RECYCLING, RUBBER

1. Introduction

In 1839, Charles Goodyear developed a technique for vulcanizing rubber. He blended natural rubber with sulfur and placed it on his wood stove, then noticed that the heat from the stove had cured the rubber into a water-impermeable sheet on one of his failed mailbags (1). In 1844, Goodyear applied for and received a patent for his invention. Because of the shortage of natural rubber at that time, a rubber-reclaiming process, based on steam pressure to devulcanize used rubber, was developed in 1858 (1). The cured ground rubber was subjected to steam pressure for 48 hours. High cost silicone rubber polymers were reclaimed in much the same way in the 1990s, although most synthetic polymers require more complicated techniques.

Rubber recycling has been extended to the use of rubber in asphalt (qv), scrap rubber as fuel, rubber pyrolysis, tire splitting, and other uses. However, the discovery of plastics and oil-extended rubbers, and a drop in crude oil prices, led to a reduction in rubber recycling during the 1970s and 1980s, except for expensive polymers, such as silicones and fluorocarbons (see SILICON COMPOUNDS, SILICONES; ELASTOMERS, SYNTHETIC–FLUOROCARBON ELASTOMERS). Pyrolysis of scrap rubber was expensive and markets were limited. It was more expensive to prepare and burn scrap rubber for fuel than to burn natural gas, fuel oil, or coal (qv). High fuel costs and petroleum scarcity in Europe and other parts of the Eastern Hemisphere have resulted in the use of recycled rubber as fuel and have made it more economical than in the 1970s and 1980s in the United States. With the technological advances of the 1990s, recycled rubber is used more and more in the United States, especially considering the regulations for handling and disposing of worn tires. With fees collected by recyclers, tire recycling is becoming more profitable. At the end of 2003, markets existed for 80.4% of these scrap tires.

Tires discarded in landfills tend to float on top of the ground; mosquito infestation and illegal tire disposal cause problems which are alleviated by recycling. Approximately 25% of scrap rubber, primarily as tires, is discarded in landfills (2,3). Private landfills may charge up to $5 per tire, and disposal costs at municipal landfills are ca $0.50–2.00 per tire (2,3), encouraging illegal disposal. As the tire piles grow, rubber recovery becomes more economical (4,5).

In the United States, 48 states have some legislation or regulations dealing with scrap tires (does not include Delamore and Alaska). These laws and regulations often have many common features which include regulation of the manner of tire disposal in landfills or stockpiles; regulations (including permitting requirements) for scrap tire haulers, processors, and end users; financial responsibility requirements for sites where scrap tires are collected, stored, or processed; provisions for market development, including financial assistance to end use markets or new entrants into the scrap tire business; provisions for financial support for implementation of the state's scrap tire management program; and provisions for clean-up of scrap tire piles.

The tire industry has consistently supported sound scrap tire legislation at both the state and federal level to ensure that scrap tires are managed in environmentally responsible ways. The tire industry has been a consistent participant in the effort to find appropriate markets for scrap tires, and to promote the expansion of those markets.

Some states have restricted the disposal of tires in landfills. Most states have enacted legislation for a surcharge on the sale of new tires to assist in proper management of scrap tires. Some communities refuse old tires; others require tire splitting or shredding to prevent floating problems in landfills. Fires resulting from the storage of tires have led to regulations governing stockpiles. Mosquito infestation caused by illegal disposal of tires has prompted Saginaw, Michigan to purchase a shredder for landfill disposal.

State landfill regulations include the following:
38 states ban whole tires from landfills.
35 states allow shredded tires to be placed in landfills.
11 states ban all tires from landfills.
17 states allow processed tires to be placed into monofills.
8 states have no restrictions on placing scrap tires in landfills.

The rate that used tires are generated is estimated at an annual replacement of 290 million tires. That translates into well over 350 million passenger tire equivalents (PTE) that require handling each year (one PTE represents a 20-lb (9.1 kg) passenger tire). Sources of used tires include dealers and stores, auto dismantlers, and factory rejects. Recovery alternatives include immediate recycle/recovery or stockpiles/landfills. Almost 95% of the scrap tires are returned by the consumer to dealers when worn-out tires are replaced by new tires. In 1990, a group called the Scrap Tire Management Council (STMC) was formed as a division of the Rubber Manufacturers Association (RMA). The STMC coordinates with tire companies to address the scrap tire challenge, works on expanding the environmentally and economically sound markets for scrap tires, and is helping to expand market development, information collection and dissemination, research, industry relations, government relations, and encouragement of new technology. The goal of the STMC is the expansion of markets to be able to utilize all scrap tires generated annually (7).

Advances in the technologies of shredding tires, reclaiming rubber, retread equipment, and energy-related projects are helping to resolve the disposal problem. In 1994 it was estimated that there were more than 700×10^6 whole tires stockpiled throughout the nation (3). Since that time, millions of tires have been removed from stockpiles as a result of clean-up programs. In 2003, the estimate was 275×10^6 tires stockpiled (6).

2. Scrap Rubber as Fuel Source

The use of scrap rubber for fuel offers the best alternative for reusing rubber, as fuel costs increase and tire disposal problems become more serious. There are four main markets for scrap rubber fuel, including fuel for cement kilns, electric utilities, pulp and paper mills, and dedicated tire-to-energy plants. Scrap tires used as supplemental fuel by these industries reduce solid waste and air pollution (2). Shredding is not expensive, therefore tires reduced to 2.50-cm chips are most economical. Tires contain more than 90% organic materials and have a heat value of ca 32.6 MJ/kg (ca 14,000 Btu/lb), compared with coal values of 18.6–27.9 MJ/kg (ca 8,000–12,000 Btu/lb). A cyclonic, rotary hearth boiler fired with whole tires was operated by the Goodyear Tire and Rubber Company from 1975 to 1977. It was designed to burn 1400 kg/h and generated 11,300 kg/h of steam (4,8).

