Recycling and pyrolysis of scrap tire

REPORT ON TRAINING VISIT

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REPORT
ON MY ACADEMIC AND SCIENTIFIC ACTIVITIES IN TRAINING COURSE
AT THE SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

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Preface

I am Asraruddin Gulzad professor of Organic Substances Technology Department of Chemical Technology Faculty of Kabul Polytechnic University. I attended a two months and ten days training visit stay from 5.10.2011 to 14.12.2011 at the Slovak University of Technology in Bratislava, Slovakia.

Main purpose of my training stay was getting familiar with new pedagogical methods, and collecting new scientific articles and books on chemical technology topics.

Activities I've done during this training stay are listed below:

- Visiting and getting familiar with chemical engineering laboratories.
- Visiting and getting familiar with organic chemistry and organic substances technology laboratories.
- Visiting and getting familiar with chemical technology factory (DUSLO ).
- Visiting organic chemistry laboratories.
- Analysis of crude oil products.
- Participating in some lectures, seminars, and laboratorial works of bachelor, master and PhD classes of chemical engineering department.
- Visiting faculty bookstore and library.
- Collecting scientific articles and books (published from 2000 to 2011) in related tire recycling topics.

I want to appreciate and thank Dr. Juma Haydary, Professor Jozef Markos, Dalibor Susa and other teachers of Chemical and Food Technology Faculty in Bratislava for their excellent cooperation and collaboration.

Some parts of collected materials are inserted in continuation of this report.

With Respect

Asraruddin Gulzad, Dr.S
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Introduction

Waste tire related environmental problems and its recycling techniques have been a major challenge to society and also the disposal of these tires becomes a serious problem. The accumulation of discarded waste tires leads to environmental pollution. A large fraction of the scrap tires is simply dumped in cities where they represent hazards such as diseases and accidental fires. Current waste tire recycling market is too small to accommodate the tire generated annually. Tires that are not beneficially reused either end up occupying valuable landfill space or worse are illegally disposed of in streams, fields, woodlands and other areas harmful to the environment and public health. While used tires are composed of relatively inert material and pose no direct harm to the environment, whole tires are banned from most landfills in highly populated areas.

A large fraction of the scrap tires is simply dumped in sites where they represent hazards such as diseases and accidental fires. For many years landfill was the main practical means for coping with the problem of waste tires.

However, landfilling of tires is declining as a disposal option, since tires do not degrade easily in landfills; they are bulky, taking up valuable landfill space and prevent waste compaction. Dumping may result in accidental fires with high pollution emissions. A low percentage of scrap tires is recycled with material recovery by methods such as retreading and reusing of tire, production of ground rubber for use in other applications and reclaiming rubber raw materials. The problem is that waste tire generation rate is much more important than the amount of material required for these alternative uses.

One of the best methods of dispose is pyrolysis of scrap tires. Pyrolysis offers an environmentally and economically attractive method of waste tires transformation into useful products and energy. Pyrolysis also represents one of the most important steps during the waste tire gasification. Thermogravimetry analysis reveals that the pyrolysis of tire rubber at atmospheric pressure starts at a temperature around 250°C and finishes at a temperature of about 550°C. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. In general, by pyrolyzing waste tire three fractions are obtained: solid residue (around 40 wt. %), liquid fraction (around 50 wt. %) and gas fraction (around 10 wt. %). The general trend is an increase in yields of liquid and gas fractions as the temperature increases. From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds containing a lot of aromatics. This liquid can be separated into light and higher fractions. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock. The main components of pyrolysis gases reported by various authors are: H₂, H₂S, CO, CO₂, CH₄, C₂H₄, C₃H₆ and other light hydrocarbons. The gas fraction can be used as fuel in the pyrolysis process. The solid
residue contains carbon black, and inorganic matter. It contains carbon black and the mineral matter initially present in the tire. This solid char may be used as reinforcement in the rubber industry, as activated carbon or as smokeless fuel.

In this report a literature and practical review of various methods of scrap tire recycling is presented.
1: Theoretical part
1.1- Methods of tire recycling

1.1.1- Tire mechanical milling

Using this technology, milling is generally made by rotating blades. The principal aim of using rotating blades is to separate rubber from the metallic part. It has been observed that by using recent plants it is possible to obtain very pure materials. No doubt low cost of the plant and absence of air emission are the major advantages, but the high consumption of electric power and limited market for the products obtained are the main drawbacks that need further research. For more information about tire mechanical milling see appendix 1.

1.1.2- Cryomechanical recycling of tire

With this process, the rubber is cooled using liquid nitrogen to a temperature ranging between −60 and −100°C. As a result of this operation, the rubber becomes fragile and thus mills easily into very fine particles by a disk or hammer mill. The main advantage of this process is the possibility of obtaining very fine powder (up to hundred microns). The high consumptions of both energy and liquid nitrogen (≈0.9 kg to treat just 1 kg of rubber), makes the process very expensive. For more information about Cry mechanical recycling of tire see appendix 2.

1.1.3- Tire devulcanization

The rubber recycling process begins with shredding. After the steel and reinforcing fibers are removed, and a secondary grinding, the resulting rubber powder is ready for product remanufacture. Until now this inert material could only be used in applications that do not require vulcanization. In the rubber recycling process, devulcanization begins with delinking of the sulfur molecules from the rubber molecules, facilitating the formation of new cross-linkages. Two main rubber recycling processes have been developed: the modified oil process and the water-oil process. With each of these processes, oil and a reclaiming agent are added to the reclaimed rubber powder, which is subjected to high temperature and pressure for a long period (5–12 hours) in special equipment and also requires extensive mechanical post-processing [3]. The reclaimed rubber from these processes has altered properties and is unsuitable for use in many products, including tires. Typically, these various de vulcanization processes have failed
to result in significant de-vulcanization, have failed to achieve consistent quality, or have been prohibitively expensive. For more information about de-vulcanization and methods of devulcanization see appendix 3.

1.1.4- Incineration of scrap tire

In general, the incineration of waste tires may be defined as the reduction of combustible wastes to inert residue by controlled high-temperature combustion. The combustion process is spontaneous above 400°C, highly exothermic and once turned on becomes self-supporting. Waste tires having a calorific value of 7500–8000 kcal/kg, are used as fuel in the incinerators [1].

The heat generated during incineration produces steam, which may be used to heat and air-condition the buildings, or for industrial processing or the production of electricity. Burning refuse in steam-generating incinerators and its use as a supplemental fuel is the most advanced and proven waste-energy utilization technologies. Design of the furnace and its effective efficiency play important roles concerning the general combustion performance. So, the incinerator has to be designed for good burning and the prevention of soot delivery. Walls and furnace beds must be able to withstand the high temperatures (approx. 1150°C) generated by the combustion process. High combustion-efficiency, defined as the ratio of thermal energy output to global energy input, usually depends upon interdependent factors, such as the fuel's physical characteristics, plant design, manufacture and operating conditions. Volatile matter content, moisture, mineral content, structural characteristics (density, area/volume ratio, design), resin content, etc. are the main physical parameters that affect the boiler's efficiency [4]. Temperature, heat-exchange surface, excess air, CO₂ content, etc., are the principal functional parameters of a combustion-facility firebox. The use of refuse as a supplemental fuel in power-producing plants offers many advantages, such as;

1. maximum heat-recovery;
2. low air-pollution emissions;
3. environmentally-acceptable process;
4. reduced power-production cost, etc.

However, the disadvantages of incinerators are:

1. large capital-investment;
2. need for flue-gas cleaning;
3. relatively high operating cost;
4. Skilled labor is required to operate the system, etc.

**Combustion technologies**

Fluidized-bed combustion is one of the most appropriate processes for the treatment of waste tires. However, high operating costs and considerable feedstock preparation make this process relatively expensive. Fluidized-bed reactor for waste tire combustion was used by a number of authors.

Rotary kiln combustion enables combustion of tires in different sizes with relatively low operating costs. The requirement of a post-combustion chamber and particulate filtration, for controlling emissions are disadvantages of combustion in rotary kiln combustors. Waste tire utilization in cement kilns brings economical benefits. However, environmental impact of this process calls for more research, especially from the view of emissions of polycyclic aromatic hydrocarbons.

Reports that energy recovery of scrap tires used by a cement kiln meets environmental standards. Giugliano et al. determined the influence of shredded tires on the combustion process in a cement kiln. Combustion in grate kilns is also used for waste tire combustion. The use of combustion in the grate kiln technology is justified economically, especially for large-sized plants [5].

**Combustion behavior and emissions**

Both combustion behavior and emissions from the combustion process of waste tires are influenced by process conditions such as temperature, oxygen enrichment, particle sizes, reactor type, etc. Using thermo gravimetric analysis and Lavenders observed that tire particles experienced an intense primary volatile combustion phase, followed by a phase of simultaneous secondary volatile combustion of less intensity and char combustion. They also found out that char burnout times were considerably shorter for tire particles than for coal. Mistral et abusing fluidized-bed combustion reported that both gas superficial velocity and partial pressure of oxygen exert influence upon the overall fixed carbon combustion efficiency. The efficiency increases slightly with the oxygen concentration and significantly if the gas superficial velocity decreases. They also burned waste tires in an atmospheric fluidized bed combustion plant with an airflow of 860 ‘l/h and 20% excess oxygen at three’ different combustion temperatures. (750, 850, and 950°C). They observed that the introduction of tires in the feeder increases the total PAH amount emitted with respect to coal emissions, with minimal variations at the combustion temperatures studied by them: thus, the higher the temperature, the lower the amount of emitted polycyclic aromatic hydrocarbons. Courtemanche et al. burned coal and waste tire crumb in an electrically heated drop-tube furnace at high particle
heating rates (104-105 K s\(^{-1}\)) and elevated gas temperatures (1300–1600 K). They found that combustion of coal generated four times more NO\(_x\) than combustion of tire crumb, in proportion to their nitrogen content. A complex study of process conditions such as temperature, O2 concentration and particle sizes on combustion behavior and pollutant emissions was not found in the literature. For disposal of waste tires by combustion with minimum environmental impact also for the prevention of fire hazards in tire landfills, more research in this area is required. Information about kinetic of pyrolysis see appendix 5a

*Emissions from the combustion of tires*

For disposal of waste tires by combustion and energy recovery the characteristics of emissions are the main factor, which must be studied. The amount of toxic emissions like SO\(_2\), NO\(_x\), CO and PAHs is affected by the process conditions and the technology used. Though emission characteristics of waste tire combustion have been studied by a number of authors, more research in this field is required. Levendis et al. comparing combustion of coal and waste rubber found that NO\(_x\) emissions from tires are 3-4 times lower than those from coal, emissions of SO\(_2\) where comparable. CO and PAH emission yields from tire derived fuel were much higher than those from coal, but the relative amounts of individual PAH components were remarkable similar in the combustion effluent of the two fuels [5]. Mistral Report that thus, the higher the temperature, the lower amount of emitted polycyclic aromatic hydrocarbons measured by fluidized-bed combustion of waste tires. Lemieux .Reviewed Emissions of organic air toxics from open burning of various types of wastes. From this review results that PAH emissions were highest when combustion of polymers was taking place. For this reason a post-combustion chamber and particulate filtration, for controlling emissions from the tire combustion is required. In addition, the conditions of the combustion process must be optimized. Appendix 5b.

1.1.5- Tire pyrolysis

Tire pyrolysis (thermal decomposition in an oxygen-free environment) is currently receiving renewed attention [7]. Recycling of tires by pyrolysis offers an environmentally attractive method. The products of the tire pyrolysis process are: Solid char (30-40 wt %), liquid residue (40-60 wt %), and gases (5-20 wt %). The solid residue contains carbon black and the mineral matter initially present in the tire. This solid char may be used as reinforcement in the rubber industry, as activated carbon or as smokeless fuel [5]. The liquid product consists of a very complex mixture of organic
components. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock or a source of chemicals. The gaseous fraction is composed of non-condensable organics as, \( H_2 \), \( H_2S \), \( CO \), \( CO_2 \), \( CH_4 \), \( C_2H_4 \), \( C_3H_6 \) etc. The gas fraction can be used as fuel in the pyrolysis process. For growing economical efficiency and enlargement of markets for pyrolysis products, further research is needed in the field of process conditions, optimization, and product characterization and treatment. Waste tires can be used directly as fuels in the incinerators. Due to their high heating value scrap tires are excellent materials for energy recovery. The use of tires directly as fuel in incinerators has the following advantages: Reduced power-production costs, maximum heat recovery and environmentally acceptable process. The disadvantages are: no material recovery, large capital investment, need for flue gas cleaning, \( CO_2 \) emission, high operating costs. Scrap tires are used also as fuel in cement kilns. More research works is needed for obtaining environmental impacts of this process, especially from the view of polycyclic aromatic hydrocarbon (PAH) emissions [5].

Waste tire pyrolysis involves the thermal degradation in the absence of oxygen. The benefit of this application is the conversion of waste tires into value-added products such as olefins, chemicals and surface-activated carbon. More than 30 major pyrolysis projects have been proposed, designed, patented, licensed, or built over the past decade, but none have yet been commercially successful. The primary barriers for this application are both economic and technical. The capital cost is high, and the products from pyrolysis do not have sufficient value and must compete with commodity materials. However, it is expected that technological innovations may break through this barrier in the near future. Developments of less costly techniques or processes for higher value added products would enable pyrolysis to become a profitable alternative for waste tire recycling. Pyrolysis is known for low emissions to the environment [2].

Char upgrading is implemented in a closed-loop activation step that yields an activated carbon and eliminates undesirable by-products and emissions. Upgrading the char produces high-surface-area activated carbon in several grades. Ash-free oil is turned into high-quality carbon black by using the furnace process. As an alternative, oils can be separated into valuable chemical feedstock by distillation.
Table 1: Composition of scrap tire pyrolysis products

<table>
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<th>Primary Products</th>
<th>wt.%</th>
<th>Content</th>
<th>Secondary Products</th>
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<tr>
<td>Pyro-gas</td>
<td>10 - 30</td>
<td>Hydrogen, CO2, CO Methane, Ethane, Propane, Propene, Butane, Other hydrocarbons, app. 1% of Sulfur</td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>38 - 55</td>
<td>High aromatic Mw 300 - 400 Low in sulfur (0.3 - 1.0%) Aromatics, Alkanes, Alkenes, Ketones, Aldehydes</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>Char</td>
<td>33 - 38</td>
<td>&gt;15 % of Ash (ZnO) 3 -5 % of Sulfur</td>
<td>Activated carbon</td>
</tr>
</tbody>
</table>

Problems:

Low Product Price: The primary products are essentially low molecular weight olefins and char. Olefins: The pyre-gas prices are low in the current market. Other chemicals are valuable, but the yield is low. High quality carbon black is also valuable but there is no particular price advantage for the same quality carbon from traditional processes. Char: Surface activated carbon is a valuable product, but there is no cost advantage compared to alternative methods (normal surface activated carbon manufacturing).

High Process Cost: The valuable chemicals from pyre-gas or oil, are generally high molecular weight substances. The purification of high molecular weight substances is expensive.

New technologies: There are two technological approaches to the problems discussed above.
(a) Higher Value Products from Pyrolysis. (High molecular weight olefins)
The production of significant quantities of valuable high molecular weight olefins to obtain curable and moldable olefins (Mw > 15,000) would overcome current economic barriers. These are typically produced in small quantities because the process temperature is high. At high temperature, vulcanized rubbers are quickly decomposed to low molecular weight olefins (Mw 300 -400). High molecular weight compounds can be generated by low temperature pyrolysis [5]. However, lower temperature will require longer process times. New technological breakthroughs will be necessary for the commercialization of low temperature pyrolysis. Four new technologies are being developed.

**Microwave pyrolysis:** Microwaves can heat objects more uniformly than conventional heating methods. Microwave heating requires shorter heating times. Microwave pyrolysis will result in relatively high molecular weight olefins and a high proportion of valuable products such as ethylene, propylene, butene, aromatics, etc. The short process time also contributes to a reduction in the process cost. Moreover, for microwave heating, the shape of the tire chip is less important compared to the requirements of conventional heating. Whole tires or larger chips can be processed using microwave pyrolysis, which greatly reduces pre-processing cost.

**Ultrasonic devulcanization:** Isayev has patented a method which minimizes heating and uses sonic energy to break down sulfur-carbon chemical bonds in tires. Chipped tires are heated to about 400 F, and then subjected to 20,000 cycles per second of ultrasonic energy (just above the highest frequency the human ear can discern) at pressures up to several thousand pounds per square inch. The rubber is transformed from a solid to a highly viscous fluid within milliseconds. With additional curative agents the viscous material can be molded into new products. A prototype machine can handle approximately 50 pounds of tires per hour [5].

**Supercritical fluid de polymerization:** Supercritical water can be used to controllably de polymerize the rubber compounds. This approach requires lower temperatures (approx. 750 F) and shorter processing times. Tire compounds are decomposed to high molecular weight olefins (Mw 1,000 - 10,000), or oils (Max. 90 %). The technique is being developed and has been tested only on an experimental scale. Because of the expensive supercritical water equipment, this application would require a relatively large initial cost.
Use of special catalysts: Use of catalysts can reduce processing temperature or time. As shown in the above applications, reduced temperature and time can result in either higher molecular weight olefins or an increasing proportion of valuable substances. The advantage of catalysts is that no new equipment or knowledge is required. Therefore cost estimation and scale-up would be easy. Some research and pilot scale experiments have been conducted recently, but the types of catalysts are highly proprietary.

Lower process cost

Surface active carbon and high quality carbon black are high value-added products. The relative process cost is the only barrier for commercial success. One approach to reduce processing cost is to operate at a high process temperature with the use of a special catalyst. Approximately 3.2 % of zinc-oxide is added to tire compounds, and the zinc-oxide remains in the char. To produce surface active carbon, the remaining zinc must be removed from the surface, and high temperature processing is able to facilitate this. Some facilities use special catalysts in order to maximize benefits.

Characteristics and composition of scrap tires

Tires are composed of rubber compounds and textile or steel cords. Rubber compounds generally consist of elastomers (natural or synthetic rubber), carbon black, hydrocarbon oils, zinc oxide, sulphur and sulphur compounds and other chemicals such as stabilizers, anti-oxidants, anti-ozonants, etc.

Pyrolysis and combustion methods and equipment Thermal decomposition of scrap tire

A number of experimental apparatus and laboratory scale plants for pyrolysis and combustion decomposition of rubber is generally studied by thermo gravimetric analysis. Both thermo gravimetric of scrap tires was presented by various authors. The behavior of the thermal (TG) and derivative thermo gravimetric (DTG) are used as standard methods for studying thermal degradation of waste rubber samples. From the thermo gravimetric analysis provided by various authors (for example: Leung and Wang,Yang et , Berrueco . results that more than one degradation temperature region during rubber pyrolysis is recorded[2]. Measurements provided in our laboratory sustain this fact (see Figure 2), however, it depends upon the composition of rubber compounds. The measured TG curves show two different mass loss regions over a temperature range of 250-550\degree C. Based on the
evaporating characteristics of individual rubber components at the temperature ranging from 250 to 380°C, additives, oils and plasticizers are lost. At the temperature ranging 400-550 NR, SBR and BR are decomposed.

Pyrolysis reactors

A number of studies have been done to investigate the pyrolysis of waste tires in both laboratory and industrial scale. Williams et al pyrolysis waste tires in a nitrogen atmosphere using a fixed-bed batch reactor at a temperature ranging from 300 to 720°C. This type reactor was also used by Berrueco et, Cunliffe and Williams and others. Rodriguez et al. Moreno et al and Laresgoiti et al. employed for paralyzing waste tires autoclaves. Kaminski and Menarche Pyrolysis waste tires in a fluidized bed reactor at a temperature ranging from 500 to700°C. Roy et al. used for the thermal decomposition of waste tires vacuum pyrolysis. Also plasma technology was employed by Tang and Huang for paralyzing waste tires[5b].

Pyrolysis of waste tires leads to the production of a solid carbon residue (char), a condensable fraction (pyre-oil) and gases. The percentage of each phase is influenced by process conditions, such as temperature, pressure, heating rate, particle sizes, heat exchange system, catalysis etc. William’s pyrolysis waste tire at a temperature between 300 and 720°C and heating rates 5 and 80 °C.min⁻¹ found that the maximum conversion of tire occurred at a temperature of 600°C. Laresgoiti found that the temperature does not significantly influence the char and gas yields over 500°C. However, temperature variations influence the gas composition. Rodriguez et al. Pyrolysis cross-section samples (2-3 cm wide), representative of whole tire, at 300-700°C. They report that Tire-pyrolysis liquids are a complex mixture of hydrocarbons, which contains 0.4 % of N and 1.2 % of S. About 30 % of such liquids is an easily distillable fraction with boiling points (70-210°C) and about 60 % of liquids have boiling point range of 150-370°C.

They analyzed the temperature influence on the global yields and the gas composition. They observed that the liquid yield increases with temperature from 400 to 500°C. However at temperatures higher than 500°C, this parameter remained almost constant. The gas yield showed a growth from 2.4 wt% at 400°C to 4.4 wt% at 700°C. A different distribution of scrap tire into yields (char, liquid and gas) was reported by Chang (30-53 wt% gas, 28-42 wt% oil and 14-28 wt% Zabanioti and Stavropoulos pyrolyzing scrap tire in a helium atmosphere in the temperature range 390-890°C and heating rates of 70-90°C. min –1found out that the char yield decreases with temperature.
reaching an asymptotic value of 20 wt% of raw material, at about 830°C. The gas yield (condensable and non condensable) increases with temperature reaching an asymptotic value of 73 wt.% of raw material, at about 830°C. Pyrolysis scrap tires in temperature range of 400-460°C, nitrogen flow rate of 0.2-0.5 m3h-1 and particle size of 2-20 mm. As optimum conditions they present 430°C, 0.35 m3h-1 and 10 mm, respectively. At these conditions the yield of char and liquid were 32.5 and 51.0 wt. %, respectively. Studied pyrolysis of waste tires with partial oxidation in a fluidized-bed reactor. They found that with increasing O₂ concentration, the gas yield increases from 22 to 43 % since CO₂ generation increases. Energy recovery is about 0.32 with O₂ concentrations up to, 6.5 %, thereafter, energy recovery is reduced to 0.24. Marina et al. carried out hydrogenative pyrolysis of waste tires for better saturation of the broken bonds. They declared that hydrogenative pyrolysis enables the use of the lowest reaction temperatures 390-430°C, the production of solid residue is minimized and the production of liquid phase is maximized. Roy et al. pyrolysis tire rubber at 500°C and a total pressure varying between 0.8 and 28.0 k Pa. They found that the yields of gas, oil and pyrolysis carbon black changed little with the pyrolysis pressure. However, the oil composition and the carbon black characteristics depended considerably on the pyrolysis pressure[6].

**Characteristics and composition of the pyrolysis products**

Use of pyrolysis as a method for recycling waste tire depends on the market for pyrolysis products. For this reason, characterization of pyrolysis products and possibilities of their application in other processes is very important. At present time, the main application for solid char is its use as active carbon, as reinforcement in rubber industry and as smokeless fuel. The liquid product is used as a fuel, or a source of chemicals, and the gas fraction as a fuel in the pyrolysis process.

**Solid residue**

The solid residue contains carbon black and the mineral matter initially present in the tire. Several studies have reported the production of chars and active carbon from waste tires. These active carbons have been used to adsorb phenols, basic dyes and metals, phenols, butane and natural gas. Active carbon from solid product of pyrolysis process is produced by activation with an activating gas at 800-100°C. Carbon characteristics (especially specific area) are greatly influenced by the degree of the activation also by nature of activating agent (steam or CO₂) and process temperature. Based on the current technology and literature results tire charre activation below 700°C
looks impractical. The particle size of the tire rubber was found to have influence on the porosity of the resultant carbon generated from steam activation [5].

Elemental analysis carried out by Zabaniotou shows that pyrolysis char contains 71 wt.% of C, 13.3 wt. % of O, 5.4 wt.% of Fe, 2.8 wt.% of S, 2.3 wt.% of Zn, 1.3 wt.% of Ca, and 0.3 wt.% of Al.

**Pyrolysis liquid product**

The liquid phase is the most important product of tire pyrolysis process. There are several papers in the literature devoted to the study of the characteristics of pyrolysis liquid products. Gas chromatography/Mass spectroscopy (GC/MS) is the most often method used not only for analyzing pyrolysis liquid product, but also for analyzing the gas yield and products of char combustion. Laresgoiti present a detailed characterization of the all pyrolysis liquids obtained at 300, 400, 500, 600, and 700°C. All, the GC/MS analysis, elemental analysis, gross calorific values and distillation data were studied. They report that tire derived liquids are a complex mixture of C6-C24 organic compounds, containing a lot of aromatics (53.4–74.8%), some nitrogenated (2.47–3.5%) and some oxygenated compounds (2.29–4.85%). Their GCV (42 MJ kg−1) is even higher than that specified for commercial heating oil’s, but the sulphur content (1–1.4%) is close to or slightly over the limit value. Significant quantities of valuable light hydrocarbons such as benzene, toluene, xylem, limonene, etc. were obtained. The concentration of these compounds increases with temperature up to 500°C and then decreases. There is also an important portion of polycyclic aromatics, such as naphthalene, phenanthrene, fluorine, biphenyl, etc.; their concentration as well as that of total aromatics increase significantly with temperature [6].

Vacuum pyrolysis of used tires produces approximately 55 wt. % of pyrolysis oil. This oil typically contains 20-25 wt. % of naphtha fraction with a boiling point lower than 200°C. The naphtha fraction typically contains 20-25 wt. % *di-* limonenes. Williams and Taylor found that the pyrolysis oil had molecular weight range from a nominal 50 to 1200.

**Pyrolysis gases**

The yield of the gas fraction obtained in different experimental systems shows important variations. For example: Berries et al., obtained the gas yield 2.4-4.4 wt.%, but Chang  wt.%. Laresgoiti, using an autoclave in a nitrogen atmosphere at temperatures between 400 and 700°C, found that the paralyzed gases consisted of CO, CO₂, H₂S and hydrocarbons such as CH₄, C₂H₄, C₃H₆ and C₄H₈, and their unsaturated
derivatives. Berries ET. Al. analyzing pyrolysis gases by gas chromatography, found that the main gases produced by the pyrolysis process are H₂, CO, CO₂ and hydrocarbons: CH₄, C₂H₄, C₃H₆ and C₄H₈. Roy et al. obtained gases by vacuum pyrolysis, mainly composed of H₂, CO, CO₂ and a few hydrocarbon gases. In general, main components of M. Juma et al. /Petroleum & Coal .pyrolysis gases were reported by various authors as: H₂, H₂S, CO, CO₂, CH₄, C₂H₄, C₃H₆ and other light hydrocarbons. For information about scrap tire pyrolysis kinetics see appendix 5b.

1.3- Tire gasification

Gasification is a partial oxidation process. Gasification of organics occurs in an atmosphere that contains some oxygen, but not enough to support complete combustion (i.e., complete oxidation of the feedstock July 1995 Cal Recovery, Inc [1]. Environmental Factors of Waste Tire Pyrolysis Final Report o carbon dioxide and water). In the gasification processes, steam reacts with the solid char in an endothermic (i.e., heat-consuming) reaction, producing gaseous carbon monoxide and hydrogen [2].

1.4- Thermogravimetry

Thermogravimetry techniques can be used to continuously measure the mass of a sample as it is heated at a controlled rate. The temperature at which water evaporates depends on its molecular environment: free water normally evaporates at a lower temperature than bound water. Thus by measuring the change in the mass of a sample as it loses water during heating it is often possible to obtain an indication of the amounts of water present in different molecular environments.

Thermogravimetry (also known by the acronym "TG"; alternative spellings include thermo gravimetric and thermogravimetry) is a branch of physical chemistry, materials research, and thermal analysis. It is based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time, and additionally of pressure and gas composition.

