have negative consequences from the associated HCl formation.

**Pyrolysis and Char-Activation Units** -- While a rotary kiln reactor has been successfully used for pyrolysis of tires, this is not likely to be the optimal solution for a high throughput system [8]. A kinetic analysis of tire pyrolysis indicates that the process is relatively fast and can be completed in under a second at 873 K. This fact would allow the use of an entrained-flow reactor, which is quite appropriate for high-throughput applications. Unfortunately, only relatively small particles can be fed into such a reactor, mainly due to heat-transfer limitations. For larger pieces of tire material, a fluidized-bed reactor operating at a lower temperature can be used. In either case, a hot cyclone is desirable to separate char particles from the oils. According to scheme presented in Figure 1, char activation by CO<sub>2</sub> takes place in a separate reactor. This has the advantage of allowing the oxides of carbon to be cycled between the activation step (producing CO) and a disproportionation step (producing CO<sub>2</sub> and carbon). In this way, CO<sub>2</sub> is periodically consumed (activation) and regenerated (disproportionation); both CO and CO<sub>2</sub> stay relatively pure in this scheme.

Another possibility is to use a moving-bed countercurrent system. While 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 CO<sub>2</sub> at the bottom (Figure 2). A temperature of about 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. Such a design, shown schematically in Figure 3, simplifies the process of feeding the tire pieces and eliminates the requirement for a hot cyclone since the oil and char come out of opposite ends of the reactor. The moving-bed concept has been employed in the large-scale gasification of coal at a plant in North Dakota which is producing synthetic pipeline gas [13]. There are some differences between the two schemes, however. The tire-processing unit would operate under atmospheric pressure since there is little or no advantage in producing activated carbon at an elevated pressure. Secondly, the coal gasification system is internally heated by introducing oxygen at the bottom and partially combusting a portion of the coal. In the tire-processing reactor, the pyrolysis gases which come off the top of the unit would be combusted externally and the hot exhaust gases (mostly CO<sub>2</sub> and H<sub>2</sub>O) would be introduced into the bottom of the reactor for char activation. The reactor would be insulated to prevent heat losses. The disadvantages of a single-reactor scheme of Figure 3 are: (1) the pyrolysis gas has a lower heating value due to dilution with the flue gas; and (2) 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 demonstrated that the final product is not very sensitive to the conditions under which pyrolysis is carried out [12]. This allows for greater design flexibility and for the possibility to consider several feasible schemes.

It was demonstrated that activation using an 8% CO<sub>2</sub>/He mixture at 1173 K for 3-10 hours was sufficient to obtain high surface area chars [12]. This residence time could be reduced by raising the temperature, increasing the CO<sub>2</sub> partial pressure, or by using steam rather than CO<sub>2</sub>. The char activation chemistry can be represented by the following two reactions:



Both reactions are endothermic and the equilibrium becomes more favorable as the temperature increases. The use of steam would offer advantages in terms of a higher reaction rate and a higher surface area product. The use of CO<sub>2</sub> would increase the production of CO from the activation step. The CO could then be subjected to the reverse Boudouard reaction for the production of finely divided carbon [14-17].

**Carbon-Black Production** -- The oils resulting from tire pyrolysis can be used to produce carbon black since their properties are known to be similar to those of the petroleum fraction used in carbon-black production [11]. 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 carbon-black properties which are important in reinforcement-material applications (e.g., in tires) are the 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 [18]. An example of a carbon-black furnace is shown in Figure 5. As an alternative to carbon-black production, tire pyrolysis oil can be used for its fuel value, although further processing to remove aromatic components would be required. The conversion of the oil stream to carbon black is a more attractive option for a number of reasons: (1) a solid product is easier to store and handle; (2) the value of the solid product is higher than any possible fuel uses; (3) little or no upgrading of the material is required; (4) possible transportation fuel uses would require upgrading because of the relatively high aromatic content of oil; and (5) since carbon black is required to make tires, the production of carbon black from the oil is a form of tire recycling and is more practical than trying to recover the original carbon black.

**Boudouard-Carbon Production from CO** -- This process step was recently discussed by Walker [14] as a 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 of a particle size much smaller than can be obtained by grinding [19]. In fact, the particle size of the Boudouard carbon is small enough to burn completely in a Diesel engine [20]. The Boudouard carbon is similar to carbon black (except for

having a zero hydrogen content) and in some cases can probably be substituted for carbon black. The envisaged applications of this product include its use as a colorant or lubricant.