In 1991, Goodyear began working with Cadence Environmental Energy (Indiana) to market a whole tire feed system to supplement fuel for cement kilns. The system is used by several cement manufacturers. In 1992, Goodyear furnished tires for a Tennessee Valley Authority (TVA) test burn at a Memphis power plant. The electric utility used tire-derived fuel (TDF) to supplement coal fuel in a cyclone boiler. These tests were successful.

Tire-derived fuel, either as whole tires or processed into chips, is the largest single current and potential market for scrap tires. Tires have a higher energy value than most coals and are cleaner burning. The materials used to construct a tire have positive energy value. With lower emissions than coal, use of TDF has an added bonus of helping reduce air pollution (qv). The final advantage for most fuel users is that TDF can be obtained at a much lower cost per Btu than conventional fuels. From an environmental standpoint, the use of TDF also helps solve a significant solid waste management problem. In 2003, 130 million tires were reused as tire-derived fuel.

2.1. Cement Kilns. The use of scrap tires as a supplemental fuel in cement kilns has had a fairly long history in Germany and Japan, where tires have been used for fuel since the early 1970s. Initially, the scrap tires were purchased by kilns for their fuel value. As the relative cost of other fuels has declined in Japan, so has the value of scrap tires, and Japanese kilns are collecting a tipping fee for using tires.

In the late 1970s and early 1980s, efforts were made to interest U.S. cement kilns in using scrap tires, either whole or processed, as a supplemental fuel. At least one conference was held on the subject, involving the cement industry, scrap tire processors, and the new tire industry. Although a report was issued by the U.S. Department of Energy (DOE), there was no substantial rush to use tires for fuel. However, some work was done privately with U.S. kilns, and at least a few began testing. By 1990, however, only a few kilns were using tires or planning to do so.

The picture has changed quickly since 1990. Currently 53×10^6 tires/year are consumed as fuel in U.S. kilns (2). Several factors caused this change: success of early pioneers caused other kilns to look at tires as a way to reduce energy costs and become more competitive; opposition to the use of other, more environmentally alarming supplemental fuels such as hazardous waste; success of foreign parent companies of many U.S. kilns in using TDF; and growing interest of state scrap tire regulators in finding sound markets coupled with a maturing understanding among regulators of the excellent environmental fit between tires and cement kilns. The Scrap Tire Management Council has been helpful through efforts to expand this market, and by facilitating access to patented Bridgestone technology (9).

Required air testing is a hurdle any cement kiln encounters as it seeks a permit to use tires as fuel. There is no standard protocol for testing cement kilns using TDF as a supplemental fuel. Each state establishes the testing to be required. The STMC had a research project underway which may remedy this situation. The results of all air emissions testing previously conducted during permitting of cement kilns is being collected and an analysis is being done to understand the emissions which might be affected using tires, and those which have been completely unaffected. The aim is to construct a testing protocol which would deal with only those emissions that might be affected by the use of tires.

2.2. Pulp and Paper Mills. The pulp and paper mill market has been one of the principal markets for TDF. Today about 26×10^6 tires/year are used in the U.S. Often such facilities are in locations where other markets for scrap tires are limited. If the volume of use is such that just one mill in a state, such as Arkansas or Maine, can use more TDF than the entire state can produce annually, the pulp and paper mill focuses on a regional, multistate TDF market. Pulp and paper mills using TDF cover the geographical range of the industry, from Idaho and Oregon, to Wisconsin, Maine, Virginia, Georgia, and Arkansas. A key issue for mills is the need for a substantially dewired, consistently sized tire chip.

2.3. Electricity Generators. The use of TDF as a supplemental fuel in electrical generation is one of the largest current and potential markets for scrap tires. Originally, many observers believed this market would follow the path established by the development of the original Oxford Energy plant (Modesto, California) which is fueled exclusively with scrap tires. Although the original facility, which consumes nearly five million tires per year, was followed by a second facility in Sterling, Connecticut, which consumes nearly 11 million tires per year, efforts by Oxford to build additional facilities in New York and Michigan ran into substantial local opposition. In the meantime, the mainstream electric utility industry began considering the use of TDF to supplement coal in a number of different types of boilers. The tire industry conducted development and testing at in-plant facilities to gauge the feasibility of using tires for energy recovery, and shared the results with electric utilities having similar boilers. The expansion of this market will be through use of tires as a supplemental fuel in existing coal-fired generation stations.

About 24×10^6 tires per year are consumed as fuel in boilers at electric utilities. In the electric utility industry, boilers typically burn coal to generate electricity. TDF is often used as a supplement fuel in electric utility boilers because of its higher heating value, lower NO_x emissions, and competitive cost as compared to coal. However, only certain types of boilers are conducive to burning TDF.

Cyclone boilers are the most used of all the utility boilers for burning TDF. They are good because they require no changes to be made to the boiler itself which reduces the capital investment. Therefore, the only additional equipment needed is a conveyer to transport the tire pieces into the boiler. Cyclone boilers cannot accept whole tires, which increases the cost of obtaining the fuel (the optimum size of the tire pieces is 1 inch × 1 inch and it must be de-wired). Stoker fired units are also economical. In the stoker boilers, the residence time of the fuel is longer so larger tire pieces can be used. The optimum size of these pieces is 2 inches square. This reduces the cost of obtaining the fuel for cyclone boilers and makes it more economical (2).

2.4. Industrial Uses. Large industrial facilities, particularly those using cyclone boilers or fluidized-bed boilers, are potential markets. In addition, several vendors of small- and medium-sized industrial energy and steam facilities are marketing units capable of using TDF. As the availability of TDF expands with new producers entering the market, it is hoped that the industrial use of TDF will also expand (7).

Approximately 17×10^6 tires per year are consumed in industrial boilers.

According to a Rubber Manufacturers Association survey in 2004, 19 industrial facilities were using TDF in their boilers to supplement their fuel usage. Industrial boilers are smaller than utility boilers and typically use a variety of fuels. When utilizing TDF, tires are typically shredded. Not all boilers are compatible with TDF. Clumping and clogging are common and preclude the use of TDF in many facilities.