A sample of material (ranging from 1 mg to 100 mg, but sometimes as large as 100 g) is placed on an arm of a recording microbalance, also called thermo balance where that arm and the sample are placed in a furnace. The furnace temperature is controlled in a pre-programmed temperature/time profile (most commonly), or in the rate-controlled mode, where the pre-programmed value of the weight changes imposes the temperature
change in the way necessary to achieve and maintain the desired weight-change rate. The most common temperature profiles are: jumping to isotherm and holding there for a specified time ("soak"); temperature ramping at constant rate (linear heating or cooling); and combination of ramp and soak segments. The profile "ORTA" ("oscillation-rate thermal analysis") is used in other methods of thermal analysis, but not in TG, due to unavoidable disturbance forces. The rate-controlled method is very time-efficient, but for some types of materials it produces incorrect results or "ghost effects"; since this method does not reveal the automatically imposed temperature profile, the users may be misled by their trust for the "sophisticated, computerized program, which saves the analysis time tremendously".

The gaseous environment of the sample can be: ambient air, vacuum, inert gas, oxidizing/reducing gases, corrosive gases, carburizing gases, vapors of liquids or "self-generating atmosphere". The pressure can range from high vacuum or controlled vacuum, through ambient, to elevated and high pressure; the latter is hardly practical due to strong disturbances [5].

The commonly investigated processes are: thermal stability and decomposition, dehydration, oxidation, determination of volatile content and other compositional analysis, binder-burnout, high-temperature gas corrosion etc. The kinetic data obtained by TG are reliable only for irreversible processes, whereas reversible ones are grossly affected by diffusion, and only special procedures can handle them. Although many industrial processes could benefit from thermo gravimetric investigations, the industry is often discouraged by the natural discrepancies between the data produced by milligram-size samples, and those of the bulk processes. In this respect gram-size and larger TG samples are more suitable for optimization research of industrial processes.

*Thermogravimeter*

NETZSCH instruments for thermo gravimetric analysis/thermo gravimetric, i.e. the thermo balances, are equipped with digital balance systems, vertically constructed with top-loading sample arrangement and direct temperature measurement at the sample. Almost all models are vacuum-tight. Besides the exact recording of mass changes as a function of temperature and atmosphere, the c-DTA® signal can optionally be calculated as a benchmark for exothermal and endothermic processes.

Almost all thermo gravimetric analyzers can be equipped with heated coupling adapters for gas analysis systems such as QMS and FTIR. The TGA models of the 400-Series can be equipped anytime with DSC and/or DTA sample carriers for full-fledged TG-DSC or TG-DTA instruments (STA).NETZSCH thermo balances fulfill the
respective instrument and applications standards, e.g. ISO 11358, ISO/DIS 9924, ASTM E 1131, ASTM D 3850, and DIN 1006.
2 : EXPERIMENTAL PART

Characteristics and composition of scrap tires

Characteristics of materials Tires are composed of rubber compounds and textile or steel cords. Rubber compounds generally consist of elastomers [natural (natural rubber NR) or synthetic (styrene butadiene rubber, SBR; butadiene rubber, BR) rubber], carbon black, hydrocarbon oils, zinc oxide, sulfur and sulfur compounds and other chemicals such as stabilizers, anti-oxidants, anti-ozonants, etc. For the experimental investigation, rubber particles from various parts of a passenger car tire (produced by the MATADOR company in Puchov, Slovakia) were used. The proximate and elemental analyses of used tire rubber material are summarized in Tables 2 and 3.

<table>
<thead>
<tr>
<th>Table 1. Proximate analysis of tire rubber material</th>
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<tbody>
<tr>
<td>Volatile (wt%)</td>
</tr>
<tr>
<td>51.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Elemental analysis of tire rubber material</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
</tr>
<tr>
<td>81.24</td>
</tr>
</tbody>
</table>

2.1-Description of laboratory pyrolysis unit

The experimental set up shown in Figure 1. Aims at the maximization of the possibility of studying the influence of different factors on the pyrolysis process. The particles of solid material are fed into the system using a feeder. Then, the particles are passed through the reactor using a screw. The residence time of the particles in the reactor is controlled by the frequency cycle of the screw. The screw is moved by an electric stepping motor controlled by a controller and a PC.

The reactor temperature is controlled by a PID controller and software. Inert atmosphere in the reactor is achieved by nitrogen flowing through the reactor in the same direction as the solid material. The flow of nitrogen is measured by a flow meter. Passing through the reactor, rubber particles are decomposed. A simple model of tire rubber decomposition
could be based on the following scheme:

\[
\text{Tire rubber} \rightarrow \text{Volatiles} + \text{Char}
\]

Secondary decomposition of high molecular compounds to compounds with low molecular weight follows:

\[
\text{Volatiles} \rightarrow \text{Tars} + \text{Gases} \\
\text{Tars} \rightarrow \text{Gases}
\]

Fig. 1 Laboratory pyrolysis unit

The volatiles are removed from the reactor at high temperature and they are led to Condenser. The solid residue is removed from the end of the reactor and collected in a jar. For laboratory tests, tire rubber without steel cords was used; however, when using tires with steel cords, steel material can be very easily removed from pyrolysis carbon black using a magnetic separator. Textile cords are decomposed under the same conditions as tire rubber. Samples of solid residue were taken for its characterization by thermo gravimetric measurements, specific surface area, porosity and pore size distribution measurements, and
ASTM standard tests for carbon black. The details of solid product characterization can be found in our previous work. The volatile fraction, after partial condensation, was further cooled in a series of scrubber type coolers and then passed through an absorber. Samples of gases were taken for measurement of their composition in a GC/MS. The liquid product was collected from the condensers for further characterization [6].

2.2-Description of Thermogravimetry unit

The behavior of the thermal decomposition of rubber is generally studied by thermogravimetric analysis (TGA). Both thermo gravimetric (TG) and derivative thermo gravimetric (DTG) methods are used as standard methods for studying thermal degradation of waste rubber samples. From TGA results provided by various authors there are more than one degradation temperature region during rubber pyrolysis recorded.

The sample was placed in the center of the furnace tube using a thin ceramic rod. This rod was standing on a digital mass balance. The temperature in the center of the particle was measured by a thermocouple located inside the ceramic rod. The temperature of the gas phase was measured by a thermocouple placed below the particle. The used thermocouples were K type (Chromega-Alomega) with a wire diameter of 0.5mm. Both the mass and the temperature of the particle were scanned with a frequency of 5 sec. A program regulated the temperature inside the tube within the range 20–10008C. The feed gas stream with the desired content of oxygen or air in nitrogen was regulated by a system consisting of two calibrated electronic flow meters.

![Thermo gravimetric experimental apparatus](image)

Figure 2. Thermo gravimetric experimental apparatus.
The volatiles are removed from the reactor at high temperature and they are led to Condenser. The solid residue is removed from the end of the reactor and collected in a jar. For laboratory tests, tire rubber without steel cords was used; however, when using tires with steel cords, steel material can be very easily removed from pyrolysis carbon black using a magnetic separator. Textile cords are decomposed under the same conditions as tire rubber. Samples of solid residue were taken for its characterization by thermo gravimetric measurements, specific surface area, porosity and pore size distribution measurements, and ASTM standard tests for carbon black. The details of solid product characterization can be found in our previous work. The volatile fraction, after partial condensation, was further cooled in a series of scrubber type coolers and then passed through an absorber. Samples of gases were taken for measurement of their composition in a GC/MS. The liquid product was collected from the condensers for further characterization [6].

Starts at a temperature from the range of 200 and 250°C and ends at temperatures between 500 and 550°C (Fig.3) At higher temperatures the residence time of the tire in the reactor can be reduced. At the same time, higher temperatures cause better decomposition of the pore structure of pyrolysis carbon black, which is an advantage for their use as reinforcement or adsorbents. However, pyrolysis at higher temperatures results in an increase of the gas to liquid ratio, energy consumption and requirement for higher quality of equipment materials. Usually, the pyrolysis temperature is chosen from the range of 550 to 700°C.

At 500°C and residence time of 3 minutes (curve 3), the reaction was not finished, The reaction conversion in the pyrolysis reactor was under these conditions 93.5%. However, at 600 °C, the reaction conversion was 98% and at 800 °C it was 99.5%. At the temperature of 550 °C, the conversion of 100% was achieved in the residence time of only 5 min.
Laboratory pyrolysis flow reactor TG curve of waste tire rubber. Laboratory pyrolysis unit. The advantage of a screw type flow reactor is in its very good heat and mass transfer conditions. Tire particles with average size of 3mm were pyrolysis under isothermal conditions in the system described above. The residence time of only 3min was set. Different pyrolysis temperatures, from 500°C to 800°C, were used. The obtained solid products were tested by thermo gravimetric analysis using a simultaneous NETZCH STA 409 PC TG/DSC analyzer for the determination of the unreleased amount of volatiles. The reaction conversion was estimated by a comparison of TG curves of the solid product and used waste rubber.
Pyrolysis at higher temperatures results in an increase of the gas to liquid ratio, energy consumption and requirement for higher quality of equipment materials. Usually, the pyrolysis temperature is chosen from the range of 550 to 700°C. Effect of temperature on the conversion of waste tire pyrolysis was observed using the laboratory unit described above. As it is shown in Figure 4, at temperatures under 500°C, tire pyrolysis is not completed. However, at temperatures above 500°C, the residence time of 5 minutes was enough for the tire pyrolysis completion. The time needed for total conversion of the material in the reactor depends on the reactor temperature, particle sizes and heat and mass transfer conditions in the reactor.
3: Results and conclusion

The laboratory unit developed enables studying the influence of a number of parameters on the amount and quality of pyrolysis products. A screw type reactor with an electric stepping motor provides very good heat and mass transfer conditions and continuous removal of pyrolysis products, which results in their better quality. The temperature range from 550 to 700 was estimated to be optimal for solid waste and biomass pyrolysis. In the developed pyrolysis unit, the residence time of 5 minutes was sufficient for the pyrolysis of waste tires completion at 550°C. The sizes of used solid particles can vary from 0.1 mm to 10 mm. As the optimal value of $dP/dR$, the value of 0.25 was estimated. The system works at the pressure slightly above the atmospheric. The minimum flow rate of inert gas was found as the optimum one. The developed laboratory pyrolysis unit enables the realization of a number of different applications related to the characterization and treatment of pyrolysis products. Influence of process conditions on the pyrolysis product yields and influence of pyrolysis temperature on the specific surface area of pyrolysis carbon black were determined. Configurations differ slightly between different facilities, but the basic process is common.

Chipped tires are heated to 1,100 - 1,500 F (600 - 800 C) in the absence of oxygen.
Primary products are pyrolysis gas (pyro - gas) oils and char. The oils and char go through additional processes to manufacture secondary, value-added products.

A versatile and modular ultra high vacuum compatible TGA–EGA–MS system has been set-up with additional features like MFC controlled gas/vapor delivery system and pulse free liquid delivery system. The UHV operating conditions and other differential pressure and flow conditions resulted in high sensitivity, low background and detection limits with minimum time delay and memory effects. This system is used to study temperature programmed decomposition of many ox anion based inorganic salts. In conjunction with off-line analytical techniques, the chemical, structural evolutions of the intermediates/products with complete kinetic/reaction pathways are determined. The non-equilibrium nature of the

EGA–MS operating condition assisted formation of Nan crystalline materials in the decomposition of many systems. This facility can also be used to study high temperature gas solid interactions, as controlled environment exposure facility for high temperature oxidation/corrosion studies and also for preparing carbide and nitride. This system is being extensively used to study the temperature programmed decomposition of inorganic solids, their kinetics and reaction mechanisms. The TGA–EGA–MS spectra were generated by plotting the continuous change of sample weight and ion intensities of product gases as a function of time and/or specimen temperature. In addition to discern various reaction stages and their temperature regimes, the EGA–MS data was also used to compute the fractional extent ‘a’ of various reaction stages. The ‘a’ vs. ‘T’ values thus deduced were used with non-isothermal kinetic expressions to arrive at the reaction control mechanisms and the corresponding kinetic parameters like activation energy and pre-exponential factors. With the knowledge of the various reaction stages, the temperature programmed decomposition was interrupted at appropriate temperatures, upon completion of each reaction stage (by monitoring the MS signal of the corresponding gas to fall to background) to enervate the reaction intermediates and final product. These residual products were subsequently subjected to off-line analysis by XRD, XPS, FT-IR and high resolution TEM. With this complementary information, complete structural–chemical transformations occurring in the course of thermal process could be mapped out. The measured curves for all samples show two different mass loss regions over a temperature range 250–550°C. Based on the evaporating characteristics of individual rubber components it is assumed that at the temperature ranging from 250 to 380°C, oils, plasticizers and additives are lost. At the temperature ranging from 400 to 550°C NR, SBR and BR are decomposed. The particle is practically de volatilized at higher temperatures than 550°C. Then, the particle contains only fixed carbon black and inorganic matter (ash).
References:


5. PYROLYSIS AND COMBUSTION OF SCRAP TIRE
M. Juma, Z. Korňová, J. Markoš, J. Annus, L. Jelemenský
Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37
February 28, 2006


4: – APPENDIX

Tire mechanical milling - Appendix 1
Recycling of waste tire-Appendix 2
Evaluation of Waste Tire de vulcanization technologies- Appendix 3
Tire incineration- Appendix 4
Kinetic modeling of pyrolysis of scrap tires- Appendix 5a
Pyrolysis and combustion of scrap tire - Appendix 5b
A Laboratory Set-Up with a Flow -Appendix 6
Preparation of Rubber Composites from Ground Tire Rubber Reinforced with Waste-Tire Fiber Through Mechanical Milling

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ABSTRACT: Composites made from ground tire rubber (GTR) and waste fiber produced in tire reclamation were prepared by mechanical milling. The effects of the fiber content, pan milling, and fiber orientation on the mechanical properties of the composites were investigated. The results showed that the stress-induced mechnanochemical devulcanization of waste rubber and the reinforcement of devulcanized waste rubber with waste-tire fibers could be achieved through comilling. For a comilled system, the tensile strength and elongation at break of revulcanized GTR/fiber composites reached maximum values of 9.6 MPa and 215.9%, respectively, with 5 wt % fiber. Compared with those of a composite prepared in a conventional mixing manner, the mechanical properties were greatly improved by colilling. Oxygen-containing groups on the surface of GTR particles, which were produced during pan milling, increased interfacial interactions between GTR and waste fibers. The fiber-filled composites showed anisotropy in the stress-strain properties because of preferential orientation of the short fibers along the roll-milling direction (longitudinal), and the adhesion between the fiber and rubber matrix was improved by the comilling of the fiber with waste rubber. The proposed process provides an economical and ecologically sound method for tire-rubber recycling. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4087–4094, 2007

Key words: adhesion; fibers; recycling; rubber; waste

INTRODUCTION

The disposal problems created by waste-rubber vulcanizates is a serious challenge to our society because they do not decompose easily. Much research has been conducted to solve this worldwide problem,1–5 and one approach is to devulcanize ground tire rubber (GTR)6–9 to break up the three-dimensional network in vulcanized rubbers. The devulcanized rubber becomes soft and can be reprocessed, shaped, and revulcanized in the same way as virgin rubber.10 One of the drawbacks of such devulcanizates is a weaker matrix. One way of overcoming this problem is the use of short fibers, which impart good strength and stiffness to the rubber matrix. Short-fiber-reinforced elastomers have been successfully used in the production of hoses, V-belts, tire treads, seals, and complex-shaped mechanical goods.11 The properties of short-fiber-reinforced composites mainly depend on the type and concentration of the fiber, the orientation and distribution of the fiber after mixing, the aspect ratio of the fiber, and the degree of adhesion between the fiber and the matrix.12,13 The interfacial bond is known to play an important role in composites because this interface is critical to the composite performance. Waste fibers represent another type of environmental problem and are normally disposed of in controlled dumps or subjected to expensive recycling processes. In the process of tire recycling, approximately 10% waste fibers are obtained. These large quantities of byproducts contain about a 30–35% loading of waste-rubber powder. A process that could use these types of wastes would represent an important environmental benefit and great economic savings for the community.

Recently, a new technique for pulverizing plastic pellets to fine powders and recycling GTR based on a stress-induced reaction has been developed in our laboratory.14–16 The technique provides high-volume production of fine or ultrafine rubber powders by pulverizing large elastomer chips or particles from scrap rubber at the ambient temperature and is feasible for rubber recycling on an industrial scale. In addition, the processing properties and compatibility of the GTR powder with other polymeric compo-
nents are improved through a stress-induced reaction due to surface activation through mechanochemical devulcanization of rubber via the breakage of \(-\text{S}=-\text{S}=-\) bonds induced by stress. The main purpose of this study is to examine the possibility of making composite materials by recycling large amounts of waste tires and waste-tire fibers produced by rubber reclamation. The effects of the fiber content, mechanical milling by the pan-milling equipment designed in our laboratory, and fiber orientation on the mechanical properties of the composites were investigated.

**EXPERIMENTAL**

**Materials**

The reclaimed rubber powder (60 mesh) used in this study was generated by cryogenic grinding of passenger-car and light-truck tires. The waste short fiber used was the byproduct of tire reclamation. Other compounding ingredients, such as zinc oxide, stearic acid, sulfur, and N-cyclohexyl benzothiazyl sulfenamide (CBS) were reagent-grade and were obtained commercially.

**Mechanical milling equipment**

GTR and its mixture with waste short fibers were milled with a pan-mill mechanochemical reactor. Figure 1 is a simple scheme of the equipment, and Figure 2 shows the structure of its key part, the milling pan. A chain-transmission system and a screw-pressure system are set to regulate the rotation speed of the moving pan and imposed load, respectively, which can strictly control two major dynamic parameters, the velocity and force during milling. Cooling water flows through the hollow interior of the pan to take away the heat generated during milling; through the control of the flow, the milling temperature is adjustable. The milling process of the solid mass in the equipment operates as follows: the materials are fed to the center of the pan from the inlet, driven by a shear force, and move along a spiral route toward the edge of the pan until they come out from the outlet; thus, one cycle of milling is finished.

**Devulcanization of GTR and comilling with waste fibers**

In this study, a pan-mill mechanochemical reactor was developed to partly devulcanize GTR at the ambient temperature. Reclaimed rubber powder was milled at the ambient temperature for a certain number of cycles at a rotation speed of 30 rpm, the average residence time of coarse rubber powder during milling was 25–40 s per cycle, and the heat produced during milling was removed by water circulation. Pan-milled GTR was sampled to measure the gel fraction. To improve the adhesion between
the fiber and rubber matrix, the comilling of waste fibers with GTR was conducted.

Preparation of the rubber mixes and vulcanizates

The formulations used for the preparation of the composites are given in Table I. Mixing was carried out on a conventional laboratory two-roll mill at a friction ratio of 1:1.2 according to ASTM D 3184-80. The roll temperature was kept at about 50°C during mixing. Waste fiber was separated manually and added in small increments to obtain a uniform dispersion. The compounds were rolled along the milling direction and resent through the mill to obtain the maximum fiber orientation in the milling direction. The sheeted rubber compound was conditioned at room temperature for 24 h before vulcanization. Each sample was cured in a hydraulic press at 150°C under 10 MPa of pressure for 15 min.

Mechanical property testing

The green strength values were determined with dumbbell-shaped samples obtained from unvulcanized composites at a crosshead speed of 500 mm/min in an Instron 4302 universal testing machine. The stress-strain properties were measured according to ASTM D 412-80 specifications with dumbbell specimens. The tear strength was determined per ASTM D 624-81 with angular tear specimens. At least five measurements for each composition were made. The hardness of the composite was measured with a Shore A durometer according to ASTM 2240.

Determination of the gel fraction of the devulcanized rubber

The gel fractions of GTR obtained at different milling cycles were measured by the Soxhlet extraction method with toluene as a solvent. The specimens (ca. 1 g) were accurately weighed (M₁), closed in filter paper, and extracted with toluene. The extracted samples were then placed in a vacuum chamber and dried at 60°C for 4 h so that the solvent would vaporize, and the dry, insoluble part was obtained. This yielded the weight of the dried sample (M). The gel fraction was determined as follows:

\[
\text{Gel fraction (\%)} = \frac{M}{M_1} \times 100\%
\]

Electron spectroscopy for chemical analysis (ESCA) measurements

To determine the introduction of the functional groups into the GTR particles, the surfaces of the GTR particles at different milling cycles were analyzed with ESCA. The ESCA measurements were made with an XSAM-800 photoelectron spectroscope (Kratos Analytical, Manchester, UK). The instrument used a nonmonochromatic Mg Kα X-ray source.

Scanning electron microscopy (SEM) observation

The morphology of the fiber surface and fractured surface of the composite was observed under a JEOL JSM-5600 scanning electron microscope (JEOL Ltd., Akishima, Japan). A thin layer of a Pd–Au alloy was coated onto the specimen to prevent charging on the surface. The scanning electron microscope was operated at 20 kV. The fractured surface of the composites was prepared through the freezing of the composite in liquid nitrogen and then rapid breaking above the surface of liquid nitrogen.

RESULTS AND DISCUSSION

Stress-induced mechanochemical devulcanization of waste vulcanized rubber

The gel fractions and tensile properties of devulcanized rubber and revulcanized rubber are shown in Table II. Pan milling has the effect of simultaneous degradation (the breakage of the carbon bonds at

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Formulations of the Vulcanized Systems</th>
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<tbody>
<tr>
<td>Material</td>
<td>Weight per 100 parts of rubber powder</td>
</tr>
<tr>
<td>Reclaimed rubber powder</td>
<td>100 (milled or without milling)</td>
</tr>
<tr>
<td>Waste short fiber</td>
<td>0, 5, 10, 15</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>2</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
<tr>
<td>CBS</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.5</td>
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</table>

<table>
<thead>
<tr>
<th>TABLE II</th>
<th>Gel Fractions and Tensile Properties of Devulcanized Rubber and Revulcanized Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Gel fraction (%) of devulcanized rubber</td>
</tr>
<tr>
<td>Without milling</td>
<td>90.3</td>
</tr>
<tr>
<td>Milled for 5 cycles</td>
<td>88.4</td>
</tr>
<tr>
<td>Milled for 10 cycles</td>
<td>86.5</td>
</tr>
<tr>
<td>Milled for 15 cycles</td>
<td>81.3</td>
</tr>
</tbody>
</table>
the backbone of the rubber) and devulcanization (the breakage of the sulfur–sulfur crosslinking bond) on GTR. The results show that for 60-mesh reclaimed rubber powder, 10 cycles of milling are optimum for the devulcanization of GTR. Up to 15 cycles, the degradation of the rubber backbone is predominant, and this results in the deterioration of the mechanical properties. Therefore, 10 milling cycles were performed for all the compositions in this study.

Effects of the waste-fiber content and pan milling on the mechanical properties

The effects of the waste-fiber content and pan milling on the tensile strength and elongation at break are shown in Figures 3 and 4, respectively. In Figures 3 and 4, “without milling” represents blends of raw GTR and waste fiber prepared in a conventional mixing manner; that is, the waste fiber was separated manually and added to the compounds during open two-roll mixing. “Milling” represents blends of pan-milled GTR and waste fiber prepared in a conventional mixing manner, and “comilling” represents GTR/waste-fiber composites in which waste fibers were comilled with GTR. The experimental results indicate that the tensile strength and elongation at break of the blends decrease with the fiber content, except for the comilled system. The deterioration of the tensile properties of the composites prepared in a conventional mixing manner can be attributed to the poor adhesion of waste fibers to the rubber matrix. During straining, voids at the ends of the fibers will be created and hence initiate crack development. The probability of failure increases as a result of the number of voids increasing with the fiber content.17

In the case of the comilling system, the reinforcement of waste fiber on GTR can be observed up to a fiber content of 15 wt %. The tensile strength and elongation at break of revulcanized GTR/waste-fiber composites reached maximum values of 9.6 MPa and 215.9%, respectively, with 5 wt % fiber. Better bonding of the short fiber to the rubber matrix is the main reason for the composites. Because of its unique structure, the pan-mill equipment acts as three-dimensional scissors during milling, exerts strong shear forces, and shows multiple functions, such as pulverization, dispersion, mixing, and activation on the materials undergoing mechanical action. During the comilling of the fibers with GTR, the size reduction and surface activation of the particles are predominant in the initial milling stage. Table III exhibits the variation of the elemental concentration on the GTR particle surface during pan milling; this was obtained from ESCA spectra. The oxygen concentration on the GTR particle surface increases with increasing milling cycles. The increase in the number of oxygen-containing groups on the surface of GTR particles indicates that reactions occur between the oxygen in air and the free radicals generated during pan milling. The introduction of the polar groups containing

### Table III
Variation of the Elemental Concentrations on the GTR Surface During Pan Milling

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without milling</td>
<td>96.46</td>
<td>3.17</td>
<td>0.37</td>
</tr>
<tr>
<td>Milled for 15 cycles</td>
<td>94.82</td>
<td>4.74</td>
<td>0.44</td>
</tr>
<tr>
<td>Milled for 25 cycles</td>
<td>94.43</td>
<td>5.10</td>
<td>0.47</td>
</tr>
</tbody>
</table>
oxygen facilitate interfacial interactions between GTR and waste fibers and thus enhance the interfacial adhesion. According to Hanafi, strong adhesion between the fiber and rubber matrix results in higher shear strength at the interface, and a stronger force must be used to overcome the shear strength at the interface, which results in a higher tensile strength.

Another reason is that the strong shear force exerted by pan milling can homogeneously distribute fibers in the matrix. Because of the brittle nature of the short fiber, extensive breakage of the fiber occurs during pan milling, and this subsequently improves fiber dispersion.

However, the tensile strength and elongation at break show that the effective reinforcement of devulcanized GTR with waste fiber takes place only below a fiber content of 20 wt %. At higher fiber contents, the matrix cannot effectively wet all the fibers, and the strength decreases.

The results for the tensile properties given in Figures 3 and 4 show that the waste fiber without commilling with GTR cannot effectively reinforce a devulcanized GTR matrix.

Figures 5 and 6 show the results of the modulus at 100% elongation and the hardness of the GTR/waste-fiber composites, respectively. The elongation at break of the without-milling system with a fiber content of 15 wt % is smaller than 100%, so its 100% modulus cannot be obtained. The addition of waste fibers to the GTR matrix leads to an increase in the 100% modulus and Shore A hardness because of the stiff nature of the short fibers. However, the tensile modulus shows a sharp decrease at a fiber content of 20 wt %. This can be ascribed to the poor dispersion of short fibers in the rubber matrix with fiber contents up to 20 wt %; the tendency of stress transfer from the matrix to the fibers decrease, so the tensile modulus decreases.

As shown in Figure 5, the comilled composites show the highest value of the 100% modulus because of the better adhesion of waste fibers in the rubber matrix and improved fiber dispersion in the matrix. The stronger adhesion at the fiber and matrix interface causes better stress transfer from the matrix into the fibers, thus leading to a higher tensile modulus.

The effects of the waste-fiber content and pan milling on the tear strength show that the tear strength of the composites increases with increasing fiber contents up to 20 wt %. The tear strength is minimum for the composite obtained without milling (Fig. 7). The experimental results for the effects
of pan milling on the mechanical properties of the composites indicate that comilling waste fibers with GTR is essential to improving the fiber dispersion in the matrix and the adhesion between the waste fiber and rubber matrix.

**Effects of the short-fiber orientation on the mechanical properties**

Table IV displays the effects of the short-fiber orientation on the tensile strength, elongation at break, 100% modulus, and tear strength of the composites and indicates that all of them have higher values in the longitudinal direction than in the transverse direction. The short fibers align themselves along the two-roll-milling direction, inducing anisotropy in the properties.\(^3\) As reported by Sreeja and Kutty,\(^4\) in the longitudinal direction, the fibers increase the overall strain resistance and hinder the growing crack front and hence higher tensile strength values; the smaller values of the tear strength in the transverse direction result from the inability of fibers aligned parallel to the crack propagation to block the advancing crack front.