**The Energy Balance** -- 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; an additional amount of heat will be generated by the production of Boudouard carbon from CO. Preliminary estimates show that the process outlined in Figure 1 will be self-sufficient from an energy standpoint. 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.

**Process Economics** -- A preliminary cost analysis for the process indicates that the proposed tire-reprocessing scheme could be profitable. The following estimates have been used: the cost of scrap tires -- about \$0.20/kg (tire-disposal charge: \$0.01-0.35/kg; transportation: ~ \$0.04/kg; size reduction: \$0.20-0.60/kg); the typical pyrolysis yields -- 35% char, 20% gas, and 45% oils; 50% carbon loss during char activation; selling prices for the activated and Boudouard carbons of \$2.22/kg and \$0.67/kg, respectively; zero profit from the high-BTU gas and oils which would be used mainly to provide the process heat requirements. These figures lead to a net income of ~ \$0.30 per kilogram of the original tire material. Of course, more detailed economic analysis needs to be performed, but even the above simplified and fairly conservative treatment demonstrates the high commercial potential of the proposed approach. It should be pointed out that, in most cases, the raw material costs for the project will be negative due to increasingly high tire-disposal charges.

For the sake of comparison, the cost of scrap-tire incineration without heat recovery is about \$0.04-0.07/kg [21]. The cost of burning used tires for energy generation 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 (DSR) can also be used as liquid fuel but, in general, depolymerization is difficult and involves extensive high-pressure treatment. Clearly, reprocessing of waste tires into fuels does not seem to be an economically attractive option.

Pyrolysis processes can be made somewhat more profitable. Nippon Zeon estimated that the break-even cost of its tire-pyrolysis pilot plant was \$0.25 per tire [22]. According to a different estimate [23], a plant processing 81,000 tons of scrap tires per year could be made profitable, based on sales of reclaimed products. As mentioned before, pyrolysis processes involving direct carbon-black recovery suffer from difficulties related to ash removal and, generally, low final-product quality. Asphalt rubber is probably the most competitive tire-derived product currently available on the market. Although nearly twice as expensive as regular asphalt pavement, asphalt rubber has already 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 [24]. Unfortunately, the estimated total demand for this product is still at about 2% of the amount of scrap tires available [21]. It can be concluded, therefore, that a large market exists for other technologies targeted at scrap-tire reprocessing into useful products.

## CONCLUSIONS

A preliminary process design was developed in which scrap tires are used as the input and in which activated carbon, carbon black (or fuel oil), Boudouard carbon and fuel gas are produced as the output. The proposed technology has the potential to convert an unmitigated waste stream of tires into marketable products (activated carbon, Boudouard carbon and carbon black). Tire-derived activated carbons could be used, for example, in waste-water treatment, stabilization of landfills and in the recovery of organic solvents and vapors. The Boudouard carbon may have a variety of uses which are yet to be explored; they include the manufacture of colorants and lubricants. The liquid stream can be utilized in the production of carbon black and/or fuel oil. The oil-derived carbon black can be reused in tire manufacturing, which forms a recycle loop for this material. Since the typical feedstocks for activated carbon and carbon black are either coal or petroleum, the proposed technology would obviate 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 both activated carbon and carbon black from used tires, with inorganic material ending up in the product with a high tolerance for this

component. Finally, following additional research, the proposed technology should be able to find applications in reprocessing other polymer wastes found in American industry (e.g., end cuttings from automobile hoses or products which do not pass quality control).