Another impediment is the metal in the tires. If not removed before combustion, it ends up in the ash and can create disposal problems. Each facility must evaluate the impact of TDF on their air emissions and ash disposal. Industrial facilities must apply for the appropriate permits from their state and/or local regulatory authorities before commencing operation (2).

2.5. Dedicated Tire-To-Energy Facilities. Approximately 10×10^6 tires per year are consumed as fuel at dedicated tire-to-energy facilities. A dedicated tire-to-energy facility is specifically designed to burn TDF as its only fuel to create energy.

According to a Rubber Manufacturers Association survey at the end of 2003, there was only 1 dedicated tire-to-energy facility operating in the U.S. The dedicated tire-to-energy facility, Exeter Energy Limited in Sterling, Connecticut burns mainly whole tires and consumes 10×10^6 tires per year. This facility serves as a major scrap tire market for scrap tires in New York and northern New Jersey. The second dedicated tire-to-energy facility in U.S. is located in Ford Heights, Illinois and was not in operation at the end of 2003.

Even though dedicated tire-to-energy facilities have been demonstrated to achieve emission rates much lower than most solid fuel combustors, there are no known facilities under construction or consideration. The length of time and cost of construction, as well as the deregulation of the utility industry hinders further expansion of this industry (2).

3. Pyrolysis

Scrap tire pyrolysis has been the subject of several studies by rubber, oil, and carbon black industries. The Tosco II process pyrolysis study sought to develop equipment to maximize pyrolytic filler production and quality (Fig. 1) (10–12). Chopped tires are fed into a rotary drum containing hot ceramic balls at 480°C in a reducing atmosphere. The rubber pyrolyzes and forms a solid residue, oil vapor, and off-gases; the condensed oil separates in a fractionator and the gas is used to heat the ceramic balls. A trommel screen separates the fine solid residue from the ceramic balls, and this residue is pelletized after steel, fiber glass, and other contaminants have been removed. The off-gas is a combination of ethylene, propylene, and butylene; the oil contains about 1% sulfur and can be substituted directly for fuel oil. Higher temperatures produce more gas and less liquid. The pilot-plant process was designed to handle 13.5 t/d of tires, generating 0.5–0.6 m^3 (3–4 bbl) of oil, 1270–1540 kg of pyrolytic filler, 190–220 kg of steel, and 154–176 kg of fiber glass. The Tosco II project was completed, but additional projects were discouraged, because the U.S. carbon black industry already had excess capacity. Furthermore, the types of pyrolysis products, eg, ZnO and other inorganic materials and glass fiber from old tires, are unpredictable. However, pyrolytic fillers must be carefully chosen to achieve specific properties in compounded rubbers, thus the residue mixture from nonvacuum pyrolysis is useful only as a low grade filler and cannot be used as a substitute carbon black source.

Other techniques include oxidative, steam atmosphere (13), and molten salt (14) pyrolyses. In a partial-air atmosphere, rubber pyrolysis is an exothermic reaction. The reaction rate and ratio of pyrolytic filler to oil products are controlled by the oxygen flow rate. Pyrolysis in a steam atmosphere gives a cleaner char with a greater surface area than char pyrolyzed in an inert atmosphere; however, the physical properties of the cured compounded rubber are inferior. Because of the greater surface area, this pyrolytic filler could be used as activated carbon, but production costs are prohibitive. Molten salt baths produce pyrolyzed char and oil products from tire chips. The product characteristics and quantities depend on the salt used. Recovery of char from the molten salt is difficult.

4. Depolymerized Scrap Rubber

In the depolymerized scrap rubber (DSR) experimental process, ground scrap rubber tires produce a carbon black dispersion in oil (15). Initially, aromatic oils are blended with the tire crumb, and the mixture is heated at 250–275°C in an autoclave for 12–24 h. The oil acts as a heat-transfer medium and swelling agent, and the heat and oil cause the rubber to depolymerize. As more DSR is produced and rubber is added, less aromatic oil is needed, and eventually virtually 100% of the oil is replaced by DSR. The DSR reduces thermal oxidation of polymers and increases the tack of uncured rubber (16,17). Depolymerized scrap rubber has a heat value of 40 MJ/kg (17,200 Btu/lb) and is blended with No. 2 fuel oil as fuel extender (18).

5. Rubber, Asphalt Modification

Ground recycled rubber has been developed as a modifier for asphalt paving materials since the 1950s in both the United States and Europe. The original developmental work was undertaken in an effort to improve the performance of asphalt paving materials, not to find a method to dispose of scrap tires, thus many different additives and modifiers have been tested with some becoming accepted practices. The utilization of various polymers has been investigated (19). Two basic processes, wet and dry, have been developed, differing in the point at which the ground rubber is introduced.

In the wet process, also called the McDonald or Arizona process after its developer and the location in which it was developed, respectively, ground rubber is prereacted with the hot liquid asphalt cement for a specified time, depending on the size of the rubber particles. During this process, the rubber particles react with and change the asphalt cement. The rubber-modified asphalt can then be used in one of several ways: as a crack sealant in pavement repair or with an aggregate chip as a cape sealant to effect temporary repair; or, in the rehabilitation of cracked pavements to prevent or reduce subsequent reflexive cracking, it can be sprayed over cracked pavements as a stress-absorbing membrane or with a thin layer of asphalt concrete as a stress-absorbing membrane interliner (SAMI) and then covered with a new friction course. Rubber-modified asphalt cement can also be mixed with the normal aggregate components to produce a rubber-modified asphalt concrete. This material can be placed in the usual manner, with some limited modifications, and used in both base and friction courses.

The dry process was originally developed in Sweden and involves using slightly larger rubber particles mixed with the dry aggregate materials. The aggregates, which must be gap-graded to allow room for the rubber particles, are mixed with normal asphalt cement to form a modified asphalt concrete. This material can be placed in the usual manner, with limited modifications, to the handling procedure (20).