The green strength values of comilled composites obtained from unvulcanized composites also confirm the preferential orientation of the fibers in the two-roll-milling direction. The green strength of short-fiber-reinforced unvulcanized composites depends on the degree of fiber orientation, and so the latter can be obtained as follows:\(^5\)

\[
\text{Fiber orientation (\%) } = \frac{S_L}{S_G} \times 100\%
\]

where \(S\) represents the green strength and subscripts \(G\), \(L\), and \(T\) represent gum, longitudinal, and transverse, respectively.

The variation of the fiber orientation percentage of the composites with various amounts of fiber is shown in Figure 8. The fiber orientation percentage increases with increasing fiber content up to 15 wt % and then decreases with further increasing fiber content. According to Geethamma et al.,\(^6\) at low levels of the fiber content, the fibers can assume a multitude of alignment directions, and the freedom of

---

**TABLE IV**

<table>
<thead>
<tr>
<th>Sample(^a)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>100% modulus (MPa)</th>
<th>Tear strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt % L</td>
<td>9.6</td>
<td>215.9</td>
<td>4.4</td>
<td>16.6</td>
</tr>
<tr>
<td>5 wt % T</td>
<td>8.2</td>
<td>202.7</td>
<td>3.9</td>
<td>12.7</td>
</tr>
<tr>
<td>10 wt % L</td>
<td>8.4</td>
<td>187.5</td>
<td>4.9</td>
<td>16.5</td>
</tr>
<tr>
<td>10 wt % T</td>
<td>7.2</td>
<td>174.6</td>
<td>4.3</td>
<td>15.2</td>
</tr>
<tr>
<td>15 wt % L</td>
<td>8.6</td>
<td>189.3</td>
<td>5.0</td>
<td>16.9</td>
</tr>
<tr>
<td>15 wt % T</td>
<td>7.4</td>
<td>197.3</td>
<td>4.0</td>
<td>14.7</td>
</tr>
<tr>
<td>20 wt % L</td>
<td>7.0</td>
<td>185.6</td>
<td>4.0</td>
<td>18.3</td>
</tr>
<tr>
<td>20 wt % T</td>
<td>6.8</td>
<td>182.5</td>
<td>4.1</td>
<td>13.5</td>
</tr>
</tbody>
</table>

\(^a\) L, longitudinal; T, transverse.

---

**Figure 8** Variation of the fiber orientation percentage with the fiber content.

**Figure 9** SEM micrograph of waste fibers.
movement is greater. When the fiber content is up to 20 wt %, the fibers cannot orient themselves in the unidirectional fashion that occurs in composites containing less fiber content because of entanglement as a result of the overpopulation of fibers.

However, the degree of anisotropy in the tensile strength is lower than that in the composite of short fibers and virgin rubber reported by Geethamma et al.\textsuperscript{22} The main reason is that the preferential orientation of fibers in the two-roll-milling direction is more prominent if the fibers are well bound to the matrix. Again, the length-to-diameter ratio of the fibers significantly decreases during pan milling, and this consequently leads to the degree of anisotropy decreasing.

**SEM observations**

Figure 9 shows an SEM micrograph of waste fibers used in this study and produced in waste-tire reclamation; the filaments are long and continuous. The waste fiber consists of adhered fiber and rubber particles, and this kind of structural feature will lead to the poor distribution of the fiber in the rubber matrix. This factor, together with the poor adhesion of waste fibers to the rubber matrix, is responsible for the deterioration of the mechanical properties of the composites without comilling.

SEM fractographs of reprocessed GTR sheets from GTR before and after mechanochemical devulcanization are displayed in Figure 10(a,b), respectively. The reprocessed GTR sheets from undevulcanized GTR exhibit a rough surface, and the rubber particle adhere loosely with many voids, which lead to poor mechanical properties. As for the reprocessed rubber sheets prepared from ground GTR obtained by pan milling, the rubber particles are tightly bond and form a continual structure because of devulcanization induced by stress, which is favorable to the improvement of the mechanical properties of the milled sample.

The improvement in the mechanical properties of the rubber composites obtained through comilling is supported by the morphology of the fractured surface. SEM micrographs of the fractured surfaces of comilled composites with 5, 10, and 20 wt % fiber concentrations are shown in Figure 11(a–c), respectively. The SEM micrographs of the comilled composites show stronger adhesion occurring at the fiber/matrix interface, at which the fiber is strongly

---

**Figure 10** SEM fractographs of reprocessed GTR sheets (a) from GTR before and after (b) mechanochemical devulcanization.

**Figure 11** SEM fractographs of GTR/waste-fiber composites prepared via comilling with various fiber contents: (a) 5, (b) 10, and (c) 20 wt %. 

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bonded to the rubber matrix, even at a fiber content up to 20 wt %. As a result, the mechanical properties of the comilled composites are improved. However, the fractured surface of similar composites prepared without comilling, displayed in Figure 12(a,b), exhibits weak interfacial adhesion between the fiber and rubber matrix. Failure will occur easily at the weak interface between the fiber and rubber matrix when stress is applied. In addition, the fiber orientation can be observed from the SEM micrographs of the composites.

CONCLUSIONS

On the basis of this investigation, it is concluded that the reinforcement of devulcanized GTR with waste-tire fibers can be achieved without any compatibilizer or fiber modification. The compatibilizing effect and adhesion between the waste-tire fiber and waste-rubber matrix can be greatly enhanced by the comilling of waste fibers with waste rubber. The variation of the elemental concentration on the GTR surface has confirmed that oxygen-containing groups are introduced onto the surface of GTR particles during pan milling and subsequently increase interfacial interactions between GTR and waste fibers. Meanwhile, the dispersion of fiber into the rubber is also improved. The mechanical properties of the composites are consequently enhanced. The reinforcement of waste-tire fiber on waste rubber is explained on the basis of the stress transfer from the matrix into the fibers according to the interfacial adhesion. The deterioration of the mechanical properties at a higher fiber loading may be attributed to the volume effect of the filler. The fiber-filled composites show anisotropy in the stress–strain properties because of the preferential orientation of the short fibers along the two-roll-milling direction (longitudinal), which is substantiated by the results for the green strength. The proposed process provides an efficient method for GTR recycling to produce rubber composites with acceptable mechanical properties.

References

Reclamation and recycling of waste rubber

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Abstract

One of the various problems which mankind faces as it enters into the 21st century is the problem of waste disposal management. Since polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem. Large amounts of rubbers are used as tires for aeroplanes, trucks, cars, two-wheelers etc. But after a long run when these tires are not serviceable and discarded, only a few grams or kilograms of rubber (<1%) are abraded out from the tire. Almost the entire amount of rubber from the worn out tires is discarded, which again needed very long time for natural degradation due to crosslinked structure of rubbers and presence of stabilizers and other additives. This poses two major problems: the wastage of valuable rubber and the disposal of waste tires leading to environmental pollution. Two major approaches to solve this problem are the recycle and the reuse of used and waste rubber, and the reclaim of rubber raw materials. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer recycling; Polymer stabilization; Polymer disposal; Polymer reuse

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1. Introduction

One of the various problems which mankind faces as it enters into the 21st century is the problem of waste disposal management. Since polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem. Large amounts of rubbers are used as tires for aeroplanes, trucks, cars, two-wheelers etc. But after a long run when these tires are not serviceable and discarded, only a few grams or kilograms of rubber (<1%) are abraded out from the tire. Almost the entire amount of rubber from the worn out tires is discarded, which again need very long time for natural degradation due to crosslinked structure of rubbers and presence of stabilizers and other additives. This poses two major problems: wastage of valuable rubber and disposal of waste tires leading to environmental pollution. Two major approaches to solve this problem are recycle and reuse of used and waste rubber, and reclaim of rubber raw materials.

2. Reuse of waste rubber products

Polymers may be divided into two main groups: thermoplastics and thermosetting materials. Thermoplastics soften when heated, and so may be molded and then cooled to obtain the desired
shape. In principle, this process may be repeated either by direct reheating or preferably after grinding into granules, of scrap products. Thermosetting materials like rubbers on processing and molding are crosslinked, and therefore cannot be softened or remolding by heating again. Chemical additives (mostly in minor quantities) are generally incorporated into both thermoplastics and thermosets as stabilizers, flame-retardants, colorants, plasticizers etc. to optimize product properties and performance. Thus thermoplastics are more readily recyclable than thermoset polymers and rubbers. Thus recycling of thermoplastics simply involves a reversible physical change by heating the resin above its processing temperature for shaping it and then cooling it to room temperature to obtain the desired recycled product. But in case of thermosetting materials like rubbers recycling is not easy. The three dimensional network of the thermoset polymer system must be broken down either through the cleavage of crosslinks, or through the carbon–carbon linkage of the chain backbone. This is a much more severe process and the fragmented products obtained by such cleavage are entirely different from the starting thermoset or even its precursor thermoplastics material. Thus recycling of thermoplastics is less troublesome and so the technology for its refabrication is both well established and economical. Thus a recycled thermoplastic material competes directly with the virgin polymer. Its commercial viability depends upon the performance/cost benefit of the finished product. In contrast, the technology for recycle of thermoset polymers including rubbers is complex, costly and less viable commercially.

In case of recycling of thermoplastics, reclaim thermoplastics are used along with virgin resins and fresh additives in the formulation to obtain desired properties in the product. As with the properties of recycled plastics which undergo significant reduction of physical property in its recycle, still it retains an acceptable fraction of virgin resin properties [1]. Similar picture is also found in reclaim rubber. Although reprocessing of thermoset is difficult still the use of reclaimed/ reground thermoset resins in new polymer formulations is found with some influence on flow and deformation characteristics during processing. Perhaps these are used as fillers. Whereas crosslinked elastomers (thermosets) are easily reclaimed to a thermoplastic mass suitable for subsequent crosslinked product although remaining present in a virgin matrix polymer. Although chemical conversion of waste thermoplastic materials can regenerate their respective monomer providing value added products but till date there is no such endeavor to regain monomeric constituent from corresponding elastomeric waste.

2.1. Waste rubber as landfills

Landfill is one of the early ways of disposal of discarded rubber products. In 1977, approximately 70% of the scrap rubber, primarily as tires, were discarded as landfills [2]. But with the decreasing scope of available sites and due to the corresponding cost explosion [3] this process of waste rubber disposal is no longer feasible. Landfilling with waste tire is, also the most unwanted due to environmental problems and has no future possibility.

The current rubber waste situation is presented in Table 1. At the end of 1950s, only about one fifth of the rubber hydrocarbon used by the United States and Europe was reclaimed. By the middle of 1980s less than 1% of the worldwide polymer consumption was in the form of reclaim. At the beginning of 20th century half of the rubber consumed was in the form of reclaim. It is expected that in 21st century most of the scrap rubber will be recycled in the form of reclaim because of day to day increase in environmental awareness. From Table 1 it is seen that except France and Italy [4] the tendency to use scrap rubber as a landfill is decreased. Some countries have already banned the use of discarded tire for landfilling. Tires discarded in landfills tend to float on top causing: mosquito breeding and illegal tire
disposal are creating problems which can be minimized by recycling. Different ingredients such as stabilizers, flame retardants, colorants, plasticizers etc. were mixed with rubber during compounding. After discarding the tires for landfilling there is a probability of leaching small molecular weight additives from bulk to the surface and from surface to the environment. These small molecular weight additives are not ecofriendly and may kill advantageous bacteria of soil. In this way landfill causes serious environmental problem.

Among various methods the least desirable disposal method is discarding the article (or material). This is a situation where not only no value is added to the waste material, but in fact, the value added is negative because of the implicit cost of: (i) transporting the material to the landfill site; and (ii) establishing and maintaining the landfill to satisfy environmental requirements.

2.2. Scrap rubber as fuel source

Sometimes scrap rubber is used as a fuel. 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 that for coal of 18.6–27.9 mJ/kg (ca. 8000–12,000 Btu/lb) [5]. Shredded tire chips have been burnt in boilers, but tire grinding and size reduction problem have set back the use of tire chips in boiler. Transportation of tire scrap can cost $0.05/kg, exclusive of grinding costs. The cost of burning one metric ton of tires per hour in an incinerator was ca. $0.20–0.40 per tire in 1974, which increased to $0.35–$0.70 per tire in 1987, and now it is increased further.

The Oxford Energy Company incinerates tires and produces electricity. The facility generates 14.4 mW of electricity and costs $38 × 10 [6]. Thus in the incineration process discarded rubber is used as a fuel to generate electricity, steam etc. This process is still in use. But it creates new problem of air pollution and is also a low value recovery process of the waste rubber.

An environmentally friendly process [6] was developed for recycling rubber waste materials such as waste tires to generate valuable fuels or chemical feedstocks in a closed oxidation process which is free of hazardous emissions. The process involves breakdown of rubber polymer materials by selective oxidation decoupling of C–C, C–S and S–S bonds by water as a solvent at or near its supercritical condition. Adkins [7] invented a method of processing used tires for the recovery of oil, steel, vinyl chloride and carbon. The process includes adding a shredded automobile tire to a batch of isocyanide, polyurethane, latex and soybean oil. The resultant mixture was then heated at 700°F for 10 min to obtain the products. The addition of soybean oil to the bath mixture provides a safer and more economical process.
3. Reclaiming from rubber products

Reclaiming of scrap rubber is, therefore, the most desirable approach to solve the disposal problem. Reclaiming of scrap rubber products, e.g. used automobile tires and tubes, hoses, conveyor belts etc. is the conversion of a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a two dimensional, soft, plastic, more tacky, low modulus, processable and vulcanizable essentially thermoplastic product simulating many of the properties of virgin rubber. Recovery and recycle of rubber from used and scrap rubber products can, therefore, save some precious petroleum resources as well as solve scrap/waste rubber disposal problems. Many attempts have been made since 1910 [8–17] for reclaiming of scrap rubber products. However, reclaiming process may be broadly classified into two groups: physical reclaiming processes and chemical reclaiming processes. In a review, Warner [18] has summarized various methods of devulcanization using chemical and physical processes.

3.1. Reclaiming of rubbers by physical reclaiming processes

In a physical reclaiming process scrap/waste rubber products is reclaimed with the help of external energy. Thus in physical reclaiming process three-dimensional network of crosslinked rubber breaks down in presence of different energy source. Due to the breaking of network structure macromolecular rubber chain is transformed into small molecular weight fragments so that it can be easily miscible with the virgin rubber during compounding. So reclaim rubber produced by physical reclaiming process may be used as a non-reinforcing filler. But if in this process a specific amount of energy is used which is sufficient to cleave only the crosslink bonds then after reclaiming a good quality of reclaim rubber will be obtained which will be thermoplastic in nature and compare well with virgin rubber properties. Different types of physical reclaiming processes are: (i) mechanical [19–21]; (ii) thermo-mechanical [22]; (iii) cryo-mechanical [23–28]; (iv) microwave [29–31]; and (v) ultrasonic [32–38].

3.1.1. Mechanical reclaiming process

In mechanical reclaiming process crumb rubber is placed in an open two-roll mixing mill and milling is carried out at high temperatures. In this process drastic molecular weight breakdown takes place due to mechanical shearing at high temperatures. In one patent by Maxwell [39] a physical process of reclaiming of vulcanized rubber and refining of the reclaimed rubber are described. The vulcanized rubber in particulate form (e.g. ground tire) is reclaimed with reclaiming agents by passing the rubber between an essentially smooth stator and an essentially cylindrical rotor arranged to provide an axial shear zone in which the rubber is frictionally propelled by the rotor action. The action may be assisted by mixing a suitable amount of previously reclaimed rubber or of vulcanized rubber with or in advance of the particulate vulcanized rubber, and/or by supplemental heating. In other aspects of the invention previously reclaimed and vulcanized rubber is similarly fed and acted upon as substitute for conventional refining operation. De and co-workers [19] reported the mechanical reclaiming process of vulcanized NR. The reclaimed natural rubber was prepared by milling vulcanized sheets at about 80°C. On a two roll laboratory mill it formed a band on the roll. Next, it was mixed with various rubber additives. In another case, mixing of reclaim rubber (RR) with fresh rubber in various proportions and study of their curing characteristics, mechanical properties etc. were done. But the Mooney viscosity of the reclaimed rubber was very high (>200, i.e. out of scale) indicating that the plasticity of rubber was very low due to the presence of higher percentage of crosslinked rubber. But the extent of reclaiming,
i.e. percentage of sol/gel fraction, molecular weight of the sol fraction, and the influence of milling parameters on the Mooney viscosity were not reported.

Study of the curing characteristics of the blends of fresh rubber with reclaim rubber indicated that with increase in the reclaim rubber content the cure rate increased but the scorch time, optimum cure time and reversion resistance decreased. As the proportion of reclaim rubber in the blends increases modulus, abrasion loss, compression set and hardness increase while tensile strength, elongation at break, tear strength, resilience and flex resistance decrease. The above result shows that increase in the proportion of reclaim rubber increases the crosslink density. As crosslink density is very high for the NR/RR (25/75) blend so modulus is high but tensile strength and flex properties are low. Thus reclaim rubber appeared to perform as a non reinforcing filler in this study.

3.1.2. Thermo-mechanical reclaiming process

This process [22] involves the thermo-mechanical degradation of the rubber vulcanizate network. The vulcanizate is swollen in a suitable solvent and then transferred to a mill to form a fine powder (∼20 μm diameter). This powder rubber is revulcanized with curing ingredients. The products thus obtained show slightly inferior properties to those of the original vulcanizates.

3.1.3. Cryomechanical reclaiming process

In the mid 1960s, the technique of grinding scrap rubber in cryomechanical process [23–28] was developed. This reclaiming process involves placing small pieces (1" × 1" × 1/2") of vulcanized rubber into liquid nitrogen which are transferred to a ball mill and ground in presence of liquid nitrogen to form a fine powder. The particle size of the cryo-ground rubber varies from 30 to 100 mesh for most products. The particle size is controlled by the immersion time in the liquid nitrogen and by the mesh size of screens used in the grinding chamber of the mill.

Generally, the cost of the ground rubber increases as the particle size decreases. The cost of 40 mesh ground rubber is usually in the mid to high twenty cents per pound area, while smaller particle sizes like 80–100 mesh cost $0.30–$0.40 per pound [40–45]. It has been reported that using 5–10 phr cryogenically ground rubber in various passenger and truck tire compounds shows some economic advantage [46]. The economic benefit for a modest usage (5%) in passenger tires and truck tires has been estimated at approximately $0.10 and $0.54 per tire, respectively. At the 10% usage level the economic benefit correspondingly doubles [47] as shown in Table 2.

In 1991 Klingensmith [48] evaluated the performances of cryogenically ground butyl rubber in the tire inner liner. He showed the effect of mesh size on percent retention of physical properties (Table 3).

3.1.3.1. Processing and mixing of cryogenically ground rubber [48]. In the processing of cryogenically ground rubber certain particle sizes are more suitable in specific applications.

**Extrusion:** 80–100 mesh cryogenically ground rubber is needed to avoid fracturing and rough edges. In extrusion of thick section 50–60 mesh cryogenically ground rubber can be used depending on the surface smoothness of the final product. The optimum level of cryogenically ground rubber to be added to fresh rubber is 5%.

**Calendering:** for optimum surface smoothness of products which are 0.060" or less thick, the compound requires 80–100 mesh cryogenically ground rubber. Where smoothness is not so important 30–60 mesh can be used. The optimum level of cryogenically ground rubber in calendering is 10%.

**Molding:** the cryogenically ground rubber in all mesh sizes can be used because all mesh sizes help in
removing trapped air during molding. The cured rubber particles provide a path for the air to escape by bleeding air from the part.

*Mold flow:* cryogenically ground rubber generally improves mold flow. Shrinkage is usually less for compounds containing cryogenically ground rubber. The shrinkage reduction is proportional to the amount of cryogenically ground rubber in the compound. So less mold flashing was found with increase in the percentage of cryogenically ground rubber.

3.1.3.2. Advantages of using cryogenically ground rubber [48]. In the cryogrinding process the equipment cost is less, operating costs are lower, productivity is increased, and the product has better flow characteristics than ambient ground rubber. The unique nature of the surface morphology of the cryoground rubber particle facilitates the ventilation of trapped air in unvulcanized rubber laminate products, particularly tires, thus reducing tendency for cure blistering. Surface oxidation of the cryoground particle is of little concern because of its inherent low surface area, thus differentiating itself from ultrafine, high surface area ambient ground filler (10–30 mesh). The particle sizes of cryoground rubber are shown in Table 4.

Mix formulations of 60 mesh cryogenically ground butyl rubber (cryofine, butyl tube reclaim) with fresh masterbatch at different proportion are shown in Table 5. Here in the compounds A–D different proportions of 60 mesh cryofine butyl rubber were mixed with master batch containing virgin butyl rubber, natural rubber, carbon black, mineral oil, stearic acid, zinc oxide, sulfur and accelerator. In formulation E, 60 mesh butyl tube reclaim was mixed with the same masterbatch.

Properties of rubber compounds of Table 5 are shown in Table 6. The data in Table 6 show that with increase in the percentage of reclaim rubber tensile strength, modulus and elongation at break decrease. Since here 60 mesh cryogenically ground rubber was used in very small amount, it should not affect that much to the tensile property of reclaim rubber containing vulcanizates. But it has been found that the tensile properties of the reclaim containing formulations (formulations B to E) are lower than those of the control formulation A.

Table 2
Cost savings per tire using cryogenically ground rubber

<table>
<thead>
<tr>
<th>Usage (%)</th>
<th>Cost savings ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In passenger tires</td>
<td>In truck tires</td>
</tr>
<tr>
<td>5</td>
<td>0.0980</td>
</tr>
<tr>
<td>10</td>
<td>0.1861</td>
</tr>
</tbody>
</table>

Table 3
Effect of mesh size on % retention of mechanical properties

<table>
<thead>
<tr>
<th>US standard screen (mesh)</th>
<th>% Retention of properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>0–5</td>
</tr>
<tr>
<td>80</td>
<td>20–30</td>
</tr>
<tr>
<td>100</td>
<td>10–25</td>
</tr>
</tbody>
</table>
Particle size also affects the tensile properties of different blends of virgin rubber with reclaim rubber, which are shown in Figs. 1–3. Fig. 1 represents for untreated ground rubber and Figs. 2 and 3 represent for treated ground rubber. From Fig. 1 it is clear that with increase in the mesh size of ground rubber tensile strength and elongation at break increase which are expected but Mooney viscosity also increases.

Table 4
Particle sizes of different cryogenically ground rubbers

<table>
<thead>
<tr>
<th>Mesh size</th>
<th>Particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>388</td>
</tr>
<tr>
<td>80</td>
<td>177</td>
</tr>
<tr>
<td>100</td>
<td>149</td>
</tr>
<tr>
<td>200</td>
<td>73.7</td>
</tr>
<tr>
<td>325</td>
<td>44.5</td>
</tr>
<tr>
<td>400</td>
<td>38</td>
</tr>
<tr>
<td>500</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 5
Mix formulations of rubber compounds

<table>
<thead>
<tr>
<th>Rubber compound</th>
<th>Formulation code</th>
</tr>
</thead>
<tbody>
<tr>
<td>(parts by weight)</td>
<td>A</td>
</tr>
<tr>
<td>Masterbatch</td>
<td>188</td>
</tr>
<tr>
<td>Cryofine</td>
<td>–</td>
</tr>
<tr>
<td>Butex (butyl tube reclaim)</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup> The amounts in percent has been calculated on 188 parts masterbatch (control). Masterbatch (phr): butyl HT-10.66: 80; RSS1: 20; N650 Carbon black: 65; Mineral Oil: 4; Durez 29095: 4; Stearic acid: 2; Sunthene 410: 8; ZnO: 3; Devil A Sulfur: 0.50 and MBTS: 1.50.

Table 6
Properties of different blends of cryogenically ground rubber

<table>
<thead>
<tr>
<th>Properties</th>
<th>Formulation code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>100% Modulus (MPa)</td>
<td>2.9</td>
</tr>
<tr>
<td>300% Modulus (MPa)</td>
<td>7.6</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>9.6</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>420</td>
</tr>
<tr>
<td>Tear strength (ppi q)</td>
<td>50</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.15</td>
</tr>
<tr>
<td>Compression set (%)</td>
<td>13.2</td>
</tr>
<tr>
<td>Air permeability (Q&lt;sub&gt;a&lt;/sub&gt;)</td>
<td>4.71</td>
</tr>
</tbody>
</table>

<sup>a</sup> Q × 10<sup>−3</sup> (ft<sup>3</sup>/0.001 in.·F psi/day).

Particle size also affects the tensile properties of different blends of virgin rubber with reclaim rubber, which are shown in Figs. 1–3. Fig. 1 represents for untreated ground rubber and Figs. 2 and 3 represent for treated ground rubber. From Fig. 1 it is clear that with increase in the mesh size of ground rubber tensile strength and elongation at break increase which are expected but Mooney viscosity also increases.
which is not desirable because with increase in the mesh size particle size of ground rubber decreases so that crosslink part in the ground rubber may also decrease. When this ground rubber is mixed with fresh rubber then plasticity of rubber compound decreases so that Mooney viscosity of the rubber compound should increase. In Fig. 2, T-608, T-609 and T-610 corresponds to 30-, 20-, 10- mesh ground rubber, respectively, with standard tire cycle treatment and in Fig. 3, T-1208, T-1209 and T-1210 corresponds to 30-, 20-, 10-mesh ground rubber, respectively, with tire cycle treatment for improved mold flow. In both
treated samples increase in tensile strength is higher but decrease in elongation at break is lower than the untreated sample. But Mooney viscosity of both the treated samples is almost same in all particle sizes.

Mix formulations of 10-, 20- and 30-mesh ground rubber at 50% loading are shown in Table 7. But from the above discussion it is clear that cryogenically ground rubber or other type of mechanically ground rubber is not possible to be used more than 10%. When higher proportion of those types of ground rubber is added with fresh rubber, the product becomes stiff and those crosslinked ground rubber site becomes the weak point of the crosslinked rubber vulcanizate. In 5–10% level it is nothing but a non reinforcing filler, because these small proportion of ground rubber cannot affect that much to the properties of finished rubber products. About 5–10% of cryoground butyl rubber have been used in

Table 7
Mix formulation of rubber compound (base formulation: zinc oxide: 5; Stearic acid: 1; Antioxidant: 2; Aromatic oil: 50; N-660: 90; MBTS: 1; Sulfur: 2 and TMTD: 0.5)

<table>
<thead>
<tr>
<th>Mesh size</th>
<th>10</th>
<th>10</th>
<th>10</th>
<th>20</th>
<th>20</th>
<th>20</th>
<th>30</th>
<th>30</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredients (phr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR 1502</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Untreated 10-mesh</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T-610</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T-1210</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Untreated 20-mesh</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T-609</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T-1209</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Untreated 30-mesh</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>T-608</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
<td>–</td>
</tr>
<tr>
<td>T-1208</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>251</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of mesh size (treated) on properties of vulcanizate (T-1208, T-1209, T-1210) (adapted from Ref. [49]).
tire innerliner but the flexing properties of mixed rubber vulcanizate have not been studied. This property is most important in tire for its long term application. When ground rubber is incorporated into fresh rubber then definitely flexing property will deteriorate because during running a tire faces cyclic stress. This cyclic stress is dissipated through the whole tire, but if some crosslinked particle is present dissipation of stress is not possible and automatically crack will generate. This is the major drawback of using cryogenically ground rubber in tire industry.

3.1.4. Other ground rubber processes

Other two types of grinding of rubber are dry ambient grinding and solution or wet ambient grinding. The first step in the manufacture of reclaim is grinding [49–52] of the rubber part to be reclaimed. It is necessary to increase the surface area of the rubber particle which increases the rate of the chemical reaction in reclaiming and also to produce more uniform product. It was found that small particle size vulcanized ground rubber could be added to the rubber compound to reduce the cost. Ground rubber used in compounding varies from 10 to 200 mesh.