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. New York Times, May 9, 1990, p. D1.
2. Schulman, B.L. and White, P.A., "Pyrolysis of scrap tires using the Tosco II process -- a progress report," Solid Wastes and Residues: Conversion by Advanced Thermal Processes (J.L. Jones and S.B. Radding, Eds.), ACS Symposium Series #76, 274 (1978).
3. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Serio, M.A., and Deshpande, G.V., Energy and Fuel 2, 405 (1988).
4. Serio, M.A., Hamblen, D.G., Markham, J.R., and Solomon, P.R., Energy and Fuels 1(2), 138 (1987).
5. Suuberg, E.M., Peters, W.A., and Howard, J.B., 17th Symp. (Int) on Combustion, The Combustion Institute, Pittsburgh, PA, 117 (1979).
6. Williams, P.T., Besler, S., and Taylor, D.T., Fuel 69, 1474 (1990).
7. Ogasawara, S., Kuroda, M., and Wakao, N., Ind. Eng. Chem. Res. 26, 2552 (1987).
8. Petrich, M.A., "Conversion of Plastic Waste to Valuable Solid Carbons", Final Report of a Project in the Innovative Concepts Program, U.S. DOE, Jan., 1991.
9. Torikai, N., Meguro, T., and Nakamura, Y., Nippon Kagaku Kaishi 11, 1604 (1979).
10. Funazukuri, T., Takanashi, T., and Wakao, N., J. Chem. Eng. Japan, 20, 23 (1987).
11. Merchant, A. and Torkelson, J.M., "Pyrolysis of Scrap Tires", Chemical Engineering Dept., Northwestern U., Spring, 1990.
12. Teng, H., Serio, M.A., Bassilakis, R., Morrison, P.W., Jr. and Solomon, P.R., "Reprocessing of used tires into activated carbon and other products," ACS Div. of Fuel Chem. Prepr. 37(2), 533-547 (1992).
13. Penner, S.S., Coal Gasification: Direct Application and Synthesis of Chemicals and Fuels, DOE/ER-0326 (1987).
14. Walker, David G., ACS Div. of Fuel Chem. Prepr. 36(3), 1129 (1991).
15. Watanabe, O., Tokunosuke, N., Bull. Inst. Phys. Chem. Research (Tokyo) 8, 288-292 (1929).
16. Donald, J.H., "An 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).
17. Hadley-Coats, Lyndon and D.G. Walker, "Boudouard Carbon: An Alternate to Gasoline and Diesel Oil," International Journal of Energy Research, 12, 2443-2451 (1988).
18. Austin, G.T., Shreve's Chemical Process Industries, 5th Edition, McGraw-Hill, New York (1984).
19. Soehngen, E.E., "The Development of the Coal Burning Diesel in Germany," Report FE/WEPO 3387-1, Purchase Order No. 3387, U.S. Energy Research and Development Administration (1976).
20. Essenhigh, H., "Coal Combustion," Coal Conversion Technology (C.Y. Yen and S. Lee, Eds.), Addison - Wesley Pub. Co., Reading, MA, 171-312 (1979).
21. Paul, J., "Rubber Reclaiming," Encyclopedia of Polymer Science and Engineering (H.F. Mark, N.M. Bikales, C.G. Overberger and G. Menges, Eds.), John Wiley & Sons, New York, vol. 14, 787-804 (1988).
22. Saeki, Y. and Suzuki, G., Rubber Age 108, 33 (Feb. 1976).
23. Bracker, G.P., Conserv. Recycl. 4(3), 161 (1981).
24. Clark, C., Meardon, K. and Russell, D., Scrap Tire Technology and Markets, Noyes Publications (1993).

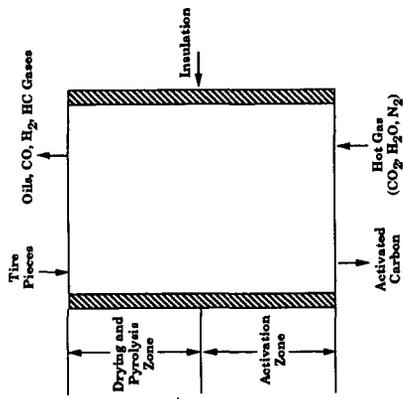


Figure 2. Schematic of the Countercurrent Moving-Bed Reactor Concept which Combines Tire Pyrolysis and Activation into a Single Unit.

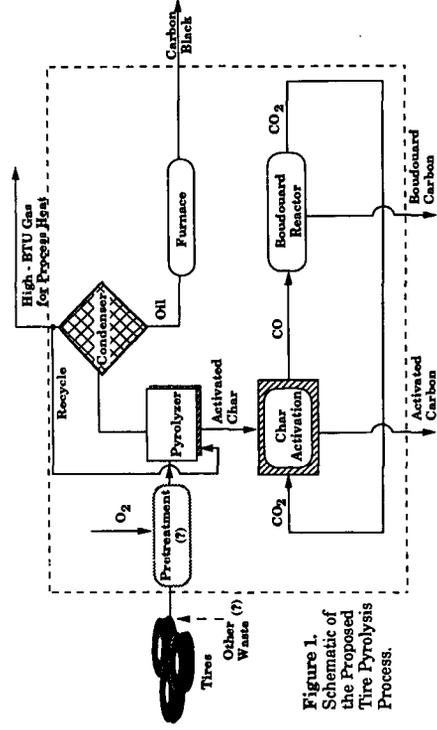


Figure 1. Schematic of the Proposed Tire Pyrolysis Process.