The largest market for ground rubber is as an additive to hot-mix asphalt concrete used as a paving material. While this use for scrap tires has been in various stages of research, development, and implementation on a small scale for a number of years, it came to the forefront of scrap tire uses with the passage of the Intermodal Surface Transportation Efficiency Act of 1991 (ISTEA). Section 1038 of the ISTEA requires all states to use scrap tire-derived ground or crumb rubber in asphalt paving in federally funded highway construction as of 1994, starting at 5% of paving and escalating to 20% by 1997. The issue has been controversial.

If the requirements of Section 1038 of the Act are fully implemented, it is estimated that 70 million tires would be required on an annual basis. If states found reason to exceed the law's minimum use of scrap tire-derived ground rubber in asphalt paving and use more on federal aid construction, or if local, county, and state governments and private parties started using rubber-modified asphalt in nonfederal aid construction, the totals could go much higher. In 2003, 220×10^6 lb (or 12×10^6 tires) were used in California and Arizona.

Asphalt–rubber is mixed and applied to roadways by several techniques. In one method, rubber and asphalt are mixed at ca 175–220°C for one to two hours. The hot mixture is applied to the roadway and covered with a layer of stone chips to form a chip seal. The rubber crumb consists of scrap tires ground into particles less than 2 mm in diameter. Rubber-modified asphalt is also used for waterproofing membranes, crack-and-joint sealers, hot-mix binders, and roofing materials. The rubber improves asphalt ductility and increases its softening point. The aggregate adhesive bond is stronger, and the asphalt lasts longer.

The use of asphalt–rubber in roadways was encouraged by the Federal Highway Administration in Arizona during the early 1970s (21). Uniroyal and other companies involved in rubber reclaiming during the late 1960s and early 1970s conducted research to develop asphalt–rubber formulations suitable for roads, joint sealer, and recreational surfaces (qv), including running tracks, tennis courts, and playgrounds.

The Arizona Department of Transportation is increasing application of a three-layer asphalt–rubber system based on test results of heavily traveled highways. Other states using/testing asphalt–rubber include New York, Massachusetts, New Jersey, Louisiana, Alabama, Florida, South Carolina, Texas, New Mexico, and Nebraska. The U.S. EPA has guidelines to encourage this development (2).

All Seasons Surfacing (Bellevue, Washington) was a licensee of Swedish technology for processing waste rubber into asphalt-paving materials called Plusride. Although no longer in business, All Seasons developed a process for paving material formed by removing portions of aggregate from asphalt and replacing it with rubber granules. In this process, 3% of 0.5-cm rubber tire chips and 20% powdered rubber dust are used. The *Rebounder*, a publication of the Rubber Pavements Association (Washington, D.C.), reported that 540 t of Plusride asphalt–rubber composition was utilized in New Jersey. The company was also exploring markets in Massachusetts and Louisiana. The material performed well in locations with severe temperature differentials; it was resistant to studded tires and chain wear and saved pavement because less sanding and salting were needed in icy conditions. Plusride was used to pave roadways destroyed by the eruption of Mt. St. Helens (Washington) in the late 1980s. In spite of the scale of operation, performance of Plusride compared well with normal usage and no maintenance has been required (21).

Ground rubber used as an asphalt modifier has been an accepted material in Arizona, California, Florida, and Texas. It requires less maintenance, produces less road noise, and shortens braking distance. Greater acceptance will require that state highway departments become familiar with rubber modification of asphalt paving materials and gain confidence in its capabilities. Efforts are underway to ensure greater technology transfer and information dissemination on asphalt–rubber issues. The National Cooperative Highway Research Program of the National Research Council established the CRM project 20-7 to provide an information network for anyone interested in crumb rubber modifiers. It is administered by the Technology Transfer Center at the College of Engineering, University of Nevada, Reno (22).

6. Cryogenic Pulverizing and Mechanical Tire Shredding

Tires must be pulverized or shredded before they can be reclaimed by devulcanization or used in asphalt and other recycling processes. The tires are mechanically ground, sometimes using cryogenic or solvent-swelling techniques to enhance grinding efficiency. In one process, a polar solvent is used to swell the rubber, followed by shearing to reduce particle size (25). Ground tire crumb rubber is commonly referred to as rubber reclaim, even though the rubber has not been devulcanized.

Cryogenics (qv) in conjunction with mechanical action has been used to make crumb rubber. Liquid nitrogen or other cryogenic fluids cool the rubber below the glass-transition temperature, and the brittle rubber is pulverized in a grinding mill. A small cryogenic system can be installed at the site to integrate the scrap rubber crumb into the compound mixing process. Cryogenic grinding of different rubber types, related costs, and rubber compound properties is available (22–26). Cryogenic grinding costs vary depending on the desired particle size and type of rubber; harder rubber is easier to grind. Ground rubber scrap can be devulcanized, pyrolyzed, or recycled directly into the rubber compound. Ground rubber is also added to plastics (27).

Air Products and Chemicals, Inc. (Allentown, Pennsylvania) developed a cryogenic process for grinding scrap tires in the mid-1960s. Midwest Elastomers installed a cryogenic system in 1980 to powder tire peels in its Wapakoneta, Ohio, plant. The equipment and materials for cryogenic processing can be expensive and have slowed expansion. Cryogenic grinding can require proximity to an air processing facility to make the use of liquid nitrogen economical.

In another grinding process, tires are mechanically ground with a two-roll, grooved rubber mill. The two-mill rolls turn at a ratio of ca 1:3, providing the shearing action necessary to rip the tire apart. The rubber chunks are screened and the larger material is recycled until the desired size is reached. Bead wire is removed by hand or with magnets. For most applications, eg, devulcanization or pyrolysis, crumb rubber particles smaller than 1.19 mm (16 mesh) are desired, and several milling steps are required. Tire fiber is removed in intermediate operations with hammer mills, reel beaters, and air tables that blow a steady stream of air across the rubber, separating the fiber. Tire grinding is highly energy-intensive and tire slitters may be used to cut the tire initially.