3.1.4.1. Dry ambient grinding. This is nothing but a mechanical grinding technique [48]. In this process vulcanized rubber pieces are placed in a serrated grinder for preparation of ground rubber of particle sizes from 10 to 30 mesh. Ambient ground rubber is largely used in tires and mechanical goods. Generally, 5–20 phr ground rubber is used. With higher particle size of ambient ground rubber, smoothness of the product decreases. Although the name of the process is ambient grinding but the grinding in fact generates some heat during processing. With high modulus or aged compounds the amount of heat generated can be higher resulting in heating of the rubber and, therefore, degradation of polymer chain takes place. So the name “ambient grinding” is not appropriate. In ambient grinding process some pendant groups are generated which become attached to the virgin rubber matrix producing an intimately bonded mixture [48].

3.1.4.2. Wet or solution grinding. This is a modified ambient grinding process [48] that reduces the particle size of rubber by grinding in a liquid medium. The process involves putting a coarse ground rubber crumbs (10–20 mesh) into a liquid medium, usually water, and grinding between two closely spaced grinding wheels. Here the particle size is controlled by the time spent in the grinding process. In this process particle sizes of 400–500 mesh have been reported. The advantage of the fine particle wet ground rubber is that it allows good processing producing relatively smooth extrudates and calendered sheets. But whether this process helps in heat dissipation through water and reduces polymer chain breakdown is not mentioned.

3.1.5. Microwave method

In the microwave technique [29–31] a controlled dose of microwave energy at specified frequency and energy level in an amount sufficient to cleave carbon–carbon bonds is used. Thus in this process elastomer waste can be reclaimed without depolymerization to a material capable of being recompounded and revulcanized having physical properties essentially equivalent to the original vulcanizate. This method is very much useful because it provides an economical, ecologically sound method of reusing elastomeric waste to return it to the same process and products in which it was originally generated and it produces a similar product with equivalent physical properties. The devulcanized rubber is not degraded when the material being recycled [53] which normally takes place in the usual commercial
processes currently being practiced. In this process they claimed that sulfur vulcanized elastomer containing polar groups is suitable for microwave devulcanization. Tyler et al. [54] have claimed their microwave devulcanization process as a method of pollution controlled reclaiming of sulfur vulcanized elastomer containing polar groups. The microwave energy devulcanization device generates heat at a temperature in excess of 260°C to yield a mass which is fed to an extruder which extrudes the rubber at a temperature of 90–125°C. The extrudate can be used per se as a compounding stock. Another process was developed for reclaiming waste elastomers by microwave radiation. The process involves the impregnation of the waste rubber with an essential oil and then heat treating the impregnated material under reduced pressure with microwave radiation [55]. The waste material must be polar in order that the microwave energy will generate the heat necessary to devulcanize. Microwave energy between 915 and 2450 MHz and between 41 and 177 W h per pound is sufficient to sever all crosslink bonds but in sufficient to sever polymer chain degradation. The tensile properties of microwave devulcanized EPDM rubber, EPDM hose and IIR are shown in Table 8. From the Table 8 it has been found that the tensile properties of devulcanized rubber and virgin rubber-devulcanized rubber blend is almost comparable. The cost of devulcanized hose and inner tube material by microwave method is only a fraction of the cost of the original compound. The transformation from waste to refined stock ready for remixing takes place in only five minutes with usually 90–95% recovery of the rubber. Therefore, it appears that this microwave technique is an unique method of reclaiming in terms of properties and fastness of the process.

3.1.6. Ultrasonic method

After the microwave techniques, ultrasonic energy was used for the devulcanization of crosslinked rubber. The first work with ultrasonic energy was reported by Pelofsky [56] in 1973 which was patented. In this process solid rubber articles such as tires is immersed into a liquid and then it was put with a source of ultrasonic energy whereby the bulk rubber effectively disintegrated upon contact and dissolved into liquid. In this process ultrasonic irradiation is in the range of about 20 kHz and at a power intensity of greater than 100 W. But in the patent information they did not mention the ultimate properties of the devulcanized rubber. Then ultrasonic reclaiming of NR vulcanizate was reported by Okuda and Hatano [57] in 1987 which was also patented. They subjected the NR vulcanizate to 50 kHz ultrasonic energy for 20 min to achieve devulcanization followed by revulcanization and obtained reclaimed rubber with similar properties to those of original rubber. But in connection with a patent on vulcanization of rubber by ultrasonic waves Mangaraj [58] indicated a possibility of rubber degradation and devulcanization by

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>EPDM</th>
<th>IIR</th>
<th>EPDM hose</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Devulcanized EPDM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>1600</td>
<td>1520</td>
<td>1190</td>
</tr>
<tr>
<td>18%</td>
<td>1340</td>
<td>1210</td>
<td>1080</td>
</tr>
<tr>
<td>26%</td>
<td>1230</td>
<td>1300</td>
<td>1075</td>
</tr>
<tr>
<td>100%</td>
<td>1430</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% virgin, devulcanized rubber blend</td>
<td>835</td>
<td>670</td>
<td>300</td>
</tr>
<tr>
<td>Devulcanized IIR</td>
<td>175</td>
<td>400</td>
<td>250</td>
</tr>
<tr>
<td>% Devulcanized EPDM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>1600</td>
<td>1520</td>
<td>1190</td>
</tr>
<tr>
<td>10%</td>
<td>1340</td>
<td>1210</td>
<td>1080</td>
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<tr>
<td>25%</td>
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<tr>
<td>10%</td>
<td>835</td>
<td>670</td>
<td>300</td>
</tr>
<tr>
<td>25%</td>
<td>175</td>
<td>400</td>
<td>250</td>
</tr>
</tbody>
</table>
ultrasonic energy. Later Isayev and coworkers reported in a number of publications [32–38] the phenomenon of devulcanization by ultrasound energy and they also patented [59,60] their developments. But in their publications the references of Pelofsky [56], Okuda et al. [57] and Mangaraj [58] are missing.

The devulcanization process requires a high energy level to break carbon–sulfur and sulfur–sulfur bonds [18]. An ultrasonic field creates high frequency extension–contraction stresses in various media [18]. Isayev and his group also made a percolation simulation of the network degradation during ultrasound devulcanization in which they have claimed an excellent agreement of experimental data for SBR and GRT with the predicted dependence of the gel fraction of devulcanized rubber on crosslink density. Curing behavior, rheological properties, structural characteristics of devulcanized rubber from model SBR and GRT rubbers as well as mechanical properties of vulcanized rubber samples were studied and a possible mechanism of devulcanization was also discussed. They characterized the degree of devulcanization by the measurement of crosslink density and gel fraction of the devulcanized rubber. Later they have published two more papers on the ultrasound devulcanization of sulfur vulcanized SBR and on vulcanization of ultrasonically devulcanized SBR elastomers [61].

Such devulcanization experiments were carried out by an ultrasound devulcanization reactor developed for the purpose. The ultrasonic reactor is a 1.5 in. rubber extruder with L/D = 11 with a co-axial cone shaped ultrasonic die attachment. There are three temperature-controlled zones. The screw is heated electrically or cooled by water pumped from a thermostat. The die and the ultrasonic horn have sealed inner cavities for running cooling water. A flush mounted thermocouple and a pressure gauge are inserted into the barrel. The temperature and pressure of the rubber at the entrance to the die are measured by a thermocouple and pressure gauge inserted into the barrel. The scrap rubber is fed into the extruder by a conveyor belt with adjustable output. A 3 kW ultrasonic power supply, an acoustic converter, a 1:1 booster and a 3 in. cone-tipped horn are used. The horn vibrates longitudinally at a 20 kHz frequency and 5–10 μm amplitude. The whole unit is mounted on four rigid bars fixed to the extruder flange.

Isayev and co-workers [32–34] studied the devulcanization of SBR vulcanizate using the above ultrasonic reactor at various temperatures viz. 121, 149 and 176°C, different clearances at various flow rates and the ultrasonic oscillation amplitudes. The extent of devulcanization was studied by measuring percentage and crosslink density of the gel fraction. It was reported that both crosslink density and the gel fraction decrease in the devulcanization process. For original ground rubber tire the measured gel fraction is 83% and crosslink density of gel is 0.21 kmol/m³, but after ultrasound treatment at 121°C barrel temperature it reduces to 64–65% with crosslink density of 0.02 kmol/m³. The crosslink density also decreases with higher residence time in the treatment zone and with higher specific ultrasonic energy.

The mechanical properties of the revulcanized sample were also studied. With decrease in the crosslink density of the devulcanized rubber, the tensile strength of revulcanized samples varies from 1.5 to 10.5 MPa and elongation at break varies from 130 to 250%. Based on the results of mechanical properties Isayev et al. [33] proposed that the devulcanized sample having a crosslink density lower than 0.06 kmol/m³ can be regarded as overtreated, and samples with crosslink density higher than 0.10 kmol/m³ can be regarded as undertreated. Thus overtreatment causes main chain breakage and undertreatment causes insufficient devulcanization. They [34] also reported that ultrasound treatment of SBR results in low molecular weights of the sol fraction: $M_n = 2–4 \times 10^3$. Ultrasonic devulcanization, therefore, causes significant degradation of polymer chains. A simple model based on a purely topological
consideration was proposed and simulation of the process was carried out [62–65]. In the model they have assumed a breakup of the main chain bond and crosslink bonds as independent random events. Such random scission of crosslinks and main chain results in the formation of soluble branched rubber chains regarded as fragmented gel structure or microgel. It is found that during ultrasound devulcanization molecular weight of sol fraction decreases from which it may be understood that during ultrasound treatment not only C–S or S–S bonds but also C–C bonds break. Levin, Kim and Isayev [37] suggested a revulcanization scheme. They concluded that devulcanized rubber contained a larger amount of sulfidized molecules which were responsible for crosslinking during revulcanization.

3.2. Reclaiming of rubbers by chemical reclaiming processes

The majority of the reclaim rubber industries use chemical reclaiming agents for the manufacture of reclaim rubbers. These are generally organic disulfides or mercaptans which are exclusively used during mechanical working at elevated temperature. Based on these chemicals many processes have been developed and subsequently patented. Apart from these a few inorganic compounds have also been tried as reclaiming agent.

3.2.1. Reclaiming by organic disulfides and mercaptans

Many attempts have been made since 1910 for reclaiming of scrap rubber products. As a result, a large number of chemical reclaiming agents for natural and synthetic rubbers, viz. diphenyl disulfide, dibenzyl disulfide, diamy1 disulfide [66,67], bis(alkoxy aryl) disulfides [68], butyl mercaptan and thienophenols [69–71], xylene thiols [70–72] and other mercaptans [73], phenol sulfides and disulfides [74] have been developed.

Cook and co-workers [75] reported the preparation, evaluation and structural correlation of alkyl phenol sulfides as reclaiming agents for styrene butadiene rubber (SBR). The effect of these alkyl phenol sulfides as reclaiming agent was compared with that of many aromatic thiols. Reclaiming of neoprene and nitrile rubbers was also evaluated using alkyl phenol sulfides. The extent of reclaiming of these two rubbers was extensively evaluated and monitored by Mooney plasticity and manual observations, such as sheet thickness, body and tackiness by numerical ratings. The reclaiming was done at 188°C (by 175 psi superheated steam) for 4 h using 5 mesh vulcanized rubber powder. Both the total and combined sulfur in the reclaimed stock were determined, but the method of sulfur estimation was not reported.

Some $N,N$-dialkyl aryl amine sulfides [74] were shown to be highly active reclaiming agents for vulcanized SBR in both neutral and alkaline reclaiming processes, and the state of reclaiming was manually assessed through thickness, body and tack evaluation. A review of science and technology of reclaimed rubber was published by Le Beau [76] in 1967. Knorr [77] has shown the action of diaryl disulfide on the natural and synthetic rubber scraps of technical goods. In this process the finely ground fabric free scrap is heated in saturated steam at a very high temperature (150–180°C) with the addition of reclaim oil and Aktiplast 6 (contain disulfides). First finely ground scrap was thoroughly mixed with diaryl disulfide and reclaim oil and allowed to swell for at least 12 h. The material was then placed on talcum powder trays. The layer thickness should not exceed 2–3 cm to allow the oxygen to penetrate the material well. A devulcanizer (or autoclave) is needed of approximately 1.5 m diameter and 3.8 m in length. The trays with scrap are rolled into the devulcanizer. Good circulation of air and steam is necessary for the process. After having sealed the lid, the autoclave is pressurized with 4 bar of
air–steam and the fan was turned on for good air circulation. The compressed air valve was then closed and 8–9 bar steam was forced in until the temperature reached 190°C. Depending on the kind of scrap the reclaiming time varied between 3–5 h per charge (200 kg).

From physical property data (Table 9) it is clear that reclaim rubber possesses very poor mechanical properties. However, the author [77] did not mention whether any curative was used with the reclaim rubber. Schnecko [78] has reviewed the present aspects of elastomers recycling and reported the development of some chemical probes for devulcanization of crosslinked rubber. These chemical probes selectively cleave carbon–sulfur and sulfur–sulfur bonds but they do not cleave carbon–carbon bonds.

Table 10 present some information on the type of chemical probes used in chemical reclaiming processes.

Saville and Watson [81] gave a reaction mechanism for breaking of polysulfide bonds in presence of propane thiol/piperidine probe as follows:

![Reaction mechanism](image)

The thiol–amine combination gives an associate, possibly piperidinium propane-2-thiolate ion

<table>
<thead>
<tr>
<th>Name of the chemical probes</th>
<th>Attacking position of the crosslink bonds</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenylphosphine</td>
<td>Polysulfide links into monosulfide and to a lesser extent disulfide links</td>
<td>[79,80]</td>
</tr>
<tr>
<td>Sodium di-n-butyl phosphite</td>
<td>Di and polysulfide crosslinks</td>
<td>[79,80]</td>
</tr>
<tr>
<td>Propane-thiol/piperidine</td>
<td>Polysulfide linkages</td>
<td>[81]</td>
</tr>
<tr>
<td>Hexane-1-thiol</td>
<td>Both polysulfide and disulfide linkages</td>
<td>[82–85]</td>
</tr>
<tr>
<td>Dithiothreitol</td>
<td>Disulfide bonds into two thiol groups</td>
<td>[86]</td>
</tr>
<tr>
<td>Lithium aluminium hydride</td>
<td>Disulfide and polysulfide bonds</td>
<td>[87,88]</td>
</tr>
<tr>
<td>Phenyl lithium in benzene</td>
<td>Polysulfide and disulfide bonds</td>
<td>[89,90]</td>
</tr>
<tr>
<td>Methyl iodide</td>
<td>Monosulfide linkages</td>
<td>[91–95]</td>
</tr>
</tbody>
</table>
pair where sulfur atoms enhance the nucleophilic character which is responsible for cleaving organic polysulfide linkages. The cleavage of polysulfide crosslinks takes place possibly due to $p_n-d_d$ delocalization of the displaced sigma electron pair of $RSS^-$

\[
R-S-S-R \xleftarrow{\text{Pr}^+} RS^+ + S - SR (\text{Fast})
\]

(3$p$-electron delocalization within $p_n-d_d$ bond)

\[
R-S-S-R \xrightarrow{\text{Pr}^+} S - R + RS^+ (\text{Slow})
\]

(no 3$p$ electron delocalization)

Triphenyl phosphine cleaves di and polysulfide bonds in the following manner.

\[
\text{Ph}_3\text{P} \rightarrow\text{R-S-S-R} \xrightarrow{\text{Ph}_3\text{P}-\text{SR}} \text{Ph}_3\text{P}^+-\text{SR} \rightarrow \text{H}_2\text{O}
\]

\[
\text{Ph}_3\text{P} = O + H^+ + \text{RSH}
\]

Trialkyl phosphites cleave di and polysulfide bonds in the following manner:

\[
x(R\text{O})_3\text{P} + R\text{SSxSR}' \rightarrow x(R\text{O})_3\text{PS} + R\text{SSR}'
\]

\[
(R\text{O})_3\text{P} + R\text{SSR}' \rightarrow (R\text{O})_3\text{P}^+\text{SR}' \rightarrow R\text{SR} + \text{OP(SR')}(\text{OR})
\]

(R = alkyl e.g., ethyl, $R'$ = alkyl or aryl)

Lithium aluminium hydride (LAH) reacts with polysulfides in an ethereal solvent at moderate temperatures and then with a weak acid, the terminal groups are liberated as thiols and interior sulfur atoms are converted to hydrogen sulfide [96–105].

\[
R-S-S_x-SR' \xrightarrow{\text{LAH}} \text{RSH} + x\text{H}_2\text{S} + \text{HSR}
\]

Lithium aluminum hydride under appropriate reaction conditions cleaves disulfide bonds in organic disulfide, which is structurally related to crosslinks [99] into two thiol groups.

\[
\text{RSSR}' \xrightarrow{\text{LAH}} \text{RSH} + \text{HSR}
\]

then $H^+$
Rubber network can easily be swollen by methyl iodide which can be removed therefrom by warming under vacuum. Meyer and Hohenemser [100,101] introduced the use of methyl iodide to estimate monosulfide linkages in vulcanized natural rubber. The level of network bound iodine after reaction for two to three days would reflect the concentration of monosulfide groups since simple saturated monosulfide group reacts as follows.

\[ \text{R}_2\text{S} + \text{CH}_3\text{I} \rightarrow \text{R}_2^+\text{SCH}_3\text{I}^- \]

Simple disulfides reacted very slowly with methyl iodide but their reaction and those of monosulfides could be catalyzed by mercuric iodide [102,103]. Di-n-propyl disulfide reacts as follows:

\[ \text{C} - \text{C} - \text{S} - \text{C} - \text{C} + 4\text{MeI} + 2\text{HgI}_2 \rightarrow 2[\text{C} - \text{C} - \text{S}^+\text{Me}_2\text{I}^-] + \text{HgI}_2 + \text{I}_2 \]

Only allylic sulfides breakdown easily to yield extractable trimethyl sulfonium salts [104–107].

Anderson [108] patented the reclaiming of sulfur vulcanized rubber in the presence of oil, water vapor and aryl disulfide peptizer at elevated temperature in the range of about 175–195°C and at a pressure in the range of about 230–260 psi for 1–4 h. Here aryl disulfide is a mixture of diphenyl disulfide, dicresyl disulfide and dixylyl disulfide. In another attempt rubber like product from rubber scrap was prepared by mixing rubber scrap with sulfur, antioxidant and antiozonants in an apparatus. The reclaiming was carried out at temperature of about 250–450°F and pressure of about 1000–3000 psi for 1–10 min. Sulfur bearing compounds as vulcanizing agents was added in place of free sulfur. The process is particularly suitable for making roofing products [109].

3.2.2. Reclaiming by inorganic compounds

Discarded tires and tire factory waste were devulcanized by desulfurization, in presence of sodium, of suspended rubber vulcanizate crumb (10–30 mesh) in a solvent such as toluene, naphtha, benzene, cyclohexane etc [110]. The alkali metal cleaves mono, di and polysulfidic cross linkages of the swelled and suspended vulcanized rubber crumb at around 300°C in absence of oxygen. As claimed by authors such treatment yielded a rubber polymer having a molecular weight substantially equal to that of rubber prior to vulcanization. Carbon black may also be recovered for reuse and the devulcanized rubber may be subjected to revulcanization without separation of the polymer from the solvent by addition of an appropriate curing composition. Although it appears from the patent that the developed process is a direct reversal of vulcanization without affecting the molecular weight of the polymer. The process may not be economically convenient. Because the process involves swelling of the Vulcanized rubber crumb in an organic solvent where in the metallic sodium in molten condition at the process temperature should reach the sulfidic crosslink sites in the bulk of the rubber crumb. Further to this isolation of the devulcanized product from the solvent may be hazardous and cause pollution. Although the patent has not described the vulcanization characteristics of the devulcanized rubber, the presence of NaS may decrease the scorch safety of the product. Yamashita and co-workers [111–114] have successfully reclaimed powder rubbers using an iron
oxide phenyl hydrazine based catalyst. In this process powder rubber from waste tires is treated with phenyl hydrazine and FeCl₂, ozonized and treated with H₂O₂ to give liquid rubber having higher viscosity and better yield than those of similar products without the phenylhydrazine–FeCl₂ treatment. For example, they reported that 100 g powder rubber from waste tires, 0.5 g phenyl hydrazine in 10 ml benzene and 0.25 g FeCl₂ in 5 ml MeOH were mixed and kept for a day at room temperature and rolled for 10 min. The above plasticized rubber was ozonized and treated with H₂O₂ to give liquid rubber having intrinsic viscosity (30°C in benzene) 0.05–0.11 dl/g in 13–25% yield compared with 0.03–0.05 dl/g and 15–20% yield for liquid rubber obtained without the phenylhydrazine–FeCl₂ treatment.

Thus from intrinsic viscosity data it is understood that molecular weight of reclaim rubber is very low. During reclaiming by the above process severe breakdown of rubber chains takes place. Kawabata and co-workers [115] have also reclaimed powder rubber using copper (I) chloride–tributyl amine catalyst. They successfully noted that the rate of degradation of isoprene rubber by copper (I) chloride–tributyl amine (Cu₂Cl₂–Bu₃N) mixtures decreased in the order of S-vulcanized rubber > ZnO and tetramethyl thiuram disulfide vulcanized rubber > organic peroxide vulcanized rubber. The sol content and crosslink density of the degradation products indicated that scission in the main chain was as important as breakdown at the crosslinking sites for the sulfur vulcanized and ZnO–TMTD vulcanized samples. But in case of peroxide cured vulcanizates the scission in the main chain was predominant. Therefore, it conclusively proves that during reclaiming process not only the cleavage of carbon–sulfur or sulfur–sulfur bonds takes place but also scission of carbon–carbon bonds of the polymer chain occurs.

A novel chemical reclaiming process has been patented wherein reclaiming of pulverized scrap rubber is carried out by a reclaiming composition consisting of reducing agent such as phenyl hydrazine (0.2–1.0 wt%) and diphenyl guanidine (0.2–0.8 wt%), ferrous chloride and a plasticizer [116] (17.5 weight % tall oil pitch). The reclaiming occurs in a solid phase in oxygenic gas at a temperature of at most 100°C by agitation in a powder mixture for about 30 min.

### 3.2.3. Reclaiming by miscellaneous chemicals

Vehicle tire scraps containing polyisoprene rubber, SBR, PBR was devulcanized by low temperature phase transfer catalyst. Both the devulcanizing agent composition and the process were patented. The novelty of this process lies in the use of low temperature phase transfer catalyst and a process temperature lower than 150°C. The devulcanized rubber of this invention is distinguishable from conventional reclaimed rubber in that the devulcanized rubber is substantially free from polysulfide crosslink which are selectively broken during the process with negligible main chain scission [117].

Kasai and co-workers [118] reported the use of thiocarboxylic acid as reclaiming agent for crosslinked rubber. In this process waste rubber powder of 30 mesh particle size is mixed with 0.5–10.0 wt% (based on rubber) of 10% thioacetic acid solution in benzene and left one day at room temperature; stripped of benzene and rolled at <120°C in air to give reclaimed rubber with good mechanical strength. A compound of rubber: 200, ZnO:5; stearic acid:1; sulfur:3; and vulcanizing accelerators: 0.7 parts was heated for 30 min at 145°C to give a vulcanizate having tensile strength 9.0 MPa and elongation at break 410%.

In a process of reclaiming by hydrocarbon solvent [119] waste tires are swollen at 188–200°C for 24–36 h in a mixture of aromatic hydrocarbons 38–48%, naphthenic hydrocarbons 12–28%, and paraffinic hydrocarbon 35–45%. The swollen rubber in the mixed solvent is passed through a 2 mm orifice of an extruder at 2–6 kN/cm² pressure to give a paste which is useful in the manufacturing of tire treads. A compound of rubber containing 40–60 parts of above prepared paste and 100–150 parts isoprene rubber,
butadiene rubber and SBR was heated for 15 min at 160°C to give a vulcanizate having 300% modulus 3 MPa, elongation at break 500% and Shore A hardness 62.

As a solution to waste tire disposal problem used tire was recycled by soaking the tire in an organic solvent e.g. 1,3,5-trimethyl benzene for a sufficient time while reducing its tensile strength by about 50%. Then the soaked rubber was disintegrated by applying a shear force to give a recycled rubber [120].

Scrap rubber containing natural and synthetic can be reclaimed by digester process with the use of a reclaiming oil having molecular weight between 200 and 1000 consisting of benzene, alkyl benzene and alkylated indanes. The composition of this reclaiming oil and the improved digester process using such reclaiming oil have been patented by Bryson [121].

Vulcanized rubber was also reclaimed by the action of transition metal alloys and derivatives [122]. In this process vulcanized rubber was swollen in an organic solvent and then treated with a size reduction agent e.g. transition metal alloy and their derivatives. In a typical composition 150 g of SBR rubber vulcanizate was allowed to swell in 1000 ml benzene for two days, placed in a ball mill in the presence of 2 g powder Mn for 20 h, then beaten in the presence of 0.1 (N) H2SO4 for 4 h, neutralized, washed, dried, homogenized and then compounded to evaluate the properties. The mixing formulation containing reclaim rubber 100; ZnO:0.3; stearic acid:0.2; aromatic oil:0.6; N-phenyl-N-cyclohexyl-p-phenylene diamine (antioxidant):0.1; accelerator:0.1; diphenyl guanidine accelerator:0.5, and sulfur:2.0 parts was vulcanized at 150°C for 45 min to give a vulcanizate having tensile strength 12.6 MPa, elongation at break 220%, Shore A hardness 70 and abrasion loss 5%.

2-Mercaptobenzothiazole was also found to be effective as reclaiming agent [123]. In this process powder rubber from waste tires was kneaded with process oil in the presence of 2-mercapto benzothiazole or its cyclohexylamine salt to give reclaim rubber, having Mooney viscosity 31 or 22, respectively. In a typical recipe a mixture of powder rubber:100; reclaiming agent:1; and process oil:10 g was rolled for 30 min. 100 g of the above product was mixed with N-cyclohexyl-2-benzothiozole sulfenamide:1.5, dibenzothiazyl disulfide:0.5, and sulfur:1.5 g, and vulcanized at 160°C for 10 min to give a vulcanizate having JIS hardness 53, tensile strength 11.9 MPa, and elongation at break 360%.

3.2.4. Reclaiming by chemical degradation [124]

Powder waste tire rubber was suspended in CHCl3 and blown with ozone containing oxygen at room temperature, and then treated with H2O2 to give –COOH group containing liquid rubber in 15–20% yield. The residue was treated similarly to give further yield of 5–9% liquid rubber. This liquid rubber was vulcanized in the presence of tris(2-methyl-1-aziridinyl) phosphine oxide at 100°C.

3.2.5. Pyrolysis of waste rubber

This technology involves pyrolysis of the rubber to generate gas and oil that can be used as a fuel and possibly for other applications. In Tosco-II process scrap rubber is pyrolyzed to generate maximum amount of carbon black [125–127]. Chopped tires are fed into a rotary drum containing hot ceramic balls at 480–549°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 carbon black from the ceramic balls. The carbon is pelletized after steel, fiberglass, 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 temperature produces more gas and less liquid. The pilot plant process was designed to handle 13.5 ton of tires per day, generating 0.5–0.6 m3 (3–4 bbl) of oil, 1270–1540 kg of carbon
black, 190–220 kg of steel and 154–176 kg of fiber glass [5]. But the types of blacks and residual constituents, e.g. ZnO, and other inorganic materials and glass fiber from old tires, are unpredictable. However, carbon must be carefully chosen to achieve specific properties in compounded rubbers. Thus the residue mixture is useful only as a low-grade filler and cannot be used as a carbon black source.