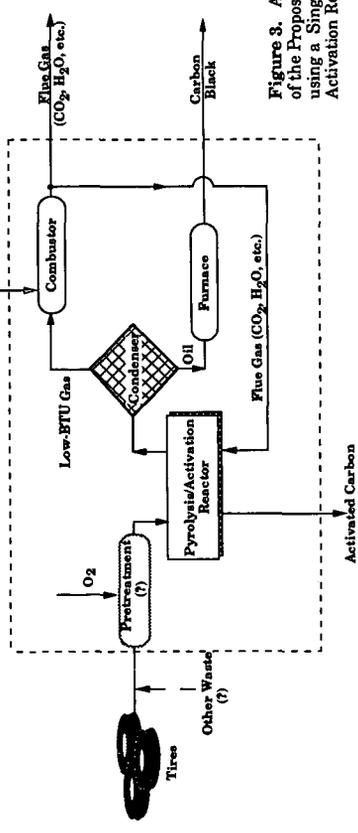


Figure 3. A Schematic Representation of the Proposed Tire-Pyrolysis Process using a Single Pyrolysis/Char-Activation Reactor.

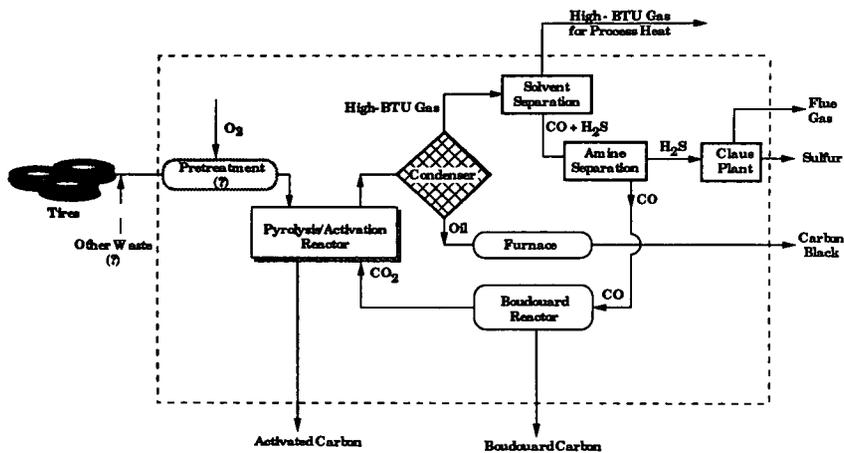


Figure 4. A Schematic Representation of the Proposed Tire-Pyrolysis Process using a Single Pyrolysis/Char-Activation Reactor and CO Separation from the Pyrolysis Gas.

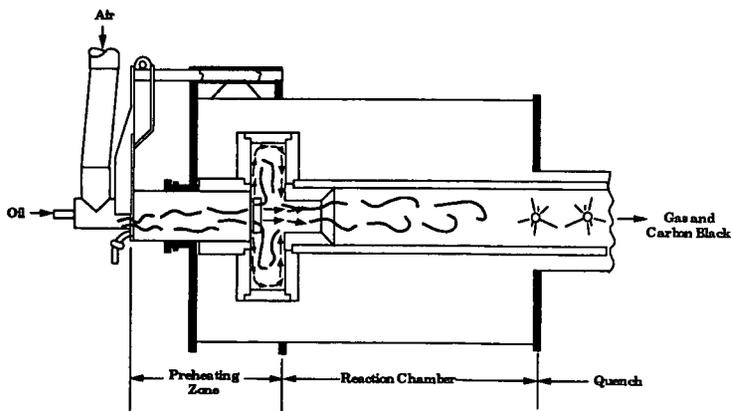


Figure 5. Flow Chart, Carbon Black Furnace Process. [Chem. Week 88 (24) 79 (1962)].