The morphology of ground rubber particles plays an important role in the ability to incorporate them into new compounds. Ambiently ground particles tend to have a more heterogeneous surface than cryogenically ground particles, the surfaces of which are more regular and cube-shaped. In practice, the adhesion of ground rubber in new compounds is a mechanical process. As a result, ambient ground materials appear to incorporate more easily into new compounds. In order to increase the reincorporation of cryogenically produced materials, work has been done to modify the surface of these particles to make them more reactive when incorporated into new compounds. Such a process has been developed and has received assistance from the U.S. Department of Energy to apply it to commercial applications (28). Given the higher cost associated with this surface modification process, a principal area of investigation is the use of this material in compounds using high value virgin elastomers (22).

In 1985, the Emanuel Tire Company in Baltimore processed more than 3×10^6 tires into chips, which are mostly sold to pulp and paper mills as a supplemental fuel; the remainder is sold to reclaiming facilities or landfilled. Only 20% of passenger tires are suitable for recapping. Nonrecappable tires are shredded into 5-cm chips. The Emanuel Tire operation is capable of reducing the 5-cm chips to smaller sizes. Shredded waste tire chips can be granulated into very fine wire and fabric-free rubber particles.

Other waste rubber products, such as production scrap from the manufacture of molded and extruded products, hose and belt manufacturers, or any other rubber products manufacturing operations, can also be reduced to ground rubber. A tire contains several types of rubber, and different rubber compounds. As a result, the chemical properties of ground rubber produced from whole tires can vary. In addition, different manufacturers use different compounds, and compounding recipes differ with the type of tire, adding to the variability possible with ground tire rubber. Production scrap or off-specification products from other nontire rubber manufacturing processes may contain only a single rubber compound. When this material is ground, it may present more uniform characteristics and be more easily utilized, including in the manufacture of the original product from which it came.

There are several uses for ground rubber: compounding rubber stocks for use in production of various molded rubber products, combining with higher cost elastomers to reduce material costs without affecting product performance, and mixing with other materials, both recycled and virgin, to manufacture products not traditionally made from rubber. Experimentally, ground rubber has been used as the basis of materials for remediation of oil spills.

Ground rubber is used in the manufacture of many products, including friction materials, floor mats and relief pads, new tire manufacture, and molded rubber products. In new tire manufacture, ground rubber is most commonly used as a processing aid. Small quantities of ground butyl rubber are used in compounding the tire inner liner to reduce air entrapment during curing. In addition, small quantities of ground rubber are used as filler materials in various tire components where its use does not compromise the performance required of the compound.

Floor mats, carpet backing, and relief mats have been traditional markets for ground rubber where the material adds resiliency at a lower cost compared to virgin compounds. Certain molded products have also been markets for ground rubber. An interesting use is the manufacture of lawn soaker hoses from ground rubber and polyurethane binder.

The key to expanding product markets for additional recycled ground rubber is customer acceptance. The auto industry is one of the largest customers of molded rubber products. Until recently, most auto industry specifications for molded rubber parts specifically prohibited the use of recycled rubber. Increasingly, the auto industry is seeking greater use of recycled materials, including recycled rubber, in the parts it purchases.

The auto industry has established a cooperative program in the field, the Vehicle Recycling Partnership (VRP). In addition, some auto manufacturers have announced specific projects that include recycled rubber.

Another need has been a technical forum in which rubber industry chemists and engineers can share information and insights into the problems raised by the expanded use of recycled ground rubber. This need is being filled by the Topical Discussion Group on Rubber Recycling, organized as part of the rubber division of the American Chemical Society. This group sponsored its first symposium in May 1995 as part of the rubber division's semiannual meeting. The Topical Discussion Group brings together producers of ground recycled rubber, with compounding and engineering personnel from rubber products manufacturers and representatives from customer industries to share information and identify needed activity.

There has been considerable interest in ground rubber as a raw material, with many experimenters and entrepreneurs attempting to develop totally new uses for the material, including using ground rubber and recycled plastics to produce a lumber substitute. Products produced in this manner have been fence posts and flooring for livestock trailers. Other investigators are experimenting with ground rubber as an additive to concrete to give greater resistance to earthquake damage.

7. Reclaiming

Originally only solid rubber scrap was reclaimed, but with the advent of pneumatic tires and fiber-reinforced rubber, methods for removing the fiber had to be developed. Although the reclaiming processes are of limited use, modified reclaiming processes may become more prevalent as recycling increases.

Acids and alkalies were used to decompose the fiber to cellulose. The alkali digester process, developed in 1899, is still used. Fiber glass reinforcement must be removed mechanically before the rubber can be reclaimed. A highly efficient method involves hammer mills and reel beaters to separate the fiber from the rubber; an air current subsequently drives off the fiber.

Until World War II only natural rubber was used in tires and reclaiming was simple. Reclaiming plasticizers penetrated the natural rubber evenly, bond cleavage was uniform, and reclaim products were soft and consistent. However, these plasticizers do not penetrate synthetic rubber particles as easily, and synthetic rubbers harden under heat and pressure. Furthermore, they are less susceptible to oxidation than natural rubber. Scrap tires contain a mixture of synthetic and natural rubbers which must be ground to a finer particle size for better oil absorption, and stronger chemical reclaiming agents must be used. Alkylphenol sulfides, aromatic amines, chlorinated mercaptans, and other strong plasticizing agents are absorbed evenly into the rubber particles, resulting in bond cleavage and a uniform smooth reclaim (Table 1).