But it is quite clear that one cannot expect to recover hydrocarbon monomers or even oligomers from the complex rubber structures by pyrolysis. If a formulation contains 30% of carbon black or white filler plus other inorganic materials, one must expect reduced yields any way. In addition there can be the size reduction necessity for articles like tires or hose in order to facilitate heat transfer, e.g. by fluid bed energy.

Although in many laboratories, pilot plant and even commercial attempts have been made to establish economical units over the last 25 years (e.g. Kobe Steel in Japan, Tosco in USA, Tyrolysis in UK, Ebenhausen in Germany and many more) [128] but none has survived. The product spectrum is well known [129,130]. There are variations by vacuum or in presence of H₂, N₂ [131] or in molten salts like NaAlO₂ [132]. Texaco opened an experimental liquefaction unit recently for a mild cracking process below 370°C at atmospheric pressure resulting in light and heavy oil fractions [133]. It has been reported that the carbon black coming out of the reactor is of poor quality and has nothing in common with those which has been used in the original recipe [134].

4. Recent developments in reclaiming of rubbers

4.1. Biotechnological processes for reclaiming of rubber

Biological attack of natural rubber latex is quite facile [135]. Man has tried time and again to consider elastomeric articles as source for microbial attack [136]. Obviously nature is able to take care of its own waste problems but as soon as man become involved and convert the natural rubber polymer into a technical material by sulfur and numerous other ingredients, biological attack is minimized [137–139]. An interesting recent approach was reported in a patent application [140,141] to utilize a chemolithiotrope bacterium in aqueous suspension for attacking powder elastomers on the surface only, so that after mixing with virgin rubber diffusion of soluble polymer chains is facilitated and bonding during vulcanization becomes again possible.

A biotechnological process was developed by Straube et al. [142]. For the devulcanization of scrap rubber by holding the comminuted scrap rubber in a bacterial suspension of chemolithotropic microorganisms with a supply of air until elemental sulfur or sulfuric acid is separated. This seems to be an interesting process which obtains reclaim rubber and sulfur in a simplified manner.

The biodegradation of the cis-1,4-polyisoprene chain was achieved by Tsuchi et al. [143–145]. They used bacterium belonged to the genus Nocardia and led to considerable weight loss of different soft type NR-vulcanzates. The microbial desulfurization [146] or devulcanization of particle surfaces was investigated in order to increase the possibility of producing high quality rubber products containing a larger percentage of recycled rubber. In a typical process rubber powder, mainly SBR of old tires with 1.6% sulfur, was treated with different species of Thiobacillus i.e. T. ferrooxidans, T. thiooxidans, T. thioparus in shake flasks and in a laboratory reactor. The sulfur oxidation depends to a large extent on the particle size. The best results were obtained with T. thioparus with a particle size of 100–200 μm. 4.7% of the total sulfur of the rubber powder was oxidized to sulfate within 40 days [146].
In a recent paper Steinbuchel [147] has studied the biological attack of microorganisms on rubber materials in order to evaluate possible contributions of biotechnology for development and recycling of used rubber products. Adaptation of microbial enrichment cultures with tire crumb material for several months resulted in enhanced growth of microorganisms especially for NR and SBR.

### 4.2. Preparation of reclaimed rubber by De-Link process

Rudi Kohler [148] reported a new technology for the devulcanization of sulfur cured scrap elastomers using a material termed De-Vulc developed by Sekhar [149]. Such technique of devulcanization was designated as De-Link process. In this process 100 parts of 40 mesh or finer crumb is mixed with 2–6 parts of De-Vulc [148] reactant in an open two roll mixing mill. De-Vulc reactant is a proprietary material and its nature and composition is not disclosed.

In Table 11, NR indicates natural rubber made from virgin materials, NR-D indicates natural rubber with 30% devulcanized rubber added to the blend. Similarly SBR is virgin material, SBR-D indicates SBR with 30% devulcanized SBR added to the blend. It is evident from Table 11 which was compiled from Ref. [132] that in 30% blend with devulcanized rubber and virgin rubber for NR and SBR, Mooney viscosity, tanδ and 300% modulus are high whereas tensile strength, elongation at break and tear resistance are low [148]. But it was claimed [148] that those tensile properties, tear resistance etc. were very similar to those for the virgin materials.

### 4.3. Reclaiming of rubbers by the use of a renewable resource material

In the chemical reclaiming process a large number of chemical reclaiming agents viz. different disulfides, monosulfides, thiols etc. have been used for treatment of scrap ground rubber crumbs or powders at an elevated temperature and under pressure. No report is available on reclaiming of rubber at around ambient temperatures. Almost all disulfides and thiols have very repelling smell and are hazardous. So handling of these disulfides and thiols are not very desirable. Being expensive also the use of such chemicals may not be economic for reclaim rubber production.

In all the above physical and chemical reclaiming processes except the ultrasound method the extent of reclaiming had not been evaluated or reported. The product of such reclaiming processes was soft and weak mass which was neither characterized nor analyzed for the composition of reclaim. Probably as a result of biased concept such reclaiming was thought to occur by scission of carbon–sulfur and sulfur–sulfur crosslink bonds. The prospect of carbon–carbon bond scission during reclaiming was not

---

**Table 11**

Mechanical properties of reclaimed rubber

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mooney viscosity ML(1 + 4) at 212°F</th>
<th>Tan δ at maximum torque</th>
<th>300% Modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tear resistance (MPa)</th>
<th>Compression set (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>61.9</td>
<td>0.056</td>
<td>13.56</td>
<td>29.14</td>
<td>543</td>
<td>3.49</td>
<td>19.5</td>
</tr>
<tr>
<td>NR-D</td>
<td>72.3</td>
<td>0.062</td>
<td>14.68</td>
<td>27.44</td>
<td>489</td>
<td>2.51</td>
<td>22.0</td>
</tr>
<tr>
<td>SBR</td>
<td>96.6</td>
<td>0.091</td>
<td>20.88</td>
<td>26.48</td>
<td>358</td>
<td>1.60</td>
<td>15.0</td>
</tr>
<tr>
<td>SBR-D</td>
<td>109.2</td>
<td>0.097</td>
<td>19.95</td>
<td>24.44</td>
<td>345</td>
<td>1.53</td>
<td>13.6</td>
</tr>
</tbody>
</table>
investigated. It is either apparent or appropriate to believe that both the physical and chemical reclaiming processes involve polymer chain scission due to mechanical shearing at low or high temperatures, chemical action at high temperatures, thermal scission, or by ultrasound energy at high temperatures. The chain scission of vulcanized rubber during reclaiming is, therefore, supposed to increase plasticity as well as the sol content. The amount of sol as well as the molecular weight of the sol portion of reclaim rubber is supposed to contribute to a great extent to the properties of the reclaim rubber. But except in ultrasound process none has reported the molecular weight of sol. Such information might help in selecting a suitable reclaiming agent as well as a process.

In view of the above state of the art in the reclaiming of waste rubbers, De [150] and Adhikari and coworkers [151–153] have developed a simple process for reclaiming of rubbers with a vegetable product which is ecofriendly and renewable resource material (RRM). The major constituent of RRM is diallyl disulfide. Other constituents of RRM are different disulfides, monosulfides, polysulfides and thiol compounds [154]. The reclaiming activity of RRM was studied in natural rubber, styrene butadiene rubber and natural rubber–polybutadiene rubber blend system and compared with the reclaiming activity of synthetic diallyl disulfide [150]. Reclaiming experiments were done using rubbers of known formulations in order to study the chemical and morphological changes occurred during reclaiming operation. The extent of reclaiming was assessed through the measurement of sol content, molecular weight of sol and Mooney viscosity of the reclaim rubber. Tensile properties of this reclaim rubber in a blend with above mentioned virgin rubbers were also evaluated before and after accelerated aging in air.

4.3.1. Reclaiming process using RRM

Vulcanized and aged ground rubber of known composition was milled in a two roll mixing mill with simultaneous addition of the RRM and spindle oil or diallyl disulfide (DADS) and spindle oil separately. The reclaiming was carried out with different concentrations of reclaiming agents for different milling times at two different temperatures. With progressive milling, band formation took place on the roll surface and the entire mass became sticky. The results in Table 12 showed that 15 min milling of

<table>
<thead>
<tr>
<th></th>
<th>NR (milling time)</th>
<th>SBR (milling time)</th>
<th>NR/PBR (milling time)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 min</td>
<td>35 min</td>
<td>15 min</td>
</tr>
<tr>
<td>Percent sol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RRM</td>
<td>18.0</td>
<td>28.0</td>
<td>19.0</td>
</tr>
<tr>
<td>DADS</td>
<td>25.0</td>
<td>29.0</td>
<td>21.0</td>
</tr>
<tr>
<td>Molecular weight $\times 10^{-4}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RRM</td>
<td>0.50</td>
<td>1.05</td>
<td>0.55</td>
</tr>
<tr>
<td>DADS</td>
<td>0.38</td>
<td>0.98</td>
<td>0.46</td>
</tr>
<tr>
<td>Mooney viscosity $ML (1 + 4) 100^\circ C$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RRM</td>
<td>97.9</td>
<td>61.5</td>
<td>170.8</td>
</tr>
<tr>
<td>DADS</td>
<td>54.1</td>
<td>26.2</td>
<td>156.8</td>
</tr>
<tr>
<td>Inherent viscosity (dl/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RRM</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DADS</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
vulcanized rubber with RRM or DADS produced lowest sol content, lowest molecular weight of sol and highest Mooney viscosity of the reclaim rubber whereas 35 min milling provided the highest sol content with the highest molecular weight and the lowest Mooney viscosity. It was found that 10 g of RRM or 2 g DADS was sufficient to obtain reasonable amount of sol with highest molecular weight as well as lowest Mooney viscosity of the reclaim rubber obtained after 35 min milling at 60°C.

It is found that the sol fraction gradually increases with the increase in milling time and the highest sol fraction is obtained at 35 min milling showing a major dependence of sol content on milling time because during milling vulcanized rubber samples undergo tremendous mechanical shearing resulting in random polymer chain breakdown. Whatever may be the process of reclaiming, either mechanical or thermal, maximum sol fraction is desirable, the molecular weight of the sol should be as high as possible for improved properties of reclaim. So in any reclaiming process proper care is necessary in setting the reclaiming conditions so that thermal or mechanical shearing has minimum effect on fragmentation of the sol. The reason for increase in sol content with progressive milling lies on the action of DADS either added externally or present as the major constituent of RRM. The DADS breaks into radicals as the temperature rises due to mechanical shearing [155], such radicals combine with the broken polymer chain radical and thereby prevent the recombination of these polymer radicals [150–152] which explains the increase of sol fraction with increase in milling time.

The molecular weight of the sol fraction obtained at lower milling time is lower than that obtained at higher milling time which seems to be little peculiar. The reason for such effect [151] was thought to be due to the action of RRM or DADS on the sol fraction. In order to investigate the reason behind such increase in molecular weight of the sol with increase in milling time the sol fraction obtained after 25 min milling during reclaiming at 60°C was separately heated at 60°C with or without RRM (10 g/100 g rubber) and DADS (2 g/100 g rubber) and the molecular weights of the heat treated sols were measured. The results are presented in Fig. 4. It is seen from Fig. 4 that when RRM or diallyl disulfide was added to the sol fraction of 25 min milled sample molecular weight of the sol fraction increased with increase in heating time. But when the sol fraction was heated without the reclaiming agent, first molecular weight increased to a certain level but then attained almost a constant value.

The Mooney viscosity of reclaim rubber decreases with increase in the milling time when reclaiming is carried out by RRM or DADS. The lowest Mooney viscosity was achieved at 35 min milling time at 60°C. It is well known that increase in low molecular weight fragments or increase in the concentration of uncrosslinked molecules helps in lubrication/plasticization during plasticity testing or during processing.

4.3.2. Mechanism for reclaiming [150,151]

Inspite of a large volume of work on the reclaiming of waste rubbers very little information on the mechanism of reclaiming of rubber supported by straightforward evidences is available. The reclaiming was thought to proceed mostly through the depolymerization i.e. the scission of C–C bonds in the original hydrocarbon chain [156]. Amberlang and Smith [157] suggested indirectly the oxidative scission at sulfur crosslinks partly on speculation and partly based on experimental results. Bennett and Smith [158] reported that an alkyl phenol sulfide reclaiming agent had little activity in the absence of oxygen. The oxygen and reclaiming agent showed exceptional activity in attacking a sulfur cured GR-S gum vulcanizate to produce soluble, low molecular weight fragments under relatively mild experimental conditions. ASTM STP 184 A [159] defined “devulcanization as a combination of
depolymerization oxidation and increased plasticity” as they usually occur during the process of reclaiming. But actually devulcanization should be the reverse process of vulcanization. In sulfur vulcanization formation of both the C–S and S–S bond takes place and, therefore, it is expected that during devulcanization only the C–S and S–S bond cleavage should occur. In view of these arguments the conversion of scrap or waste rubbers into usable form by all these above physical and chemical processes may be called reclaiming processes.

The role of disulfide compounds and thiols used in the reclaiming process is not established till date. Adhikari et al. have proposed the following mechanism of reclaiming of rubber [150].

Step 1 describes the homolytic scission of the disulfide reclaiming agent producing sulfur radicals [154,160] (a or b). Simultaneously polymer radicals of the types (c), (c’), (d), (e) or (f) are generated at reclaiming temperature through the steps 2 and 3. Although earlier workers have indicated thermal and oxidative scission of C–C bonds of the original hydrocarbon chain (depolymerization) and sulfur-crosslink bonds, but they have not measured the molecular weight of reclaimed rubber [76,156,157]. Since the bonds in the polyisoprenyl chain of natural rubber are of the lowest strength [155], it is, most likely to undergo rupture at the –CH₂–CH₂– bonds. This is due to the lower dissociation energy than that of the usual single C–C bond by the resonance energy of the mesomeric alkenyl radicals [155] which are produced when these bonds are broken. Adhikari et al. have also noticed molecular weight reduction of NR on thermal treatment in presence of RRM or DADS [151].

Fig. 4. Effect of heating on molecular weight of sol with and without the addition of RRM and DADS (adapted from Ref. [152]).

\[
\begin{align*}
M.W. \text{ of sol. fraction} \times 10^3 \\
\text{Heating Time of sol. fraction (min)}
\end{align*}
\]

- By adding DADS,  - Without adding DADS
- By adding RRM,  - Without adding RRM
Step 1: thermal decomposition of the disulfide reclaiming agent

\[ R\text{-}S\text{-}S\text{-}R \xrightarrow{\Delta} 2R\text{-}S\cdot \quad (a) \]

(b)

Step 2: depolymerization

(c) \[ \text{Mechanical Shearing} \]

(c')

Step 3: thermal scission of sulfur crosslinks

(d)

Step 4: radical coupling reaction

(A) \[ R\cdot \text{ or } RS\cdot \text{ or } R\text{-}S\text{-}S\cdot + \text{(c) or (f)} \xrightarrow{\Delta} \quad (d) \]

\[ x = 1 \text{ or } 2 \]

(B) \[ R\cdot \text{ or } RS\cdot \text{ or } R\text{-}S\text{-}S\cdot + \text{(c) or (f)} \xrightarrow{\Delta} \quad (e) \]

\[ z = 0 \text{ or } 2 \]
During the actual reclaiming process it is likely that the thermally generated polymer radicals (c, c', d, e or f) are scavenged by the sulfur radicals thereby preventing the recombination of these polymer radicals (Step 4). This may be supported by the peptizing action of organic thiol compounds during mastication of raw rubbers where shear generated polymer radicals are prevented from recombination by the action of thiol radicals [155]. The sulfur analysis of rubber before and after the treatment of DADS in this study [151] has shown the increase of combined sulfur of the treated rubber. This may be explained due to the attachment of DADS fragments with the rubber molecules. It also appears that above sequences of reactions may occur irrespective of any reclaiming temperature or any reclaiming agent.

4.3.3. Mechanical properties of virgin rubber reclaim rubber blend

Suitability of the reclaim rubber obtained by the reclaiming action of RRM on NR vulcanizate was studied by blending with fresh rubbers like NR, SBR and NR/BR blends. A representative mix formulation using fresh NR is shown in Table 13. The amount of additives such as ZnO, stearic acid, CBS and S were used based on 100 g fresh rubber irrespective of the amount of reclaim rubber used in the compound, because the RR matrix was thought of as a matrix having no additive originated from its parent compound. The suitability of the reclaim rubber alone in making a product was also verified in the curing of a NR reclaim without using any additive which showed very poor tensile properties [150]. Tensile properties, Mooney viscosity and swelling value of NR/RR blends are shown in Table 14. It is clear that with increase in the proportion of reclaim rubber 100% and 200% moduli increase but tensile strength and elongation at break decrease [150]. The reason for higher 100 and 200% moduli may be due to higher crosslink density of rubber vulcanizates which is also corroborated by swelling value data. The lower tensile strength may be attributed to the presence of crosslinked gel in the matrix originated from the reclaim rubber gel which is difficult to disperse in the fresh rubber matrix. Such gel remains as weak sites for stress concentration resulting in a lower tensile stress. From Table 14 it is also found that the tensile strength value is higher for DADS reclaim rubber containing vulcanizate than RRM reclaim containing vulcanizate. Similar trend of mechanical properties was also observed when SBR reclaim and NR-PBR reclaim were incorporated in fresh SBR and fresh NR-PBR blend, respectively.

4.3.4. Aging characteristics [150]

Aging characteristics of vulcanizates containing reclaim rubber (RR) should be given proper attention because reclaim rubber itself is a degraded product. In view of this reclaim rubber obtained by the use of
RRM was tested for its aging performance. Such RRM reclaim rubber–fresh rubber blend showed improved aging properties which were measured after 24, 48 and 72 h aging at 70 ± 2°C in an air aging oven. The aging results for NR-RR compounds are shown in Table 15. It was found that 40% inclusion of NR reclaim in fresh NR showed 60% increase in 200% modulus and 17% decrease in tensile strength for RRM reclaim containing stock. The RRM reclaim rubber showed better aging resistance than those of DADS reclaim rubber. The same trend is also found in aging resistance of RR-SBR [153] and RR-NR/PBR [150] compounds. These results indicate that the inclusion of reclaim rubber in making rubber products may avoid the usage of antioxidant.

5. Preparation of thermoplastic elastomers from reclaimed rubbers and low density polyethylene

Thermoplastic elastomers (TPE) were prepared [161,162] from reclaimed tire rubber (RR) and...
LDPE by blending in a Brabender plasticorder or a roll mill in the presence of vulcanizing agent. The hardness, tear strength, tensile stress at 100% elongation and tensile strength of TPE increased with increasing LDPE content in the blend while the elongation at break decreased. In the (90–10):(10–90) RR-LDPE weight ratio range the blend showed thermoplasticity, when RR-LDPE weight ratio was in (90–60):(10–40) range, the blends were rubber like, but the blends became resin like when weight ratio decreased.

A thermoplastic material was prepared from a blend of granular scrap material and a thermoplastic polymer [163] such as butadiene–styrene block copolymer in the ratio of about 1:1. Plastic rubber composite was prepared by mixing particulate rubber having a size less than about 10 mesh with a thermoplastic material and a coupling agent [164]. The coupling agent being present in an amount less than 3% by weight of the material to be coupled. A thermoplastic blend comprising of ground vulcanized rubber from both natural and synthetic rubber and polyolefin resin with one or more functionalized olefin polymer was developed. Both the composition and the process were patented [165].

Lal [166] obtained an unexpected increase in green strength of an unvulcanized blend of reclaimed rubber with polyethylene or polypropylene. Unexpected improvements in solvent resistance and molding properties of uncured blends are also achieved. The reclaimed rubber, utilized in the blend have been devulcanized by mechanical energy, heat, microwave energy, and or chemical agents.

Before blending with plastics surface modification of reclaim rubber can be done either by chemical means or by mechanical means. It was reported that high energy radiation such as plasma [167–169], corona [170–172] and electron beam radiation [173–175] can modify the surfaces and bring about better miscibility. Addition of GRT (Ground Rubber Tire) to a number of thermoplastics shows poor compound properties [176]. It was found that silane treated GRT showed better mechanical properties than that of untreated GRT [177]. It was reported that addition of natural rubber increases the adhesion between GRT and polypropylene [177,178]. The precoating of GRT surfaces with ethylene–acrylic acid copolymer and ethylene–glycidyl methacrylate copolymer increased the impact energy [179–181]. With decrease in particle size of GRT from 0.6 to 0.074 mm there is a minor increase in the impact energy (17%) while the MFI drops from 2.7 to 1.7 g/10 min. But the addition of surface modified GRT (4 wt%) by ethylene–glycidyl methacrylate copolymer, increases the impact energy and MFI of the

<table>
<thead>
<tr>
<th>NR Vulcanizate</th>
<th>Percent retention value after 72 h aging</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200% Modulus</td>
</tr>
<tr>
<td></td>
<td>140</td>
</tr>
</tbody>
</table>

**RRM reclaim containing vulcanizate**

- NR/RR:75/25 155 101 70
- NR/RR:60/40 138 105 78
- NR/RR:50/50 138 93 75
- NR/RR:40/60 128 100 75

**DADS reclaim containing vulcanizate**

- NR/RR:75/25 136 82 80
- NR/RR:60/40 156 91 87.5
- NR/RR:50/50 128 107 87.5
- NR/RR:40/60 128 88 63

Table 15

Aging characteristics of different NR/RR blends

composites which is corroborated from Table 16. But when surface modified GRT is used for the preparation of thermoplastic composites following results was observed.

The higher value of impact energy and MFI for surface modified GRT may be due to coupling action of GRT with ethylene–glycidyl methacrylate copolymer. It is interesting to note that in LLDPE-GRT composite the changes in the impact energy and MFI, as a function of particle size, are similar for composites with or without the coupling agent. It has been found from Table 16 that rubber particle size has only a minor effect on impact energy and viscosity. Adhesion of polymer–filler interface can be improved by the surface modification of the filler particle. If the modified surface has more oxidized species they may react with the glycidyl groups in the LLDPE matrix. Electron beam radiation resulted in a significant increase in surface oxygen concentration and composite impact strength. The impact energy of the composites prepared from all the surface modified GRT with LLDPE and ethylene–glycidyl methacrylate copolymer are shown in Table 16.

Among the various methods of GRT surface modification, only the composites prepared from electron beam radiation-treated GRT give better impact energy. There is no change in impact energy of the composites if the intensity of the radiation changes from 10 to 25 kGy. The composites based on electron beam radiation treated GRT with ethylene–glycidyl methacrylate copolymer shows a lower stiffness than untreated GRT with ethylene–glycidyl methacrylate copolymer composite. The reason for such behavior may be due to the formation of low molecular weight compound during electron beam radiation treatment. These compounds probably act as plasticizer and reduce the relative stiffness. Again the composites from electron beam radiation treated GRT shows much higher displacement than those of untreated GRT which proves that electron beam radiation treatment increases the surface chemical functionality (–OH, –COOH, –CHO etc.) on the GRT. These functional groups can easily react with ethylene–glycidyl methacrylate copolymer and therefore increases the ductility of the composite. In this way ground rubber tire can be used properly with thermoplastics and thus tire disposal problem can be minimized to a lesser extent. Because the surface modification procedures are expensive the cost of ultimate product should be very higher.

6. Comparative study of recent reclaiming processes

Recently three processes viz. ultrasound devulcanization, devulcanization by De-Link process and reclaiming by renewable resource material (RRM) and diallyl disulfide have been developed for preparation of reclaim rubber from scrap/waste rubber products. A comparative evaluation of these three processes are presented in Table 17.
Table 17
Comparative evaluation of the recent developments

<table>
<thead>
<tr>
<th>Condition and properties</th>
<th>Ultrasonic energy</th>
<th>De-Link process</th>
<th>Reclaiming by RRM and DADS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>121, 149, and 176</td>
<td>Ambient temperature</td>
<td>40, and 60. Near ambient temperature</td>
</tr>
<tr>
<td>Pressure</td>
<td>Die pressure is substantially reduced as the amplitude of ultrasound is increased</td>
<td>Not required</td>
<td>Not required</td>
</tr>
<tr>
<td>Additives</td>
<td>Ultrasound energy (20 KHz) and amplitude (5-10 microns)</td>
<td>De-Vulc being proprietary in nature</td>
<td>Renewable resource material (RRM) and dially disulfide (DADS)</td>
</tr>
<tr>
<td>Environmental concern</td>
<td>No pollution</td>
<td>?</td>
<td>No pollution</td>
</tr>
<tr>
<td>Instrument required for reclaiming</td>
<td>Ultrasonic reactor</td>
<td>Either two roll mill or internal mixer</td>
<td>Either two roll mill or internal mixer</td>
</tr>
<tr>
<td>Sol content of reclaim rubber (SBR)</td>
<td>36%</td>
<td>Not mentioned</td>
<td>For RRM as reclaiming agent 32% and DADS as reclaiming agent 35%</td>
</tr>
<tr>
<td>Molecular weight of sol (SBR)</td>
<td>( M_n = 2 - 4 \times 10^3 )</td>
<td>Not mentioned</td>
<td>For RRM as reclaiming agent ( M_v = 1.13 \times 10^4 ) and DADS as reclaiming agent ( M_v = 1.02 \times 10^4 )</td>
</tr>
<tr>
<td>Crosslink density of gel (SBR)</td>
<td>0.06 kmol/m³</td>
<td>Not mentioned</td>
<td>Not determined</td>
</tr>
<tr>
<td>Mooney viscosity of reclaim rubber (SBR)</td>
<td>Not mentioned</td>
<td>104 Mooney units</td>
<td>For RRM as reclaiming agent 120.2 Mooney units and DADS as reclaiming agent 70.6 Mooney units</td>
</tr>
<tr>
<td>ML (1 + 4)100°C</td>
<td>For SBR reclaim 1.5–10.5 MPa</td>
<td>For SBR reclaim 6.99 MPa</td>
<td>For NR reclaim when RRM as reclaiming agent 4.34 MPa and when DADS as reclaiming agent 3.52 MPa</td>
</tr>
<tr>
<td>Tensile strength of revulcanized sample</td>
<td>For SBR reclaim 130–250%</td>
<td>For SBR reclaim 311.5%</td>
<td>For NR reclaim for RRM = 283% for DADS = 300% for RRM = 21.4 MPa for DADS = 21.6 MPa</td>
</tr>
<tr>
<td>Elongation at break of revulcanized sample</td>
<td>Not determined</td>
<td>27.44 MPa</td>
<td>For RRM = 500% for DADS = 500%</td>
</tr>
<tr>
<td>Tensile strength of virgin rubber reclaim rubber blend (NR/RR = 70/30)</td>
<td>Not determined</td>
<td>489%</td>
<td>Not determined</td>
</tr>
<tr>
<td>Elongation at break of virgin rubber, reclaim rubber blend (NR/RR = 70/30)</td>
<td>Not determined</td>
<td>Not determined</td>
<td>Not determined</td>
</tr>
<tr>
<td>Mooney viscosity of virgin rubber, reclaim rubber blend (NR/RR = 70/30)</td>
<td>Not determined</td>
<td>72.3 Mooney units</td>
<td>For RRM = 30.4 Mooney units, for DADS = 32.5 Mooney units</td>
</tr>
</tbody>
</table>
Thus from the above table it is clear that very high temperature is required for ultrasound devulcanization. But Isayev and co-workers have not mentioned the effect of temperature only without ultrasound energy on devulcanization. But in De-Link process and RRM process nearly ambient temperature is required for reclaiming which is advantageous because at low temperature less energy is consumed for reclaiming and simultaneously polymer degradation can be minimized. For ultrasound devulcanization a special type of ultrasonic reactor is required whereas in De-Link and RRM process only internal mixer or two roll mixing mill is sufficient. Again sol content and molecular weight of sol obtained by ultrasonic devulcanization and RRM process are almost same.