The three rubber-reclaiming processes are digester, heater or pan, and reclaimator processes (29). Goodyear has devulcanized and reclaimed scrap rubber with the help of microwaves (30). Tires are most commonly reclaimed by digesting (Fig. 2). Two-roll mills or other grinding devices reduce whole tires to uniform particles, and fiber is mechanically separated from the rubber with hammer mills, blown into collectors, and baled. Metal chlorides may also be used to reduce tire fiber chemically during digesting. Oils and processing aids are blended with the crumb rubber in ribbon blenders or similar mixers and are transferred to a digester, a steam-pressurized tank equipped with horizontal mixing paddles. The blend is mixed continuously at steam pressures of 1.01–1.70 MPa (10–17 atm) for four to six hours. The pressurized digester batch is forced into a blowdown tank, washed, and dried. Compounding ingredients, eg, carbon black and clay, are added to modify and maintain certain properties required for specific applications. Metal and other contaminants are strained from the digested rubber by extruders. High friction refining mills provide the smoothness and physical properties needed in the final product. The reclaim is baled, extruded into pellets, or formed into slabs for shipment. A typical reclaim formulation is shown in Table 2.

Innertubes of butyl and natural rubber and other fiber-free scrap rubbers are reclaimed by the heater or pan process. Brass tube fittings and other metals are removed from the scrap which is mechanically ground, mixed with necessary processing aids (see Table 1), loaded into pans or devulcanizing boats, and autoclaved at steam pressures of 1.01–1.42 MPa (10–14 atm) for three to eight hours. The product is refined by milling, extruded, and milled again in much the same way as in the digester process. A typical reclaiming formulation is shown in Table 3.

In the Reclaimator, a high pressure extruder, fiber-free rubber is heated to 175–205°C with oils and other ingredients. High pressure and shear between the rubber mixture and the extruder barrel walls effectively devulcanize the mixture in one to three minutes. In the Lancaster-Banbury method, high temperature, pressure, and shear are applied to the rubber in a batch process that is otherwise similar to the Reclaimator process. In another high pressure process, scrap rubber is devulcanized at 5.5–6.9 MPa (54–68 atm) for ca five minutes. The product is milled, baled, or pelletized as in other processes.

Natural rubber (NR) scrap is reclaimed with solvent naphthas, terpenes, dipentenes, and resins that swell, tackify, and promote bond cleavage (see RUBBER, NATURAL). Tires, mainly synthetic styrene–butadiene rubber (qv) (SBR), are less susceptible to oxidation (see BUTADIENE). Aryl disulfides, phenyl disulfides, high molecular weight mercaptans, and other sulfur-containing chemicals are used to swell and lubricate the bonds and devulcanize the rubber by chemical oxidation and bond cleavage. The oils control the properties of the product, soften the rubber, and increase the elongation. These properties are also affected by reinforcing agents and fillers (qv), eg, carbon black, aluminum silicate, and calcium carbonate. Nonreinforcing fillers reduce the tack of devulcanized rubber and facilitate handling. They abrade vulcanized particles during the final milling, resulting in a smooth texture. Reinforcing fillers increase the tensile strength of the reclaimed material. Typical reclaiming formulations are shown in Table 4.

Tires, natural rubber tubes, and butyl tubes are the main sources of scrap and reclaim (see ELASTOMERS, SYNTHETIC–POLYISOPRENE). Specialty reclaim materials are made from scrap silicone, chloroprene (CR), nitrile–butadiene (NBR), and ethylene–propylene–diene–terpolymer (EPDM) rubber scraps (see ELASTOMERS, SYNTHETIC–POLYCHLOROPRENE; ELASTOMERS, SYNTHETIC–ETHYLENE–PROPYLENE–DIENE RUBBER). Tires, hoses, belts, molded and extruded goods, and asphalt products consume ca 80% of the reclaimed rubber manufactured. Typical properties of reclaimed rubbers are shown in Table 5.

Until the 1960s, reclaimed rubber was an important raw material in molded and extruded rubber products, eg, tires, rubber mats, and hard rubber battery cases. With the advent of vinyl, other plastics, and less expensive oil-extended synthetic polymers, reclaimed rubber sales stabilized and decreased. In 1973, the oil embargo and rising energy costs increased costs of the energy-intensive rubber reclaiming process to the point where they matched virgin polymer costs. Increased radial tire production required crack resistance that could not be provided by reclaimed rubber compounds (28).

8. Civil Engineering Market

The civil engineering market for scrap tires encompasses several distinct uses. Whole tires have been used to construct retaining walls and crash barriers.

One publicized use is the construction of houses and at least one motel (6). Whole tires have been used in erosion control, to construct breakwaters and artificial reefs and have been used as crash barriers at race tracks and marinas.

Jai Tire patented a process that, upon adding crumb rubber to soil, improves turf by providing aeration and reducing compaction (31). Superior Environmental Products, Inc. developed a material that contains 40% of scrap tire rubber. The material can control chemical, oil, and gasoline spills (32).

A broader use of scrap tires as an engineering material is in the formation of chipped or shredded scrap tires as a fill material, especially useful where light weight is needed. Notable projects include the fill over an underground garage in Minneapolis and the use of shredded tire fill to construct a ramp to an interstate highway where the ramp passes over a closed landfill. The lighter weight of the tire fill is expected to reduce settling as the landfill matures. Research is also being conducted in the use of shredded tires to backfill retaining walls, and as an insulating material under roadbeds in cold climates.

Expansion of the civil engineering markets depends on the availability of standard engineering data for shredded tire material; fortunately, several projects are being undertaken by university-based researchers who are generating this data. Another limiting issue is concern about potential leachates that might result from any of these uses; again, data is being developed which so far has demonstrated no difficulties with tires in these uses.

Several state highway departments have undertaken road construction-related fill projects using tire chips, including Oregon, Colorado, North Carolina, Virginia, Maine, Minnesota, and Wisconsin. Minnesota has achieved considerable private use of tire chips as fill material, as has Vermont. Several states have approved the use of tire chips in private septic systems as backfill for leach fields, including Iowa, Georgia, and South Carolina. Whole used tires are used for a thick flow zone for leachate and as a protective barrier at the Pen Argyl landfill in Pennsylvania (33).