7. Applications of recycled/reclaimed rubbers

7.1. Ground rubber in civil engineering applications

A large amount of crumb rubber is used in civil engineering projects [182], such as play ground surface, parking lots, bank stabilization, fill under road surface and asphalt modifier because the scrap tire chips have properties that road builders find essential: light weight, low earth pressure, good thermal insulation and good drainage properties. Another important thing is its better damping property which is good for running vehicles. The scrap tire management council estimates that eight million scrap tires were used in civil engineering application in 1996 [182]. But recently fires have set back the use of ground scrap rubber for many of these applications. Waste tires and tubes were incorporated into asphalt for making an asphalt composition [183]. A rubber modified asphalt was developed, for use as a paving compound, by reacting very fine ground particulate rubber with paving grade asphalt at a temperature range of 300–400°F within 25 min. Such treatment forms a free flowing mixture which can be held at normal asphalt working temperatures for at least 96 h without degradation [184].

Ground tire rubber is used as an additive in various types of asphalt pavement construction [185]. Approximately 480 million tons of asphalt are used each year in the United States [186] and in 1986 25,200 tons of rubber were used in asphalt. Rubber modified asphalt is advantageous to increased durability, reduced reflective cracking, thinner lift and increased skid resistance. Again day to day burden placed on national highways is increased due to higher tire pressure and increase traffic volumes. So there is a need to improve conventional asphalt concrete mixes. Rubber modified asphalt concrete has been shown to increase durability and fatigue resistance. Asphalt rubber is also used for water-proofing membranes, crack and joint sealers, hot mix binders and roofing materials. The rubber improves asphalt ductility and increases the temperature at which asphalt softens. The aggregate adhesive bond is stronger, and the asphalt lasts longer.

Asphalt rubber is mixed and applied to roadways [187] by several techniques. In one method, rubber and asphalt are mixed at 175–220°C for 1–2 h. The hot mixture is applied to the roadway and covered with a layer of stone chips to form a chip seal. The rubber crumb which is used in this process is usually less than 2 mm in diameter. Typically about 2 ton of rubber is used for 1 km of roadway. Generally in two processes viz. wet process and dry process crumb rubber is mixed with asphalt. In the dry process crumb rubber is mixed with asphalt cement mixture to replace some of the aggregates in the mixture and in the wet process crumb rubber is added to the asphalt cement mixture to modify the physical properties and chemical properties of the asphalt cement. Rubberized
asphalt mixtures were developed by Nielson et al. [188] by dissolving/dispersing relatively large proportion of reclaim rubber into molten paving asphalt in presence of a minor proportion of a highly aromatic, high boiling, high flash point mineral oil. Such a mixture finds application to road ways in the form of stress-absorbing membrane interlayers between old, damaged pavement surfaces and over layer of new asphalt concrete, for providing chip-seal coatings over old pavement, as crack fillers in portland cement concrete or asphalt concrete pavements and bridge deck water-proofing membranes [189–194].

Reclaim rubbers from old and worn tires, tire scrap, inner tube scrap, tire peel, retreading scrap, tire carcass, rubber buffing and other rubber scraps have been converted to an asphalt rubber stable thixotropic emulsion for application as a pavement repair material [195]. The emulsion is capable of flowing as a liquid upon gentle agitation. Such emulsion involves the steps of heating asphalt and rubber to form a jellied reaction product followed by admixing an asphalt-rubber soap consisting essentially of water, an anionic water soluble emulsifying agent, and an alkali metal or alkaline earth metal halide to form the thixotropic emulsion.

Excellent weathering, wear and chemical resistant construction products, viz. paving or tile for drive ways, or a shingle for roof tops have been developed from recycled tire crumbs and siliceous crystalline grains. The process comprises the steps of granulating rubber tires to form coarse rubber crumbs followed by mixing the coarse rubber crumbs with coarse siliceous grains in presence of a polymerizable liquid binder to provide a viscous slurry. The viscous slurry was cast into sheets followed by curing to give an environmentally stable construction product [196].

Currently two types of dry processes are adopted in rubber asphalt paving. One is the Plus Ride system and another is the TAK system. In the Plus Ride system rubber modified asphalt concrete paving mixture is prepared by using 3% granulated coarse and fine rubber particles to replace some of the aggregates in the mixture. The purpose of using this mixture now-a-days is to improve durability, to resist the excessive wear, to increase flexibility and durability and to overcome the problem of the early reflection of fatigue cracking in resurfaced asphalt pavements. This mixture shows extended durability at thinner lifts during testing at laboratory and field [197,198] and also indicated a potential for greatly increased pavement fatigue life as a result of the elasticity of the material [199]. The surface texture and protruding rubber granulate are reported to give the pavement improved skid resistance under icy conditions [200,201]. Ice deposition in roadway surface becomes a serious problem in urbanized areas with high traffic volumes. Costs of maintaining ice-free pavements with chemicals or improving traction through sand applications are high. By using rubber modified asphalt pavement this problem can be minimized.

### 7.1.1. The TAK system

The TAK System originated after its inventor. This process was developed by Takallou in 1986 [202]. In this process rubber modified asphalt concrete paving mixture is prepared by adding 3% by weight of fine and coarse rubber particles to a dense graded aggregate mixture. The rubber granulate is prepared from whole tire recycling. The average net yield of rubber from a used passenger car tire is about 12 lb (after steel and fabric removal). Hence five tires are required to obtain 60 lb of granulated tire rubber which is necessary for production of one ton of rubber modified asphalt concrete mix. Therefore, rubber obtained from 16,000 tires is consumed per mile in a two lane highway with 3 in. of rubber modified asphalt concrete pavement.
7.1.2. The wet process

This process (Arizona Refinery System) [203] was developed to overcome the problem of fatigue cracking in resurfaced asphalt pavements. The idea is based on using a composite material of hot asphalt cement with 1% by weight of total mixture of ground crumb rubber and diluted with an oil extender for ease of application. At elevated temperatures (300–400°F) for periods of one-half hour to one hour this reaction forms a thick elastic type material which is then diluted with 5% kerosene to aid in application. At room temperature this asphalt rubber composition is a tough rubbery and elastic binder material. The elastic quality of this mixture is most probably maintained by undissolved rubber particles that serve as units of elastic interference to the propagation of cracking. When a crack begins to propagate through the membrane then it encounters with elastic rubber particle and is stopped or its path of propagation is changed where it will encounter with another elastic rubber particle and so on. Thus propagation of crack is not possible.

7.2. Uses of cryogenically ground rubber

Cryogenically ground rubber is used in tires, hoses, belts and mechanical goods, wire and cable and in various other applications. It is especially useful in producing a product for tire innerliners. The particle size chosen is controlled by cost and fineness needed to produce the desired processing. The finer the particle size, the smoother the calendered sheets and the finer an edge that can be produced on extrusions.

8. Advantages of using reclaimed rubber

Although reclaim rubber is a product of discarded rubber articles it has gained much importance as additive in various rubber article formulations. It is true that mechanical properties like tensile strength, modulus, resilience, tear resistences etc. are all reduced with the increasing amounts of reclaim rubber in fresh rubber formulation. But at the same time the reclaim rubber provides many advantages if incorporated in fresh rubber.

8.1. Easy breakdown and mixing time

During reclaiming process reclaimed rubber has already been plasticized due to a large amount of mechanical working. Therefore, in the consumers hands it mixes easily than new rubber at lower mixing time with less heat generation. This is particularly advantageous with compounds containing high carbon black loading. In the mixing of tire carcas and side wall stocks also this property is very advantageous because during first banbury pass reclaim rubber is not added rather added during second banbury pass along with the curing agents to a position of the master batch obtained from the first banbury pass. The second pass is much shorter than the first, therefore, an increase in mixing capacity of as much as 40% occurs with a 30% banbury cost saving per pound of rubber. With increase in the ratio of reclaimed RHC to new RHC, the mixing cycle decreases. Furthermore, an all reclaim stock mixes in just one half the time required for an all new rubber stock.
8.2. Low power consumption during breakdown and mixing

Reclaimed rubber consumes less power during breakdown and mixing than new rubber. Rubber Reclaimers Association has done a series of experiments to study the power saving during mixing with reclaim rubber.

The first series compared whole tire reclaimed rubber with natural rubber and SBR 1712. Each was mixed with black, filler and oil in proportions to stimulate the composition of the reclaim. Banbury time was kept constant. The savings in power cost per 1000 pounds of reclaim were:

- 20% vs Natural Rubber
- 34% vs SBR 1712

The second series show that a mixture of SBR 1712 and BR (without any additives) plus a small proportion of reclaim rubber shows 12% less power consumption than by SBR 1712 alone and 14% less power consumption than for the combination of SBR 1712 + BR, the mixing time being constant in all the cases.

The third series shows that SBR 1712 alone, and SBR 1712 plus increasing proportions of tire reclaim rubber upto 50% on RHC basis, result in increasing power savings for a constant mixing time.

<table>
<thead>
<tr>
<th>% Reclaim RHC</th>
<th>% Power saving</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>9.6</td>
</tr>
<tr>
<td>50</td>
<td>18.7</td>
</tr>
</tbody>
</table>

8.3. Advantages in calendering and extrusion

Reclaimed rubber stocks can usually be processed at a lower temperature than those containing virgin rubber alone. It provides generally faster processing during extruding and calendering. Due to the presence of crosslinked gel in reclaimed rubber, it is less thermoplastic than new rubber compounds. Thus when extruded and cured in open steam they tend to hold their shape better. Extruder die swell and calender shrinkage reduce with a proper use of reclaim rubber due to its lower nerve. Fresh rubber calendered sheets show 6–10% shrinkage. Using of reclaim rubber in tire carcass stocks permits high speed calendering and results in smooth uniform coating. The use of substantial proportion of reclaim rubber in automobile floor mat stocks permits maximum calender speeds which is sometimes twice as large as when very high proportions of SBR are used. Reclaim rubber in tire carcass compound gives better penetration in the fabric and chord than a non-reclaim compound.

8.4. Influence on tack behavior

The tack of a non-reclaim compound may disappear within 24 h after calendering whereas, reclaim rubber compound tend to maintain their tack longer than non-reclaim compound. Non-reclaim
Compounds become more tacky in hot weather and dry in cold weather. On the other hand, reclaim rubber compounds are less influenced in tack variation in hot and cold weather. This characteristic of reclaim rubber is exploited for its usefulness in pressure sensitive tape.

8.5. Influence on curing and aging

Reclaim rubber containing compounds help to retard and reduce sulfur bloom from both uncured and cured stocks. It cures faster than virgin rubber compound, probably due to its combined sulfur and active crosslinking sites. Energy savings thus obtained constitute its usefulness in commercial purpose. During vulcanization reclaim rubber containing stocks show less tendency to revert indicating better aging resistance. Ball and Randall [204], Adhikari et al. [153,205,206] and Dierkes [207] observed antiaging characteristics of reclaim rubber. Adhikari et al. observed around 90% retention of tensile properties of NR, SBR and NR-PBR reclaim rubber without using any antioxidant. As per Ball and Randall such aging resistance of reclaim rubber is due to the severe treatment of oxidation, heating, digestion and mechanical shearing which appear to stabilize the hydrocarbon against further changes.

8.6. Cost and energy savings

Finally, it may be stated that incorporation of reclaim rubber into new rubber compound, not only reduces the cost of the finished product but also saves our united resource of fossil feed stock. Energy consumption in the tire production is 25 l of oil equivalent/tire. But much less energy is consumed in the production and utilization of recycled rubber products than direct production of rubber articles from the virgin raw materials. Energy consumption in reclaim production from truck treads is 0.09 l of oil equivalent/kg and 0.12 l equivalent/kg from whole tire. These data show that negligible amount of energy in terms of oil equivalent is consumed for reclaim production.

9. Conclusion

Among various methods of disposal of scrap/waste rubber products recycling or reclaiming of rubber is the most positive approach, because it not only saves our limited resource fossil feedstock but also maintain our environmental quality. In almost all types of reclaiming process except microwave technique degradation of polymer chain takes place. So microwave technique is unique to get better quality product. The vegetable product (RRM) may find better place as a reclaiming agent at around ambient temperature after thorough investigation.

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Executive Summary

This report presents the results of the evaluation of waste tire devulcanization technologies performed by CalRecovery, Inc. under contract with the California Integrated Waste Management Board.

Devulcanization is a potential method of recycling waste tire rubber. Devulcanized rubber is a highly valued form of waste rubber since devulcanized material can be revulcanized into useful products.

Approximately 25 potential devulcanization technology researchers and developers were identified throughout the world and North America, including three in California. However, only a very small number of devulcanization systems are now operating. These are primarily small-capacity systems, which are devulcanizing natural or synthetic rubbers (as opposed to devulcanizing the mixture of rubbers recovered from waste tires).

The general types of devulcanization technologies identified and analyzed in the study are shown below.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Basis of Processing</th>
<th>Zone of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Chemicals/chemical reactions</td>
<td>Surface of particles</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Ultrasonic waves</td>
<td>Throughout particles</td>
</tr>
<tr>
<td>Microwave</td>
<td>Microwaves</td>
<td>Throughout particles</td>
</tr>
<tr>
<td>Biological</td>
<td>Microorganisms</td>
<td>Surface of particles</td>
</tr>
<tr>
<td>Other</td>
<td>Mechanical Steam</td>
<td>Surface of particles</td>
</tr>
</tbody>
</table>

Key Findings

- Reliable information and data on devulcanization of waste tire rubber are difficult to obtain due to proprietary claims, efforts to hide poor or infeasible process performance and product quality, and the limited number of technology researchers and developers and of peer-reviewed data. Reliable data relating waste tire characteristics, devulcanized rubber quality, end product performance, and production costs is scarce.

- Only a very small number of low-capacity devulcanization systems are operating in the United States (at approximately 100 lb/hr, all R&D scale, mechanical, or ultrasonic). No proven commercial capacity units could be found that are currently devulcanizing waste tires, for example, at 1000 lb/hr or greater. The likely reasons include insufficient product quality and high costs of production.

- In terms of the potential of producing high-quality devulcanized rubbers (for example, high strength), the best technology appears to be ultrasonic, based on the current state of the art.

- Devulcanization of single rubbers has much more history than that of multi-rubber mixtures such as waste tires. Only a few companies devulcanize single formulation rubber as a result of captive conversion or merchant scrap recovery from manufacturing. The production of devulcanized rubber from home manufacturing scrap ranges from 100 to 200 million pounds annually, which represents about 1 to 2 percent of total U.S. rubber consumption. The largest volume devulcanization activity supports the domestic tire and rubber companies. Examples
of devulcanized single-product rubber applications are tire bladders, seat spring covers, various molded goods, and foam crack sealer. The quality of devulcanized single rubbers is higher than that of devulcanized multiple rubbers.

- Markets and uses for devulcanized waste tire rubber are generally scarce, opportunistic, and lack history and standards. Based upon limited market history and potential, devulcanized tire rubber would be expected to find uses in molded goods, binders for plastics, and applications needing a better surface finish. Examples of product areas are footwear soles, rubber sheeting, car mats, and inner liner compounds. Potential uses of devulcanized rubber of especially high quality and performance could include tread and sidewalls of tires; this level of high quality has not been demonstrated. Devulcanization that depends on surface devulcanization technologies (for example, chemical and mechanical) appears destined in the near term to produce low- or medium-quality devulcanized rubber material.

- The estimated cost for producing devulcanized materials from waste tires is $0.7 to $1.2/lb ± 30 percent, including the cost of crumb rubber feedstock. This range of production costs is significantly greater than that of virgin rubbers.

- All things considered under current and likely near-term future conditions, devulcanization faces an uphill struggle to be competitive with virgin rubber.

**Key Research Needs**

- Sponsor waste tire devulcanization projects that secure reliable and comprehensive data that document and relate feedstock characteristics, operating conditions, environmental impacts, cost, and type and quality of products, with the objective of producing high-quality devulcanized rubber.

- Identify methods that reduce the cost of production, while at the same time yielding high-quality devulcanized rubber and/or manufactured compounds or end products.
Chapter 1. Introduction

Devulcanization of rubber has a long history, but renewed interest in the subject has arisen during the past five to ten years due to increased regulatory and public concern for properly managing waste tires.

Devulcanization is a potential method of recycling waste tire rubber. As its name implies, in the process of devulcanization, the structure of the vulcanized waste rubber is modified. The resulting material can be revulcanized or transformed into useful products (see complete definition on page 4). Devulcanized rubber is a highly valued form of waste rubber.

The evaluation begins with a review of research and development as determined by a search of the literature. Subsequently, types of devulcanization technologies are described and analyzed in terms of technical aspects, cost, market situation, and environmental considerations. Barriers to waste tire devulcanization are then discussed, along with potential methods of resolving them. Lastly, major conclusions and recommendations of the study are offered at the end of the report.

An overriding consideration of the evaluation is devulcanization of waste tire rubber, as opposed to single types of rubber. The reason is that tires are composed of mixtures of multiple rubbers (as well as other constituents), which renders devulcanization of waste tires much more challenging than that of single rubbers.
Chapter 2. Status of Research and Development for Devulcanization Technologies

Introduction

Methods of devulcanizing elastomers (or rubber) have been researched almost since the time of the discovery of the rubber/sulfur vulcanizing process by Charles Goodyear in 1839. Many papers have been published on subjects relevant to devulcanization. Additionally, a number of patents have been issued on topics concerning devulcanization processes. The discussion below describes the results of a review of the status of research and development performed in the area of devulcanization.

Devulcanization has been applied to different types of elastomers. The purpose of this analysis is to describe the development of devulcanization processes in general and to relate those developments to the potential for devulcanizing waste tire rubber. Waste tires are composed of a number of different constituents, including vulcanized natural and synthetic rubber compounds, steel, fiber, and other materials. The status of devulcanization must also be measured against the potential uses of devulcanized waste tire rubber and the ability of the devulcanization processes to achieve yields and quality of rubber necessary to make devulcanization feasible.

Definitions

There is some discrepancy in the literature among key terms that will be used in this analysis and in their definitions. In the discussion on research and development of devulcanization, CalRecovery uses the following terms:

Vulcanization is the thermo-chemical process that incorporates sulfur and sulfur crosslinks into a mixture of rubber molecules in order to provide the elasticity and other properties that are desired in manufactured rubber products. In the process, sulfur atoms are chemically bonded to the carbon molecules of rubber molecules and serve as crosslinks (chemical bonds) between the sulfidic rubber molecules. The vulcanization process is irreversible at standard atmospheric conditions of temperature and pressure. The vulcanization process also uses primary and secondary accelerators, typically sulfur-containing organic compounds and activators such as zinc oxide and stearic acid.

Reclaiming is a procedure in which scrap tire rubber or vulcanized rubber waste is converted—using mechanical and thermal energy and chemicals—into a state in which it can be mixed, processed, and vulcanized again. The principle of the process is devulcanization (Franta, 1989). Historically and practically, in the concept of rubber reclaiming, devulcanization consists of the cleavage of intermolecular bonds of the chemical network, such as carbon-sulfur (C-S) and/or sulfur-sulfur (S-S) bonds, with further shortening of the chains also occurring (Rader, 1995). This description of devulcanization is different than that given below, which is limited to chemical interactions involving sulfur atoms.

Devulcanization is the process of cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds) of vulcanized rubber. Ideally, devulcanized rubber can be revulcanized with or without the use of other compounds. The different types of devulcanization processes also modify other properties of the rubbers. These processes cause diminution of some properties over those of the parent rubber. Ideally, devulcanization would
yield a product that could serve as a substitute for virgin rubber, both in terms of properties and in terms of cost of manufacture.

**Methodology**

In order to establish the status of research and development for devulcanization technologies, CalRecovery used a number of resources. CalRecovery could not rely solely on the peer-reviewed literature to provide the greatest capture of information covering devulcanization of sulfur-cured rubber or of waste tires. The project team consulted the following sources, both in North America and internationally, listed below:

- Popular and peer-reviewed literature.
- Waste tire processors.
- Patents.
- Tire manufacturers.
- State and federal agencies.
- Universities and research institutes.
- Associations and organizations.
- Website search engines.
- Subconsultants of CalRecovery.

Based upon the data and information collected among the various sources, the research and development status of devulcanization was determined for a variety of technologies and processes.

**Composition of Waste Tires**

A typical tire compound contains the following constituents:

- Natural and synthetic rubber.
- Reinforcing fillers.
- Oils.
- Antioxidants.
- Zinc oxide.
- Accelerators.
- Sulfur.

**Grinding and Pulverization Technologies**

Use of waste rubber in a vulcanized state most often requires reduction of particle size or increase in surface area. One of the widely used methods for doing this with scrap rubbers and wastes is a grinding process.

The three current methods of grinding waste rubber are: (1) ambient grinding, (2) cryogenic grinding, and (3) wet-ambient grinding (Harshaft, 1972). Vulcanized scrap rubber is first reduced
to a 2 x 2 inch or 1 x 1 inch chip. Then a magnetic separator and a fiber separator (cyclone) remove all of the steel and polyester fragments. The waste rubber can then be further reduced using an ambient ground mill, or it can be ground into fine particles while frozen using cryogenic grinding (Klingensmith & Baranwal, 1998).

One method for obtaining fine-mesh rubber is cooling scrap tires in liquid nitrogen below their glass transition temperature and then pulverizing the brittle material in a grinder. Cryogenically-ground rubber has a fine particle size, varying from 30 to 100 mesh. Except for inexpensive rubbers such as tire rubbers, the process is not economical because of the substantial quantities of expensive liquid nitrogen or other cryogenic liquids needed to freeze the rubber (LaGrone, 1986).

However, the process may be economical for expensive rubbers such as fluorocarbon rubbers. Little or no heat is generated in the process, resulting in less degradation of the rubber. In addition, the most significant feature of the process is that almost all fiber or steel is liberated from the rubber, resulting in a yield of usable product and little loss of rubber (Klingensmith & Baranwal, 1998).

Ambient mechanical size reduction by chopping and grinding often uses a conventional high-powered rubber mill set at close nip. The vulcanized rubber is sheared and ground into small particles. Using this relatively inexpensive method, it is common to produce 10- to 30-mesh material, which is a relatively large crumb.

In addition, multiple grinder passes can be used to further reduce the particle size. Ambient grinding produces an irregularly shaped particle with many small hair-like appendages that attach to the virgin rubber matrix, producing an intimate bonded mixture (Szilard, 1973). The lower particle limit for the ambient grind process is the production of 40-mesh material. The process, however, generates a significant amount of heat. Excess heat can degrade the rubber. If the rubber is not cooled properly, combustion can occur upon storage.

A process using a wet grinding method to achieve a crumb fineness of approximately 200 mesh has been reported (Lynch & LaGrone, 1986). Wet or solution process grinding can yield a very small particle size, ranging from 400 to 500 mesh. The advantage of fine particle wet ground rubber is that it allows good processing, producing relatively smooth extrudates and calendered sheets (Lynch & LaGrone, 1986).

Grinding processes for tire rubber are well developed. They are widely used for recycling of tire rubbers and rubber wastes. Also, industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved.

Pulverization techniques for rubbers are also being developed based on the concept of polymer pulverization that was originally proposed for plastics. The process manufactures polymer powder using a twin-screw extruder, imposing compressive shear on the polymer at specific temperatures that depend on the polymer (Enikolopian, 1985).

Based on this method, the solid-state shear extrusion pulverization method of rubber waste using a twin-screw extruder and a single-screw extruder has also been proposed [(Khait & Torkelson, 1999; Khait, 1994) and (Bilgili, et al., 2000; Bilgili, et al., 1999; Bilgili, et al., 2001, pp. 265–276; Bilgili, et al., 2001, pp. 277–289), respectively]. The pulverized rubber particles were fluffy and exhibited a unique elongated shape.

In solid-state pulverization, the rubber granulates are fed into the hopper of the extruder and conveyed into the compression zone, where they are subjected to high compressive shear. Under simultaneous action of this compressive shear and torsion due to the screw rotation, the
granulates are pulverized. They emerge from the pulverization zone as a rubber powder with smaller particle size. Surface oxidation of the rubber particles and initiation of agglomeration of a fraction of the produced particles may occur. The particles produced exhibit irregular shapes with rough surfaces and have a porous structure. The particles obtained in this process can be molded into products after exposure to high heat and high pressure for a period of at least one hour (Arastoopour, et al., 1999; Bilgili, et al., 2003).

The pulverization technologies have been developed on laboratory scale only. Currently, efforts are underway to develop machines for a large-scale production of pulverized tire rubbers. During this process, the tire rubber is apparently only slightly devulcanized, mainly in the proximity of the surface layer of rubber particles. The main disadvantage of the technology is the generation of tremendous amounts of heat due to compression and shearing actions in the pulverization zone that are difficult to control.

It should be noted that all such grinding processes produce little chemical change in the rubber beyond the degradation that occurs as a result of exposure to heat during the process. The ground rubber thus produced functions essentially as a filler when compounded with virgin rubber. The one advantage it may have over other fillers, such as carbon black or clays, is that it will be able to chemically bond with the new rubber to some extent in the vulcanization process. Used alone, its applications are limited to products requiring relatively low physical and mechanical properties.

Types of Devulcanization Technologies Identified

A search of the literature and patents was performed to determine the status of devulcanization technology and processes. In summary, the information is grouped into the following categories:

1. Chemical.
2. Ultrasonic.
3. Microwave.
4. Biological.
5. Other.

Results

The results of the status evaluation are discussed below under each of the respective categories of devulcanization processes.

Chemical

Organic Solvent Only

One type of chemical method proposed (Hunt & Kovalak, 1999) is based on the use of 2-butanol solvent as a devulcanizing agent for sulfur-cured rubber under high temperature and pressure. The authors of the study claim that the molecular weight of the rubber is retained and its microstructure is not significantly altered during the devulcanization process. However, the process is extremely slow and requires separation of the devulcanized rubber from the solvent. The process is applicable to devulcanization of finely ground tire rubber, but so far it has been carried out only on a very small laboratory scale.

Another type of chemical technology (Benko & Beers, April 2002; Benko & Beers, May 2002; Benko & Beers, October 2002) uses a solvent to treat (devulcanize) the surface of crumb rubber
particles of sizes within about 20 to 325 mesh. This is similar to the proposal by Hunt and Kovalak. The process is carried out at a temperature range between 150°C to 300°C (300°F to 575°F), at a pressure of at least 3.4 Mega Pascals (MPa), in the presence of solvent selected from the group consisting of alcohols and ketones. Among various solvents, 2-butanol exhibited the best ability to devulcanize sulfur-cured styrene-butadiene rubber (SBR) rubber. Duration of the process is about 20 minutes.

Reported data on surface devulcanization experiments were obtained by treating small amounts of crumb rubber in the gas chromatography column. The solvent suitable for this process should have a critical temperature in the range of about 200°C to 350°C (400°F to 650°F). The process produces a slurry of the surface devulcanized crumb rubber that has to be separated from the solvent. In this process, a preferential breakage of S-S and C-S bonds appears to take place, with little breakage of the main chains. The obtained surface modified crumb rubber was subjected to vulcanization as obtained and also in blends with virgin rubber. The vulcanizates exhibited a good retention of mechanical properties in blends with virgin rubber. However, this process has been tested only on a small laboratory scale.

**Oils and Chemicals**

The De-Link technology for the devulcanization of sulfur-cured scrap elastomers uses 100 parts of 40-mesh or finer crumb mixed with 2 to 6 parts of De-Link reactant in an open two-roll mixing mill (Kohler & O’Neill, 1997; Sekhar & Kormer, 1995). The De-Link reactant, called De-Vulc, is a proprietary material and its nature and composition are not disclosed. No evidence is available to demonstrate that the De-Link process is used beyond laboratory or pilot scale.

Diallyl disulfide is the major constituent in a simple process for reclaiming rubber using a vegetable product that is a renewable resource material (De, et al., 1997; De, et al., 2000; De, et al., 1999). Other constituents of this material are different disulfides, monosulfides, polysulfides, and thiol compounds.

Sulfur vulcanized natural rubber (NR) can be completely recycled at 200°C to 225°C (392°F to 437°F) by using diphenyldisulphide (Knorr, 1994). A 1999 report (Verbruggen, et al.) listed the efficacies of various disulphides used as recycling agents for NR and ethylene propylene diene monomer rubber (EPDM) vulcanizates. While complete devulcanization was observed on sulfur-cured NR at 200°C (392°F), a decrease on crosslink density by 90 percent was found when EPDM sulfur vulcanizates and diphenyldisulphide were heated to 275°C (527°F) in a closed mold for two hours. At the same time, EPDM cured by peroxide showed a decrease in crosslink density of about 40 percent under the same conditions.

**Inorganic Compounds**

In addition to the use of organic chemicals, rubbers can be devulcanized by means of inorganic compounds. Discarded tires and tire factory waste have been devulcanized by desulfurization of suspended rubber vulcanize crumb (10 to 30 mesh) in solvents such as toluene, naphtha, benzene, cyclohexane, etc. in the presence of sodium (Myers, et al., 1997). The alkali metal cleaves mono-, di-, and polysulfidic crosslinks of the swollen and suspended vulcanized crumb rubber at around 300°C (575°F) in the absence of oxygen.

However, this process may not be economical because it involves swelling of the vulcanized crumb rubber in an organic solvent. In this process, the metallic sodium in a molten condition should reach the sulfidic crosslink sites in the crumb rubber. In addition, the solvents may cause pollution and become hazardous. Another proposed method uses an iron oxide phenyl hydrazine-based catalyst to reclaim powder rubbers (Kawabata, et al., 1981) and copper (I) chloride-tributyl amine catalyst (Kawabata, et al., 1979).
The devulcanization process by use of inorganic compounds is suitable for devulcanization of finely ground tire rubber. However, devulcanization is accompanied by a severe breakdown of the rubber chains. So far, the process has been carried out only on a small laboratory scale.

**Ultrasonic**

Rubber devulcanization by using ultrasonic energy was first discussed in Okuda and Hatano (1987). It was a batch process in which a small piece of vulcanized rubber was devulcanized using 50 kHz ultrasonic waves after treatment for 20 minutes. The process apparently could break down C-S and S-S bonds, but not carbon-carbon (C-C) bonds. The properties of the revulcanized rubber were found to be very similar to those of the original vulcanizates.

One continuous process for devulcanization of rubbers is based on the use of high-power ultrasound electromagnetic radiation. This is a suitable way to recycle waste tires and waste rubbers. The ultrasonic waves, at certain levels, in the presence of pressure and heat, can quickly break up the three-dimensional network in crosslinked, vulcanized rubber. The process of ultrasonic devulcanization is very fast, simple, efficient, and it is free of solvents and chemicals. The rate of devulcanization is approximately one second. This may lead to the preferential breakage of sulfidic crosslinks in vulcanized rubbers. (Isayev, 1993; Yu. Levin, et al., 1996; Isayev, et al., 1997; Yun, et al., 2001; Yun & Isayev, April 2003).

Under a license from the University of Akron for the ultrasonic devulcanization technology, NFM Company of Massillon, Ohio, has built a prototype of the machine for ultrasonic devulcanization of tire and rubber products (Boron, et al., 1996; Boron, et al., 1999). It was reported that retreaded truck tires containing 15 and 30 weight percent (percent by weight) of ultrasonically-devulcanized carbon black-filled SBR had passed the preliminary dynamic endurance test (Boron, et al., 1999).

Extensive studies on the ultrasonic devulcanization of rubbers, and some preliminary studies on ultrasonic decrosslinking of crosslinked plastics, showed that this continuous process allows recycling of various types of rubbers and thermosets (Isayev, 1993; Hong & Isayev, 2002 (pp. 160–168); Shim, et al., 2002; Shim & Isayev, 2003; Gonzalez-de Los Santas, et al., 1999).

As a consequence of the process, ultrasonically-devulcanized rubber becomes soft, therefore enabling this material to be reprocessed, shaped, and revulcanized in very much the same way as virgin rubber. This new technology has been used successfully in the laboratory to devulcanize ground tire rubber (commonly referred to in the industry as GRT) (Isayev, et al., 1995; Yun, et al., 2001; Boron, et al., 1996), unfilled and filled rubbers N (Hong & Isayev, 2001; Yu. Levin, et al., 1996; Isayev, et al., 1997; Diao, et al., 1998; Shim, et al., September 2002; Ghose & Isayev, 2003), guayule rubber (Gonzalez-de Los Santas, et al., 1999), fluoroelastomer, ethylene vinyl acetate foam, and crosslinked polyethylene (Isayev, 1993; Isayev & Chen, 1994). After revulcanization, rubber samples exhibit good mechanical properties, which in some cases are comparable to or exceeding those of virgin vulcanizates.

Structural studies of ultrasonically-treated rubber show that the breakup of chemical crosslinks is accompanied by the partial degradation of the rubber chain; that is, the C-C bonds (Isayev, et al., 1995; Tukachinsky, et al., 1996; Yu. Levin, et al., 1997 (pp. 641–649); Yushanov, et al., 1998). The degree of degradation of C-C bonds can be substantial, depending on conditions. The mechanism of rubber devulcanization under ultrasonic treatment is presently not well understood, unlike the mechanism of the degradation of long-chain polymer in solutions irradiated with ultrasound (Suslick, 1988).

Ultrasonic devulcanization also alters the revulcanization kinetics of rubbers. The revulcanization of devulcanized SBR appeared to be essentially different from those of virgin SBR (Yu. Levin, et
al., 1997, pp. 120–128). The induction period is shorter or absent for revulcanization of devulcanized SBR. This is also true for other unfilled and carbon black-filled rubbers such as ground rubber tire (GRT), SBR, natural rubber (NR), ethylene propylene diene monomer (EPDM), and butadiene rubber (BR) cured by sulfur-containing curative systems, but not for silicone rubber cured by peroxide.

Ultrasonically-devulcanized rubbers consist of sol and gel. The gel portion is typically soft and has significantly lower crosslink density than that of the original vulcanizate. Due to the presence of sol and soft gel, the devulcanized rubber can flow and is subject to shaping. Crosslink density and gel fraction of ultrasonically-devulcanized rubbers were found to correlate by a universal master curve (Yushanov, et al., 1996; Diao, et al., 1999; Yushanov, et al., 1998). This curve is unique for every elastomer due to its unique chemical structure.

**Microwave**

Microwave technology has also been proposed to devulcanize waste rubber (Fix, 1980; Novotny, et al., 1978). This process applies the heat very quickly and uniformly on the waste rubber. The method employs the application of a controlled amount of microwave energy to devulcanize a sulfur-vulcanized elastomer—containing polar groups or components—to a state in which it could be compounded and revulcanized into useful products such as hoses.

The process requires extraordinary or substantial physical properties. On the basis of the relative bond energies of C-C, C-S, and S-S bonds, the scission of the S-S and carbon-sulfur crosslinks appeared to take place. However, the material to be used in the microwave process must be polar enough to accept energy at a rate sufficient to generate the heat necessary for devulcanization. This method is a batch process and requires expensive equipment.

Recently, thermogravimetry was employed to study the changes occurring in rubber vulcanizates during devulcanization. These were carried out by microwave treatment (Kleps, et al., 2000). This study determined the degree of degradation of the polymer chains in response to microwave treatment. It also established the conditions of devulcanization needed to obtain the best properties of rubber devulcanizates for reuse in rubber processing.

**Biological**

Biological processing of vulcanized rubber has been used in some cases, although vulcanized materials are resistant to normal microbial attack (Adhikari, et al., 2000). Several researchers have reported using different types of microorganisms to attack the sulfur bonds in vulcanized elastomers. One process uses a chemolithiotrope bacterium in a liquid solution to depolymerize the surface of powdered elastomers. The polymer chains then are available to bond again during the vulcanization process. The same type of bacterium has been shown to devulcanize crumbed scrap rubber when held in an aerated liquid suspension of microorganisms (Straube, et al., 1994).

Reportedly, sulfur can be recovered in this process, as well as devulcanized rubber. Loffler and colleagues studied the devulcanization of high-quality rubber products by different species of *Thiobacillus* in 1993. The rate of devulcanization was found to be a function of particle size, with best results secured for particles in the range of 100 to 200 microns. However, only a small percentage of the sulfur links were broken after 40 days of exposure.

In 2003, Bredberg investigated and reported on the ability of sulfur-oxidizing bacteria *Acidithiobacillus* and sulfur-reducing *P. furiosus* to break sulfur crosslinks in vulcanized rubber materials. The report covered the effect of grinding methods on reaction rates. Apparently, these types of biological devulcanization processes are exclusively or primarily limited to the surface
layers of the elastomers (Christiansson, et al., 1998). This circumstance may explain the overall low rates of desulfurization based on total mass processed.

Several researchers have reported on devulcanization of vulcanized cis-1,4-polyisoprene, a primary constituent of natural rubber (Tsuchii, et al., 1985; Tsuchii, et al., 1997; Tsuchii & Takeda, 1990). This process employed a bacterium of the species Nocardia, and a white rot fungus, C. subvermispora (Sato, et al., 2003). Holst, et al. in 1998 gives nine other groups or mixtures of microorganisms that have been used for desulfurization of GRT or constituents thereof.

Naturally occurring microorganisms are susceptible to the environmental conditions within the processing system. Thus, toxicity to chemical compounds in the substrate (that is, waste tire rubber) is an overriding concern. Maintenance of proper environmental conditions (availability of nutrients, operating temperature, etc.) during processing is another concern. In fact, methods of determining and preventing biodegradation of rubber have been investigated extensively (Cundell & Mulcock, 1973; Cundell, et al., 1973; Keursten & Groenevelt, 1996; Williams, 1986). Some effort has been expended on isolating and enriching microbial cultures for devulcanizing NR and SBR using biotechnology. Other studies focused on controlling the microbial toxicity of rubber constituents (Bredberg, 2003; Bredberg, et al., 2002).

**Other**

**Mechanical**

A mechanical or reclaimator process has been used for the continuous reclaiming of whole tire scrap (LaGrone, 1986; Szilard, 1973; Bryson, 1979; Klingensmith, 1991; Leyden, 1991). Fine rubber crumb (typically, 30 mesh), mixed with various reclaiming oils, is subjected to high temperature with intense mechanical working in a modified extruder for reclaiming the rubber scrap.

**Steam With or Without Chemicals (Digester)**


The wet process may use caustic and water mixed with the crumb rubber, while the dry process uses steam only. If necessary, various reclaiming oils may be added to the mixer in the vessel. The dry digester has the advantage of less pollution being generated. Scrap rubber containing natural and synthetic rubbers can be reclaimed by the digester process, with the use of reclaiming oil having molecular weights between 200 and 1,000. These consist of benzene, alkyl benzene, and alkylate indanes. The composition of this reclaiming oil and the improved digester process using such reclaiming oil have been patented (Bryson, 1979).

**Biological and Microwave**

Both microbial oxidation and microwave energy have been employed in a two-stage system developed and patented by the Westinghouse Savannah River Company, LLC, for the purpose of devulcanizing waste tire rubber (Fliermans & Wicks, 2000). The process has developed only to the point of proving conceptual feasibility based on limited testing (Westinghouse Savannah River Company, 2004).
Technology Researchers and Providers

In preparing the literature review and consulting other sources, CalRecovery identified a number of entrepreneurial groups and technology suppliers that have developed (or attempted to develop) and/or researched devulcanization processes. These are listed in Table 1. As far as could be determined from the available information, all of the processes listed in Table 1 are at the research or developmental level. None are applied to devulcanizing waste tires on a continuous commercial basis.

The history of rubber devulcanization is checkered with research on various types of technologies. Certain technologies have been discontinued for a variety of reasons, and some researchers have maintained secrecy about their findings. Numerous licensing agreements are in existence. Thus, the listing given in Table 1 likely contains not only the names of the primary technology developers, but also those that license the technologies for use as is or with some type of modification. In many cases, CalRecovery found it difficult to identify or determine the developer of the technology, as opposed to those marketing or licensing the technologies.

As shown in Table 1, CalRecovery identified technologies with apparent origins in North America, including three in California, and in several other countries.

Table 1. Identified Devulcanization Technologies

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Rubber Technologies, Inc.</td>
<td>Florida</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>BF Goodrich Company</td>
<td>Akron, Ohio</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>Exxon</td>
<td>USA</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>Goodyear Tire &amp; Rubber Company</td>
<td>Akron, Ohio</td>
<td>Microwave</td>
</tr>
<tr>
<td>Goodyear Tire &amp; Rubber Company</td>
<td>Akron, Ohio</td>
<td>Chemical/Thermal</td>
</tr>
<tr>
<td>Guangzhou Research Institute</td>
<td>Guangzhou, China</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>LandStar Rubber, Inc.</td>
<td>Scottsdale, Ariz.</td>
<td>Proprietary license</td>
</tr>
<tr>
<td>Levgum, Ltd.</td>
<td>Israel</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>Ultramer/National Feedscrew &amp; Machining, Inc.</td>
<td>Massillon, Ohio</td>
<td>Ultrasonic/Mechanical</td>
</tr>
<tr>
<td>NRI Industries</td>
<td>Toronto, Ont., Canada</td>
<td>Mechanical</td>
</tr>
<tr>
<td>Pacific Northwest National Laboratory (RubberCycle)</td>
<td>Richland, Wash.</td>
<td>Biological</td>
</tr>
<tr>
<td>POLYMERight, Inc.</td>
<td>Fremont, Calif.</td>
<td>Chemical/Mechanical</td>
</tr>
<tr>
<td>Quantum Polymer</td>
<td>Cleveland, Ohio</td>
<td>Chemical</td>
</tr>
<tr>
<td>Redwood Rubber, LLC</td>
<td>Corte Madera, Calif.</td>
<td>Ultrasonic</td>
</tr>
<tr>
<td>Revulcon</td>
<td>Germany</td>
<td>Mechanical</td>
</tr>
<tr>
<td>Rubberworks International</td>
<td>New York</td>
<td>Ultrasonic/Mechanical</td>
</tr>
<tr>
<td>Santee River Rubber Company</td>
<td>South Carolina</td>
<td>Mechanical/unknown</td>
</tr>
<tr>
<td>SoftStone</td>
<td>Pottsboro, Tex.</td>
<td>Same as Levgum</td>
</tr>
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<tr>
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</tr>
<tr>
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</tr>
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<tr>
<td>Company</td>
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<td>Process</td>
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<td>Ultrasonic</td>
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<td>Watson Brown HSM, Ltd.</td>
<td>Glossop, England</td>
<td>Mechanical</td>
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<tr>
<td>Westinghouse Savannah River Company</td>
<td>Aiken, S.C.</td>
<td>Biological/Microwave</td>
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</tbody>
</table>
Chapter 3. Technology Descriptions and Analysis

Introduction
As described in Chapter 2, several types of devulcanization technologies have been applied to the devulcanization of waste tire rubber. Other technologies may have the capacity for devulcanization based on processing of other rubber or thermoplastic feedstocks. Various types of these technologies are described in this chapter, including performance of devulcanized materials or mixtures where such data could be found.

Methodology
Information for this task was primarily secured using the following resources:

- Popular and peer-reviewed literature.
- Waste tire processing equipment manufacturers.
- Websites of devulcanization entrepreneurs and other sources of devulcanization technologies.
- Telephone calls and e-mail communications to researchers and technology vendors.

Despite a concerted effort to collect detailed data and information on the various types of devulcanization technologies, only limited information was found to be in the public domain or of a non-proprietary nature. Consequently CalRecovery, in a number of cases, synthesized general technology descriptions based on the best non-proprietary data that was available and on its engineering judgment.

Few lab-scale or commercial-scale devulcanization systems exist in the United States. Test or performance data released in the public domain is limited, and researchers maintain tight-fisted control of data to protect actual or perceived technical know-how and competitive advantage. In most cases where reports of data and information on devulcanization appear in the available literature, conditions (feedstock characteristics, operating, analytical, etc.) are insufficiently described. These circumstances limited CalRecovery’s attempts to interpret the data and technologies in the current study.

Devulcanization Systems
The process of devulcanizing waste rubber can be broken down into two separate sequential and integrated steps. The first (or pre-processing) step is size reduction. The waste is reduced in size so that it can be fed into the system that actually performs most if not all of the chemical bond-breaking. The second step is the devulcanization process, or the breaking of the chemical bonds (primarily the sulfur bonds). The output product from the process is devulcanized rubber.

Devulcanization system suppliers may supply only the devulcanization process itself, or in combination with a size reduction process.

Pre-Processing of Feedstock (Step 1)
Regardless of the specific type of devulcanization technology (biological, ultrasonic, etc.), devulcanization systems in general are composed of several subsystems. Common to essentially all devulcanization technologies is the need for a finely sized, vulcanized rubber feedstock. This is because the chemical, thermal, or biological conversion subsystems accept only finely sized
feedstock for devulcanization. Also, finely sized feedstock creates substantial surface area for devulcanization reactions to take place.

Consequently, the developers of devulcanization technologies either assume that their operation will procure appropriately sized feedstock from a third party or they must include size reduction equipment as part of their overall devulcanization system. Very generally, a typically desired particle size of feedstock for the devulcanization process is on the order of 10 to 30 mesh. However, there are exceptions to this generality, as discussed later.

There are three primary commercial methods of grinding waste rubber:

1. Ambient grinding.
2. Cryogenic grinding.
3. Wet-ambient grinding.

Generally, several stages of size reduction are used to prepare waste tires or vulcanized scrap rubber for devulcanization. The first stage of size reduction typically reduces the rubber feedstock to a nominal 1- to 2-inch particle size. When processing waste tires, a magnetic separator and a fiber separator are subsequently used to remove the steel and fiber constituents (contamination). The resulting clean, primary-grind product is then further reduced in size using an ambient ground mill, or ground into fine particles while frozen using cryogenic grinding.

One method for producing fine-mesh rubber is cooling scrap tires in liquid nitrogen, and then pulverizing the brittle material in a high-speed hammermill. The ground rubber has a fine particle size, in the range of 30 to 100 mesh.

Another method of producing finely sized rubber is ambient mechanical size reduction using a high-powered rubber mill set at close nip. This method produces 10- to 30-mesh material. Multiple grinder passes can be used to further reduce the particle size.

Lastly, wet or solution process grinding can be used to produce rubber particle size distributions in the range of 200 to 500 mesh.

Grinding processes for tire rubber are well developed. They are widely used for recycling of tire rubbers and rubber wastes. Also, industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved. With waste tire size reduction comes high energy requirements. This is a significant issue if finely-sized rubber feedstock is needed, as is diminution of rubber properties due to heat generation during size reduction.

**Devulcanization Processes (Step 2)**

The following devulcanization processes are described in this chapter:

- Chemical.
- Ultrasonic.
- Microwave.
- Biological.
- Other.
Chemical

Chemical agents have been used to devulcanize scrap rubber since the 1960s. Early research was performed by the Malaysian Rubber Producers Research Association (MRPRA) (Warner, 1994). Initial studies performed by Saville and Watson (Warner, 1994) on low molecular mass compounds paved the way for later researchers to investigate the action of chemical probes. Further studies have been carried out to ascertain which bonds, specifically, were being cleaved by the chemical processes.

Most chemical devulcanization processes are batch processes that involve mixing size-reduced rubber particles and chemical reactants in a temperature- and pressure-controlled mixer. Generally speaking, rubber is fed into a mixer with a devulcanizing agent and heated. In the case of abandoned technology of the mid-1990s (namely, the De-Link Recycling System promoted by STI-K Polymers), the recommended ratio of chemical agent to a finely sized (for example, 40 mesh) rubber feedstock was approximately 2 to 6 parts by weight chemical to 100 parts rubber (Kohler & O’Neill, 1997; Sekhar & Kormer, 1995; Findians Oy, 2003). Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A flow diagram of the process is given in Figure A.

Figure A. Schematic Diagram of a Chemical Devulcanization System

Various chemical agents have been used in the chemical devulcanization processes developed over the years. The agents include petroleum-based solvents (for example, toluene), thiol-amine reagents, hydroxide, disulfide compounds, or chlorinated hydrocarbons. With some chemical agents, a catalyst is also used to promote the desired reactions.

The following two chemical devulcanization processes are indicative of the current commercialization efforts, lab-scale systems, or both.

POLYMERight, Inc., a California-based company, is developing a rubber reclaiming process where a measured amount of proprietary devulcanization chemical agent (DB-26) is added to a mixer and heated with a corresponding amount of vulcanized rubber. After the requisite exposure time is elapsed, the slurry is forced through an extruder at temperatures between 500° and 600°F (260° and 315°C). Once cooled, the now devulcanized rubber is ready for sale. According to company information, POLYMERight’s technology has been demonstrated on a laboratory scale (10 to 15 lb/hr), but it has yet to be demonstrated on a commercial scale.

Another company marketing a chemical devulcanization technology is Tires2Oil, Inc. (T2O). The T2O process takes place in a mixer or reactor. In the case of tire rubber, granulated rubber (approximately 30 mesh) is separated from the fiber and metal fractions and loaded into a reactor.
The rubber is then mixed with a proprietary solvent and treated at thermodynamically critical conditions of temperature and pressure.

When the requisite reaction time has elapsed, the mixture is cooled and the gases vented and stored. The oil and solvent fraction is drained from the reactor, and the carbon black is removed for additional processing. The solvent is then separated by distillation—or other means—for reuse. The sulfur, which has been collected from the mixture and scrubbed from the gases, reportedly can also be sold. Carbon black recovered from the process can also be further processed by T2O for resale. T2O also claims to have developed additional processes that are capable of recovering the other chemical constituents of vulcanized rubber; for example, oils, solvents, and sulfur (Tires2Oil, 2004).

**Ultrasonic**

Most companies marketing ultrasonic devulcanization technologies are utilizing very similar technologies involving cold feed extruders and varying physical arrangements of ultrasonic equipment. The recent technologies are continuous processes, as opposed to batch.

Ultrasonic devulcanization technology is actually composed of a “devulcanization system”—namely, extrusion and ultrasonic processing. Many of the designs are similar. Two key differences in some cases are the equipment and materials used to generate the ultrasonic energy required for the process, and the positioning of the transducer(s) relative to the extruder.

Two different arrangements of ultrasonic devulcanization systems are shown in Figures B and C. In this type of devulcanization system, size-reduced rubber particles are loaded into a hopper and are subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and softens the rubber. As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy.

The resulting combination of heat, pressure, and mechanical mastication is sufficient to achieve varying degrees of devulcanization. The time constant of the devulcanization process takes place in seconds. Essentially all of the rubber entering the process is discharged from the extruder in semi-solid product stream. Process losses would be primarily those due to emissions of fine particulates or of gases, if any, generated due to the mechanical and thermal processes occurring during the devulcanization process. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried.
In terms of laboratory or commercial ultrasonic processing systems that are operational or were in the last five to eight years, the following descriptions are representative examples.

The University of Akron has a laboratory-scale ultrasonic devulcanization system that utilizes mechanical extrusion and ultrasonic energy to devulcanize scrap rubber. The extruder reportedly has a capacity of approximately 50 lb/hr (Isayev, 1993; Isayev & Chen, 1994; Isayev, et al., 1995; Tukachinsky, et al., 1996; Yun, et al., 2001). The required particle size of the scrap rubber feedstock is generally 10 to 30 mesh. Processing rates during laboratory test runs of about 5 lb/hr have been reported when processing tire rubber (Hong and Isayev, 2002, pp. 160–168). At these processing rates, the system requires approximately 1 to 1.5 kW ultrasonic energy (20 kHz) source.
Under a license from the University of Akron’s ultrasonic devulcanization technology, Ultramer, Inc., of Massillon, Ohio, has reportedly built a prototype machine for ultrasonic devulcanization of tire and rubber products. The project manufactured retreaded truck tires containing 15 and 30 weight percent of ultrasonically devulcanized carbon black-filled SBR.

Also, Redwood Lumber, LLC, Corte Madera, Calif., has reportedly constructed and operated a proprietary ultrasonic devulcanization system. The process is based on the use of “magnetostriction-based” ultrasound (Ruhman, et al., 2000). The processing capacity is low but unknown as of this writing.

**Microwave**

Microwave technology has also been proposed to devulcanize waste rubber. This process applies the heat energy very quickly and uniformly on the waste rubber. However, any vulcanized rubber used in the microwave process must be sufficiently polar in structure so that the microwave energy can be absorbed at a rate adequate to generate the heat necessary for devulcanization. This method is a batch process; a schematic diagram of the general process flow is shown in Figure D. Microwave energy requirements are in the range of .041 and 0.177 kW/lb in the case of devulcanizing EPDM using microwave frequencies between 915 and 2450 MHz. Processing times are approximately five minutes, with 90 to 95 percent recovery of rubber (Adhikari, et al., 2000).

**Figure D. Schematic Diagram of a Microwave Devulcanization System**

The only rubber used in tires that is sufficiently polar to be effectively devulcanized by microwave energy is EPDM. This represents a small fraction of the rubber used in tires, probably well under 5 percent, because it is primarily used in whitewalls and raised white letters. Most types of rubber used in tire manufacture (natural rubber/polysisoprene, styrene-butadiene rubber, polybutadiene, polyisobutylene) are not sufficiently polar to be devulcanized by microwave technology because sufficient heating of the rubber constituents cannot be obtained to promote devulcanization.

The only reasonable use for microwave devulcanization is on compounds containing primarily a polar rubber, such as EPDM hose. Goodyear obtained a U.S. patent for the use of microwave energy to devulcanized rubber in 1978 (Novotny, et al., 1978). The process was used to devulcanize EPDM hose scrap for some years, then was abandoned due to unfavorable economics (Klingensmith, 1996).

**Biological**

The concept of utilizing bacteria to devulcanize scrap rubber has been investigated for at least 30 years. For example, Beckman, Crane, Kay, and Laman concluded an in-depth evaluation of the biodegradation of rubber in 1974 (Warner, 1994). Although vulcanized materials are resistant to normal microbial attack and compounded rubber can act as a biocide, several researchers have reported using different types of microorganisms to attack the sulfur bonds in vulcanized elastomers.
Bacterial devulcanization is performed by mixing finely ground rubber with media containing the appropriate bacterium in a temperature-controlled bioreactor. The slurry is then maintained at a prescribed temperature and pressure for the duration of the treatment. Biological contact time is approximately ten to a few hundred days. Solids content of the slurries used in research are approximately 5 percent by weight (Holst, et al., 1998; Christiansson, et al., 1998).

Once processed, the newly devulcanized material is rinsed and filtered to remove the microorganisms, then dried for sale. An important fact of note is that this technology requires an extremely fine feedstock in order to achieve useful degrees of devulcanization [for example, 200 mesh (75 microns) (Romine, 1997) or 100 to 200 microns (Loffler et al., 1993)]. A generic processing diagram for a biological devulcanization system is shown in Figure E.

Figure E. Schematic Diagram of Biological Devulcanization System

Other

Mechanical

Mechanical devulcanization is achieved through the repeated deformation of rubber particles under specific conditions of temperature and pressure.

One mechanical process implemented by Toyoda Gosei (TG) utilizes a “modular screw-type reactor” to manipulate and stress the rubber until it is plasticized and then ultimately devulcanized (Fukumori et al., 2002). By manipulating screw configuration and rotational speed, and processing temperature, researchers are able to control the duration of the treatment. In this way they can, to some extent, control the properties of the devulcanizate.

The TG process can accept and process rubber feedstock up to about 5 to 10 mm. According to the developers, the process requires about 100 Kw (kilowatts) to process 200 to 300 kg (kilograms)/hr of rubber, or approximately 0.4 kW/kg. The TG process has been primarily, if not exclusively, used to devulcanize specific types of rubber compounds, such as NR and SBR.
**Steam With or Without Chemicals (Digester)**

Steam devulcanization of crumb rubber uses a steam vessel equipped with an agitator for continuous stirring of the crumb rubber while steam is being applied. There are two variants of the basis steam process, namely, “wet” and “dry.” The wet process uses caustic and water mixed with the rubber crumb, while the dry process uses only steam.