Small tire chips have also been utilized as a soil amendment to improve athletic playing fields (see RECREATIONAL SURFACES). A patented process marketed under the trade name Rebound (Jai Tire) combines crumb rubber from scrap tires with composted organic material to reduce soil compaction, resulting in better athletic playing surfaces (34). Installations have been made in Florida, California, Colorado, Hawaii, Maryland, Michigan, Missouri, Nevada, Virginia, and Wisconsin.

The Americans with Disabilities Act (ADA) has opened another market for scrap tires in resilient playground surfacing. Many schools and recreation facilities are reconfiguring playgrounds to make them more accessible, including the use of resilient surfaces which can be traversed by wheelchairs.

The goal of most scrap tire utilization projects is to find markets for scrap tires so that they do not end up in landfills or on stockpiles. Ironically, one potentially significant use of tires is in the construction and management of landfills. Both shredded and whole scrap tires have been approved in various states for use in constructing leachate beds in landfills. Approval has also been given in some states for the use of shredded tire material as a partial replacement for required daily cover (22). This is a growing application.

Scrap whole tires have been used to form artificial fishing reefs, oyster beds, and as a floating breakwater. Goodyear has installed more than 2000 fishing reefs made from old tires. In Ft. Lauderdale, Florida, one of the largest reefs is made of 3×10^3 tires; it stretches ca 2.4 km (35). Tires are also used in playgrounds, flower planters, and shoe soles. The tire splitting industry cuts tires into pieces for gaskets, shims, dock bumpers, shock absorbers, blasting mats, and other articles. Rubber is sliced from tire tread to make strips for floor mats.

9. Tire Retreading and Other Uses

In 2003, about 16.5×10^6 tires were retreaded (2). Retreading has been the most cost-effective alternative to recycling rubber. After retreading, 290×10^6 scrap tires are generated. However, worn retreaded tires usually are discarded in a landfill. Approximately 10% of discarded tires are retreaded (36).

10. Economic Aspects

Scrap tires are used in a number of productive and environmentally safe applications. From 1990 through 2003, the total number of scrap tires going to market increased from 11×10^6 (24.5%) of the 223×10^6 generated to 233×10^6 (80.4%) of the 290×10^6 generated.

The 2003 market breaks down as follows

130×10^6 (44.7%) are used as fuel.
56×10^6 (19.4%) are recycled or used in civil engineering projects.
18×10^6 (7.8%) are converted into ground rubber and recycled into products.
12×10^6 (4.3%) are converted into ground rubber and used in rubber-modified asphalt.
9×10^6 (3.1%) are exported.
6.5×10^6 (2.0%) are recycled into cut/stamped/punched products.
3×10^6 (1.7%) are used in agricultural and miscellaneous uses.

The EPA's Jobs through Recycling (JTR) Program site contains information on markets for scrap tires.

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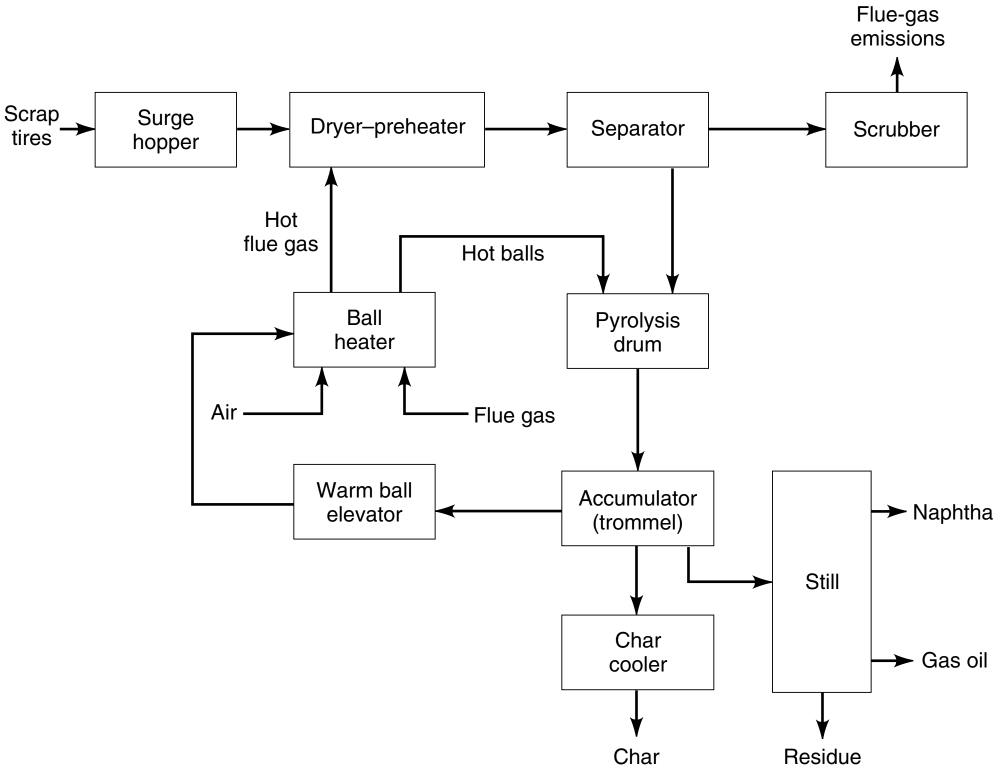

Fig. 1. The Tosco II process.

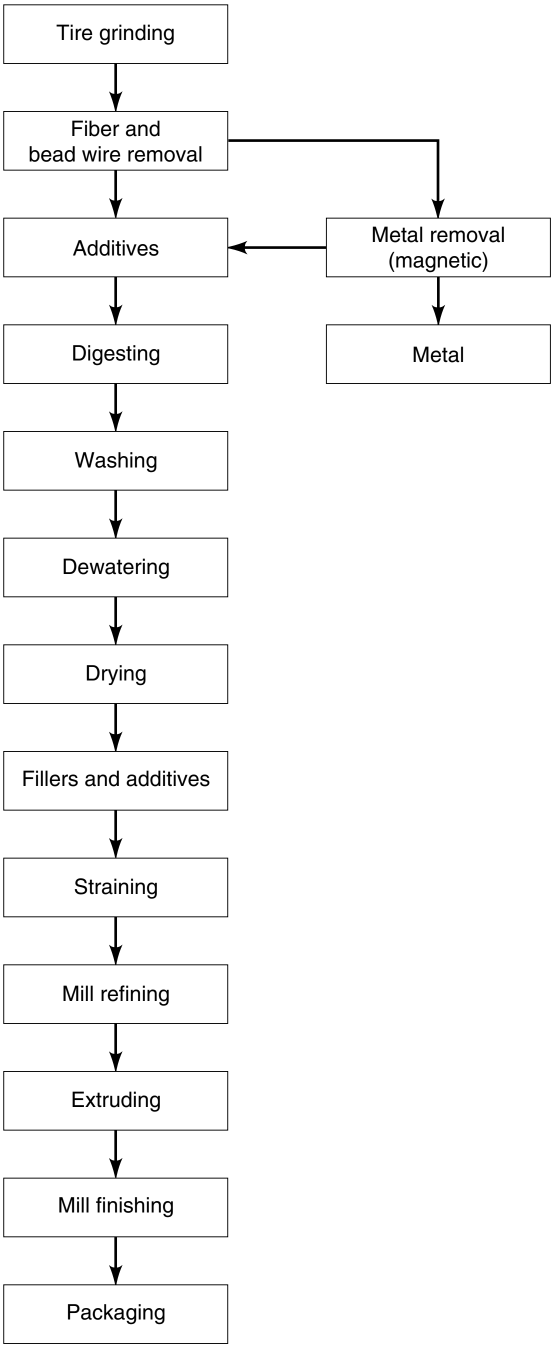

Fig. 2. The reclaim digester process.

Table 1. **Oils and Processing Aids for Reclaiming Rubber**

Material	Composition	Action
Paraflux	saturated plasticizer, polymerized hydrocarbon	plasticizer
tall oil pitch		
Tarene[a]	mixed terpenes, a pine-tar product	extender; plasticizer aids in dispersion of fillers; softens product and improves processing
Solvenol	monocyclic terpenes	processing aid; nonstaining reclaim oil and solvent; swells and penetrates rubber; dissolves and disperses heavy oils
Pitt Consol 500	aryl disulfides in petroleum oil	peptizer; shortens devulcanizing time by oxidizing rubber bonds
300′ mineral rubber	bituminous petroleum product	extender, plasticizer, and softener; aids in processing reclaim
resorcinol	resorcinol	tire formulations; promotes adhesion of rubber to cord; reduces stain in whitewall tires when used with formaldehyde
Corray 40	cycloparaffinic hydrocarbon	processing aid; softens, swells, and smooths reclaim
carbon black		reinforcing filler
Triton × 100[b]	alkylaryl polyether alcohol	emulsifier; aids in dispersing oils over rubber particles
clay	aluminum silicate	inert filler; hardens and stiffens reclaim
limestone whiting	calcium carbonate	inert filler; hardens and stiffens reclaim
liquid caustic[c]	sodium hydroxide	devulcanizing agent; removes free sulfur and acts as curing aid

[a] Trademark of Harwick.

[b] Trademark of Rohm and Haas.

[c] 30% NaOH solution.

Table 2. **Formulation for Reclaiming Whole SBR Tires**[a]

Ingredient	Parts, phr
SBR[b]	100.0
Paraflux	5.4
tall oil pitch	6.0
Solvenol	2.0
Pitt Consol 500	2.0
300′ mineral rubber	1.7
carbon black	4.0
resorcinol	0.06
Triton × 100	0.06

[a] Digested for 5 h at a steam pressure of 1.01 MPa (10 atm).

[b] Styrene–butadiene rubber reduced to <1.19-mm (16-mesh) particles.

Table 3. **Formulation for Reclaiming Butyl Rubbers**[a]

Ingredient	Parts, phr
IIRh[b]	100
Corray 40	2
clay	3
water	2

[a] Devulcanized for 5 h at a steam pressure of 1.01 MPa (10 atm).
[b] Butyl tubes reduced to 6.25-mm particles.

Table 4. **Formulation for Reclaiming Natural Rubber**

Ingredient	Parts, phr
Carbon black[a]	
NR black[b]	100
Tarene	3
limestone whiting	10
liquid caustic[c]	2
water	2
Neutral rubbers[d]	
NR neutral[e]	100
Corray 40	3
clay	2
liquid caustic[c]	2
water	2

[a] Devulcanized for 5 h at a steam pressure of 1.01 MPa (10 atm).
[b] Black NR tubes reduced to 6.25-mm size particles.
[c] 30% NaOH.
[d] Devulcanized for 5 h at a steam pressure of 1.4 MPa (14 atm).
[e] NR elastic bands and thread reduced to 6.25-mm size particles.

Table 5. **Properties of Reclaimed Rubbers**

Polymer	Specific gravity	Mooney viscosity	Tensile strength, MPa[a]	Elongation, %	Ash, %	Acetone extract, %
NR[b]						
neutral	1.19	45	9.0	500	29	9
black	1.19	25	8.6	400	13	11
SBR, whole tire[b]	1.18	50	6.9	280	7	22
IIR, tubes[c]	1.17	65	9.0	540	7	

[a] To convert MPa to psi, multiply by 145.

[b] Rubber Reclaimers Association (RRA) cure test recipe for mixed elastomer and NR reclaim; cured 20 min at 141°C.

[c] RRA cure test recipe for IIR reclaim, cured 30 min at 160°C. IIR is isobutylene–isoprene rubber (butyl rubber).