If necessary, various reclaiming oils may be added to the mixture in the reaction vessel. In one case, a wet process using diaryl disulfide and reclaiming oils with saturated steam at 190°C (374°F) was fed finely ground NR and synthetic rubber scraps. A charge of about 440 lbs. was partially devulcanized after 15 to 17 hours of processing. This process required 12 hours at ambient temperature for pre-treatment and 3 to 5 hours for steam or high temperature treatment (Adhikari, et al., 2000).

The dry process digester has the advantage of generating less pollution than the wet process. Scrap rubber containing natural and synthetic rubbers can be reclaimed by the steam digestion process. Reclaiming oil used for this process has molecular weights between 200 and 1000, consisting of benzene, alkyl benzene, and alkylate indanes. A generic processing diagram for steam devulcanization is shown in Figure F.

**Figure F. Schematic Diagram of a Steam Devulcanization System**

![Steam Devulcanization System Diagram]

**Product Characteristics**

**Processing Parameters and Compound Properties**

**Background**

The properties of devulcanized rubber, and properties of materials manufactured from this substance, depend on the results of the devulcanization process. These properties also depend on the other constituents of the product that incorporates the devulcanized rubber. In the industry, the formulation process is referred to as compounding.

Compounding is important in determining the characteristics of products manufactured with devulcanized rubber. Therefore, we include a section on compounding and its influence on material properties as an introduction to the discussion of devulcanized product characteristics. The discussion also serves as a backdrop to the assessment presented in Chapter 5, Market Analysis.
Compounding

Compounding is the process of combining rubber with all of the ingredients that will be present in the final vulcanized product. A compound is the recipe that is mixed and milled, then extruded, calendered, or molded into the desired shape, and cured at high temperature. This recipe would include the carbon black and/or other fillers, extender oil, antioxidants, antiozonants, sulfur, and other curatives, such as accelerators and activators.

The term “compound” typically refers to rubber that has been pre-mixed and milled to be shaped and cured into a finished product. For example, “custom compounders” produce compound and sell it to manufacturers of finished rubber goods. A tire retreader would buy “tread compound” already extruded into the approximate shape of a tread, apply it to a tire carcass, and then vulcanize it in a mold. The term is also used to refer to a cured compound. For example, all of the properties in the examples given below are properties of the cured compounds.

The compounding of rubber is a synthesis of art and science. While much has been learned and published about rubber compounding, the practice still involves both intuition and trial-and-error. General principles provide at least a good starting point for compound development. For example, carbon black is a “reinforcing” filler. Carbon black increases the tensile strength of rubber up to a point, usually to the loading level of approximately 50 parts per hundred (phr). With most mineral fillers, tensile strength drops as the level of filler is increased.

The following examples of compound properties for different applications give some specifics as to how compound properties vary with the amounts of fillers and oils used (Vanderbilt Rubber Handbook, R.T. Vanderbilt Company, 1990). This standard reference has dozens of typical rubber compounds for many different applications, some of which could be used as the basis for test compounds using devulcanized rubber.

Examples

The loading of carbon black and minerals affects properties of natural rubber. As indicated in Tables 2 and 3, values of hardness and modulus increase as loading levels increase, while elongation and tensile strength decrease. Tensile strength begins to drop off when carbon black loadings exceed the 50 parts per hundred (phr) range. This is why most high-strength applications use this range of carbon black loading.
<table>
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<tr>
<th>Constituent and Loading</th>
<th>300% Mod, MPa (psi)</th>
<th>Tensile MPa (psi)</th>
<th>Elong. (%)</th>
<th>Hard. (Shore A)</th>
<th>Tear, kN/m (psi)</th>
<th>Compr. Set (%)</th>
<th>Mooney (t5/ML)</th>
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<td>2.8 (400)</td>
<td>22.1 (3200)</td>
<td>660</td>
<td>43</td>
<td>28.2 (160)</td>
<td>13</td>
<td>14/11</td>
</tr>
<tr>
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<td>4.4 (640)</td>
<td>21.4 (3100)</td>
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<td>45.8 (260)</td>
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</tr>
<tr>
<td>75 phr</td>
<td>6.3 (920)</td>
<td>18.8 (2730)</td>
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<td>42.2 (240)</td>
<td>14</td>
<td>9/17</td>
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<tr>
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<td>15.3 (2200)</td>
<td>530</td>
<td>80</td>
<td>44.9 (255)</td>
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<td>11.6 (1580)</td>
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<td>59.9 (340)</td>
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<td>74</td>
<td>73.9 (420)</td>
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</table>

Base Compound:
- SMR-5
- Vanplast R
- Stearic Acid
- Zinc Oxide
- Agerite Stalite S
- Sulfur
- Altax
- Methyl Tuads

All compounds cured 10 minutes at 153°C (307°F).
Tear measured on Die A samples.
Compression set measured after 22 hours at 70°C (158°F).
Mooney measured at 132°C (270°F).
Table 3. Effect of Mineral Loading Materials in Natural Rubber

<table>
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<tr>
<th>Constituent and Loading</th>
<th>300% Mod., MPa (psi)</th>
<th>Tensile MPa (psi)</th>
<th>Elong. (%)</th>
<th>Hard. (Shore A)</th>
<th>Tear, kN/m (pli)</th>
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<td>65</td>
<td>40.5 (230)</td>
<td>44</td>
<td>15/78</td>
</tr>
</tbody>
</table>

Base Compound:
- SMR-5
- Vanplast R
- Stearic Acid
- Zinc Oxide
- Agerite Stalite S
- Sulfur
- Altax
- Methyl Tuads

All compounds cured 15 minutes at 153°C (307°F).
Tear measured on Die A samples.
Compression set measured after 22 hours at 70°C (158°F).
Mooney measured at 132°C (270°F).

Higher quality compounds of rubber use lower levels of carbon black and mineral loading. Therefore, these compounds possess higher proportions of rubber, as shown by way of examples for SBR compounds in Tables 4A and 4B. As indicated by the data in Tables 4C and 4D, respectively, the automotive mat compound has about six times as much filler (325 phr) as the high-quality shoe sole compound (50 phr).
### Table 4A. Properties of Some Compounds Used to Manufacture High-Quality Conveyor Belt Cover (phr)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mix 1</th>
<th>Mix 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR extended with aromatic oil</td>
<td>137.5</td>
<td>--</td>
</tr>
<tr>
<td>SBR extended with carbon black</td>
<td>--</td>
<td>162.5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Vanax NS accelerator</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Methyl Tuads accelerator</td>
<td>0.4</td>
<td>--</td>
</tr>
<tr>
<td>Carbon black</td>
<td>70</td>
<td>--</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>10</td>
<td>--</td>
</tr>
</tbody>
</table>


### Table 4B. Properties of Some Compounds Used to Manufacture Medium-Quality Conveyor Belt Cover (phr)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mix 1</th>
<th>Mix 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR extended with aromatic oil</td>
<td>137.5</td>
<td>--</td>
</tr>
<tr>
<td>SBR extended with oil and carbon black</td>
<td>--</td>
<td>245</td>
</tr>
<tr>
<td>Carbon black</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>40</td>
<td>--</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>--</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Agerite Superflex antioxidant</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Antozite 67P antiozonant</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vanax NS accelerator</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Methyl Tuads accelerator</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4C. Properties of Some Compounds Used to Manufacture Automotive Mat (phr)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR extended with naphthenic oil</td>
<td>150</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>4</td>
</tr>
<tr>
<td>Agerite Superflex antioxidant</td>
<td>1.5</td>
</tr>
<tr>
<td>Vanwax NS special protective wax</td>
<td>3</td>
</tr>
<tr>
<td>Glycol activator</td>
<td>2</td>
</tr>
<tr>
<td>Clay, calcium carbonate, silica fillers</td>
<td>325</td>
</tr>
<tr>
<td>Naphthenic plasticizer</td>
<td>30</td>
</tr>
<tr>
<td>Amax accelerator</td>
<td>2</td>
</tr>
<tr>
<td>Methyl Tuads accelerator</td>
<td>0.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4</td>
</tr>
</tbody>
</table>


Table 4D. Properties of Some Compounds Used to Manufacture Shoe Sole (phr)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>High-Quality</th>
<th>Medium-Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR (45-55 ML4)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Naphthenic oil</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vanox MBPC antioxidant</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Altax accelerator</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Unads accelerator</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Glycol activator</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>Silica filler</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Pliolite S6-B high-styrene resin</td>
<td>--</td>
<td>25</td>
</tr>
<tr>
<td>Dixie clay</td>
<td>--</td>
<td>120</td>
</tr>
</tbody>
</table>

Properties of natural rubber compounds for two different applications are shown in Tables 5 and 6. The radial truck tread described in Table 5 has about half the fillers of the first extrusion compound (AA 515), described in Table 6, and nearly twice the tensile strength. Note also that the second extrusion compound (AA 725) described in Table 6 shows a considerable increase in strength and modulus with the use of more carbon black in place of the clay. This is a good illustration of the reinforcing effect of carbon black, compared with that obtainable with non-reinforcing clay.

Finally, the characteristics of two EPDM hose compounds are presented in Table 7 in order to show one of the most extreme examples of loading levels and their influence in rubber manufacturing. The “highly extended” EDPM hose compound described in the table has 600 phr oil and filler, or about 11 times as much oil and filler as the “steam hose” compound (55 phr), and less than half the strength (6.4 vs. 13.0 MPa) and modulus (2.2 vs. 4.9 MPa). This example shows how much rubber can be saved when property requirements are not critical for product end uses.

Table 5. Characteristics of Radial and Bias Truck Tread Recipes

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Radial</th>
<th>Bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSR 20 natural rubber</td>
<td>100</td>
<td>--</td>
</tr>
<tr>
<td>Budene 1207</td>
<td>--</td>
<td>50</td>
</tr>
<tr>
<td>Plioflex 1712</td>
<td>--</td>
<td>68.75</td>
</tr>
<tr>
<td>SAF black (N-110)</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Antozite 67P</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Agerite Resin D</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>Vanax H Special</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>4</td>
<td>12.5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>4</td>
<td>3.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.55</td>
</tr>
<tr>
<td>Durax</td>
<td>1.75</td>
<td>--</td>
</tr>
<tr>
<td>Vantard PVI</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>Morfax</td>
<td>--</td>
<td>1</td>
</tr>
<tr>
<td>Methyl Tuads</td>
<td>--</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>169.50</strong></td>
<td><strong>200.75</strong></td>
</tr>
</tbody>
</table>

**Rheometer at 150°C (300°F)**

| t_{s1} (minutes) | 7.4 | 12.2 |
| t_{c90} (minutes) | 12.0 | 36.8 |

**Physical Properties**

**Cured 22 minutes at 150°C (300°F)**

| Stress at 300%, MPa (psi) | 12.3 (1790) | 11.8 (1710) |
| Tensile strength, MPa (psi) | 27.1 (3920) | 17.6 (2550) |
| Elongation at break (%) | 550 | 415 |
| Rebound\(^a\) at 22°C (72°F) (%) | 81.9 | 70 |

\(^a\) ASTM D1054, cured 32 minutes at 150°C (300°F).

<table>
<thead>
<tr>
<th></th>
<th>ASTM D 2000</th>
<th>AA 515</th>
<th>AA 725</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR-5</td>
<td></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Agerite Stalite S</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Vanfre AP-2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Vanplast R</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Circo light oil</td>
<td>8</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>Neophax A</td>
<td>30</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>FEF black (N-550)</td>
<td>30</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>McNamee Clay</td>
<td>40</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.75</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>Amax</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Methyl Tuads</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

**Cured 10 minutes at 153°C (307°F)**

- 300% modulus, MPa (psi) 5.4 (780) 16.6 (2400)
- Tensile strength, MPa (psi) 13.8 (2000) 18.8 (2730)
- Elongation (%) 570 370
- Hardness (Shore A) 50 68
- Tear die A, kN/m (pli) 21.1 (120) 28.2 (160)

**Cured 5 minutes at 160°C (320°F)**

- 300% modulus, MPa (psi) 5.4 (790) 16.1 (2340)
- Tensile strength, MPa (psi) 14.5 (2110) 18.7 (2720)
- Elongation (%) 530 380
- Hardness (Shore A) 50 67
- Tear die A, kN/m (pli) 56.3 (320) 33.4 (190)

**Mooney at 121°C (250°F)**

- Scorch, t5 (minutes) 10 9
- Plasticity (ML) 15 28

**Compression Set after 22 hrs at 70°C (158°F)**

- % set 38 22

Table 7. Properties of EDPM Hose Compounds

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Highly Extended Hose Compound</strong></td>
<td></td>
</tr>
<tr>
<td>Nordel® 2760P</td>
<td>100.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Oil and Fillers</strong></td>
<td></td>
</tr>
<tr>
<td>Atonite whiting</td>
<td>200.0</td>
</tr>
<tr>
<td>GPF black (N-650)</td>
<td>200.0</td>
</tr>
<tr>
<td>Cincosol 4240</td>
<td>200.0</td>
</tr>
<tr>
<td>Paraffin</td>
<td>2.0</td>
</tr>
<tr>
<td>Altax</td>
<td>1.5</td>
</tr>
<tr>
<td>Butyl Zimates</td>
<td>3.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.0</td>
</tr>
<tr>
<td>Vanax A</td>
<td>1.0</td>
</tr>
<tr>
<td>Methyl Tuads</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Mooney Scorch, MS 121°C (250°F)</strong></td>
<td></td>
</tr>
<tr>
<td>Minimum viscosity</td>
<td>13</td>
</tr>
<tr>
<td>Time to 10 pt. rise (minutes)</td>
<td>17</td>
</tr>
<tr>
<td><strong>Vulcanizate Properties, Press Cure, 177°C (350°F), 5 min</strong></td>
<td></td>
</tr>
<tr>
<td>100% modulus, MPa (psi)</td>
<td>2.2 (310)</td>
</tr>
<tr>
<td>Tensile strength, MPa (psi)</td>
<td>6.4 (920)</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>460</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steam Hose Tube Compound</strong></td>
<td></td>
</tr>
<tr>
<td>Nordel® 2522</td>
<td>100.0</td>
</tr>
<tr>
<td>Agerite Resin D</td>
<td>1.5</td>
</tr>
<tr>
<td>Zn stearic</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Oil and Fillers</strong></td>
<td></td>
</tr>
<tr>
<td>FEF black (N-550)</td>
<td>55.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
</tr>
<tr>
<td>Vanax MBM</td>
<td>1.0</td>
</tr>
<tr>
<td>Varox DCP-40C</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>Mooney at 132°C (270°F)</strong></td>
<td></td>
</tr>
<tr>
<td>Scorch, t5 (minutes)</td>
<td>6.5</td>
</tr>
<tr>
<td>Viscosity (ML)</td>
<td>39.0</td>
</tr>
<tr>
<td><strong>Cured 8', 177°C (350°F) Original Properties</strong></td>
<td></td>
</tr>
<tr>
<td>100% modulus, MPa (psi)</td>
<td>4.9 (710)</td>
</tr>
<tr>
<td>Tensile, MPa (psi)</td>
<td>13.0 (1885)</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>190</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>74</td>
</tr>
</tbody>
</table>

Many more examples illustrating the effect of compounding on properties are available in the *Vanderbilt Rubber Handbook* and other similar reference sources. Such reference sources can give guidelines to compounders as a starting point in developing a new compound. They are also helpful in determining the compound properties required for specific applications. In the case of devulcanized rubber, they can offer target properties to determine which applications might be most appropriate.

**Properties**

When considering the use of devulcanized rubber in various applications, the properties of the rubber are critical to both its processing characteristics and its suitability in the final application. This is true of tires, mechanical goods (belts, hoses, seals, etc.), or lesser applications such as floor mats, insulation, etc. Most of the published data identified in this study has been associated with the following properties: Mooney viscosity (ML-4), tensile strength, modulus, and elongation. While these properties are indeed important, many other rubber properties are equally important in characterizing a rubber.

Another key performance property is hysteresis behavior, which in rubber relates to the amount of heat produced with repeated flexing. Hysteresis is particularly important in tire sidewalls, and it is partly for this reason that natural rubber is a major ingredient in most sidewall compounds. This is because natural rubber has better hysteresis properties than most synthetics.

Two other key properties relating to tire building are tack and green strength. Tack is the extent to which an unvulcanized compound will stick to itself or to another unvulcanized compound. Green strength is the strength of the “green,” or unvulcanized, compound. Because devulcanization changes the molecular structure of the rubber, the effect of the devulcanization process on these properties is important.

Other important properties involve the aging properties of a rubber, particularly its oxygen and ozone resistance. Antioxidants and antiozonants are chemicals added to rubber compounds to provide such resistance. Little information has been reported with regard to whether or not these chemicals are removed or destroyed during devulcanization, or whether their effectiveness is reduced, thus making it necessary to add more of them to the devulcanized rubber.

Other processing-related properties are not as easily quantified. The time and temperature required to mix a compound and the amount of energy required for mixing, as well as the curing time and temperature required, are difficult to gauge. Some of these processing characteristics for devulcanized rubber will probably be different from those of virgin rubber of the same type.

Part of the difference is that some portion of the original compound ingredients, including curatives, antioxidants, antiozonants, oil, and fillers, will still be present in the devulcanized rubber. These differences also mean that the quantities of curing ingredients required will most likely be different. For example, how much of the original sulfur remains in the rubber in a chemically active state, and how much was lost? And, how much of the original accelerator and activator is still present and is still chemically active? To the extent that some of these chemicals are still present, less of them will need to be added to cure the devulcanized rubber.

All of the properties mentioned in the preceding paragraphs are critical to how well a devulcanized rubber can be used as a complete or partial substitute for virgin rubber. Therefore, a competent rubber laboratory should test the devulcanized rubber to characterize these properties and determine what compound changes are needed to effect the desired cure, provide the desired properties both for processing and for the cured compound, and provide adequate protection against the effects of oxygen and ozone.
Another critical area of laboratory testing is the determination of how the addition of a proportion of devulcanized rubber to virgin rubber affects the properties of the final blend. For example, how much devulcanized rubber, with lower mechanical properties, can be added before the mechanical properties of the blend are significantly reduced? This will determine the practical limits on the levels of devulcanized rubber that can be used in various applications.

Testing will also help to determine the economic viability of using devulcanized rubber in these applications. Some of the data presented later in this report show substantial reduction in tensile strength with the addition of devulcanized rubber. In other cases, little or no reduction in properties occurs. Such large discrepancies in data show that more work is needed to better understand these effects.

Mechanical properties such as tensile strength, modulus, and elongation are not measured on the pure rubber, but on a cured compound. Consequently, a critical point is that these properties are dependent not only on the rubber itself, but on the amount and type of fillers and extenders used, as well as the state of cure.

For example, a tire tread compound of SBR would have much higher mechanical properties than an SBR carpet underlay compound. Even though the same rubber is used, the tread compound would typically have about 45 to 50 parts of carbon black and 5 to 10 parts of extender oil per 100 parts of rubber. The carpet underlay might have 200 or more parts of fillers, usually clay, calcium carbonate, and possibly even some crumb rubber, and 50 or more parts of oil per 100 parts of rubber. Some hose compounds contain as much as 400 parts of fillers and 200 parts of oil per 100 parts of rubber. Compounds used in rubber matting typically use equally large amounts of fillers, often including crumb rubber.

Another important point is that these “lower-value” products do not use poorer quality rubber, but they use less rubber by increasing the amount of fillers and oil in the compound. Just enough rubber is used to achieve the desired properties, while lower-cost fillers and oils extend the rubber to allow the compound cost to be kept competitive. To use an application of devulcanized rubber, with its lower properties, in these products, a little more rubber (and, thus, fewer fillers) may be necessary in order to achieve the desired mechanical properties. This is another area where laboratory compounding and testing would be needed to determine some of the possible applications.

**Chemically or Chemically/Mechanically Devulcanized Rubber**

Little information is available in the public domain about the properties of rubber compounds formulated with chemically devulcanized waste tire rubber. Some data that were identified during the course of the study are shown in Table 8. The reported data reflect two different types of chemical devulcanization technologies.

Unfortunately, a detailed accounting of test materials, performance parameters, and conditions is lacking, thus inhibiting the extent of interpretation of the data. Comparisons of data are primarily limited to comparing the properties of virgin rubbers with compounds containing the virgin and devulcanized material at concentrations of about 30 percent devulcanized material. As shown by the data in the table, the properties of the mixtures containing devulcanized material are in general moderately lower than those of their virgin counterparts.
Table 8. Properties of Waste Tire Rubber Devulcanized Using Chemical or Chemical/Mechanical Technology

<table>
<thead>
<tr>
<th>Technology Type</th>
<th>Technology Surrogate</th>
<th>Test Rubber Compounds</th>
<th>% Devulc (or Ground) Mat’l</th>
<th>Mooney Viscosity (ML-4 @ 212°F)</th>
<th>Tensile Strength (lbs/in²)</th>
<th>300% Modulus (lbs/in²)</th>
<th>Elongation to Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>STI-K Polymers DeLink</td>
<td>NR</td>
<td>0</td>
<td>61.9</td>
<td>4,270</td>
<td>1,987</td>
<td>534</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NR w/devulc NR</td>
<td>30</td>
<td>72.3</td>
<td>4,020</td>
<td>2,151</td>
<td>489</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Virgin SBR (1520)</td>
<td>0</td>
<td>96.6</td>
<td>3,880</td>
<td>3,059</td>
<td>358</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SBR (1520) w/devulc SBR</td>
<td>30</td>
<td>109.2</td>
<td>3,580</td>
<td>2,923</td>
<td>345</td>
</tr>
<tr>
<td>Chemical/Mechanical</td>
<td>LandStar/ Guangzhou Research Institute</td>
<td>NR</td>
<td>100</td>
<td>28.4</td>
<td></td>
<td></td>
<td>680</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SR</td>
<td>100</td>
<td>17.2</td>
<td></td>
<td></td>
<td>514</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AMR Powder (devulc. additive)</td>
<td>100</td>
<td>23.9</td>
<td></td>
<td></td>
<td>640</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tread Tire Compound</td>
<td>0</td>
<td>20.3</td>
<td></td>
<td></td>
<td>772</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Light Duty Truck Tire Compound</td>
<td>0</td>
<td>23.8</td>
<td></td>
<td></td>
<td>536</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a Kohler &amp; O'Neill, 1997.</td>
<td>b Howlett, 1999. Basis of data: Xingru, 1997.</td>
<td>c AMR is assumed to mean activated-modified rubber.</td>
<td>50 NR + 30 SR + 20 CIS-BR + 40 AMR.</td>
<td>30 NR + 70 SR + 0 CIS-BR + 40 AMR.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ultrasonically Devulcanized Rubber

Similar to the case for chemically devulcanized rubbers, CalRecovery found limited data in the public domain related to the performance of mixtures containing devulcanized waste tire rubber. A summary of some performance data is presented in Table 9 for some rubbers used in tire construction. As was noted in the case of chemically devulcanized rubbers, a general diminution occurs in properties of mixtures containing devulcanized rubber versus the virgin equivalents. For the conditions of the University of Akron research, data in the table show the following:

1. Substantial diminution of some properties as percent devulcanized rubber is increased.

2. That the percentage reduction in properties between virgin mixtures and those containing devulcanized product generally decreases as the percentage of devulcanized product is increased.
Table 9. Properties of Waste Tire Rubber Devulcanized Using Ultrasonic Technology

<table>
<thead>
<tr>
<th>Technology Surrogate</th>
<th>Test Rubber Compounds</th>
<th>% Devulc or (Ground) Mat'l</th>
<th>Mooney Viscosity (ML-4 @ 212°F)</th>
<th>Tensile Strength (lbs/in²)</th>
<th>100% Modulus (lbs/in²)</th>
<th>300% Modulus (lbs/in²)</th>
<th>Elongation to Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U of Akron</td>
<td>SBR 1848&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0</td>
<td>2,415</td>
<td>740</td>
<td>780</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR (1848) w/devulc</td>
<td>10</td>
<td>1,075</td>
<td>790</td>
<td>540</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR (1848) w/whole train reclaim&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(10)</td>
<td>1,940</td>
<td>760</td>
<td>660</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SBR (1848) w/30 mesh buffings&lt;sup&gt;a&lt;/sup&gt;</td>
<td>(10)</td>
<td>1,440</td>
<td>780</td>
<td>480</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100% NR (SMR CV60) &amp; 0% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>3,263</td>
<td>116</td>
<td>670</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR (SMR CV60) &amp; 25% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>1,885</td>
<td>123</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25</td>
<td>580</td>
<td>123</td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NR (SMR CV60) &amp; 50% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>406</td>
<td>131</td>
<td>390</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Technology Surrogate</td>
<td>Test Rubber Compounds</td>
<td>% Devulc or (Ground) Mat'l</td>
<td>Mooney Viscosity (ML-4 @ 212°F)</td>
<td>Tensile Strength (lbs/in²)</td>
<td>100% Modulus (lbs/in²)</td>
<td>300% Modulus (lbs/in²)</td>
<td>Elongation to Break (%)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------</td>
<td>-----------------------------</td>
<td>---------------------------------</td>
<td>---------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50</td>
<td>363</td>
<td>123</td>
<td>320</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR (SMR CV60) &amp; 75% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>363</td>
<td>145</td>
<td>295</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>75</td>
<td>276</td>
<td>131</td>
<td>250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>290</td>
<td>152</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% SBR (23.5% bound styrene, and Duraden 706)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>100</td>
<td>290</td>
<td>138</td>
<td>180</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Boron, et al., 1996.
<sup>b</sup> Adapted from Hong & Isayev, 2002 (pp. 160–168).
Chapter 4. Cost Analysis

This analysis of the costs associated with the production of devulcanized rubber is based on information available in the public domain and on the experience of the members of the project team in conducting similar analyses for a variety of processing systems.

Detailed cost data for devulcanization, and associated technical data as mentioned previously, are sparse in the available literature. Breakdowns of capital and operating costs by cost category are essentially not available. In addition, comprehensive mass balance descriptions are lacking, thus substantially restricting the ability to estimate yield of devulcanized rubber and production of process by-products.

Consequently, cost estimates, when found in the literature, could not be analyzed and judged for completeness, reasonableness, and accuracy. Unit production “costs” found during the performance of the study were typically in the range of $0.20 to $0.50/lb. These costs were inadequately documented. In fact, it was not possible to determine if the costs were all-inclusive or if they included reasonable costs for feedstocks, profit, revenues from waste tire disposal fees, and fees for disposal of process residues.

Given the lack of information in the literature, the CalRecovery team opted to construct engineering cost estimates for devulcanization based on descriptions of devulcanization systems identified during the study and described earlier in the report. The cost estimates are based on a synthesis of information and data from multiple sources for a given generic type of technology; for example, chemical.

The team found that this approach was the best method available for approximating the cost of devulcanization. The team consulted multiple sources of information because no source provided anything approaching adequate information and data that would be needed for a third-party analysis of production cost and system performance. Thus, the estimates of cost given in this section are not for a specific (for example, proprietary) devulcanization technology. However, they should be generally applicable for a group of similar types of technology; for example, chemical. Since the majority of information in the available literature is reported in research and development studies, the cost analysis reflects systems using low (that is, laboratory-scale) processing rates.

The analysis was generally performed by determining the costs (capital and operating and maintenance) of the processes and equipment described in the available literature. The cost analyses were conducted for three technologies that use different processing approaches: chemical, ultrasonic, and mechanical.* The key processing elements of each of these technologies have been described in Chapter 3 of this report, and they serve as the primary basis of estimating capital and operating and maintenance costs.

In cases where sufficient equipment or other processing information was not found in the literature, the study team used its professional judgment to complete the processing system design, operating plan, etc. The results of the analysis are presented in Table 10. The processing rates used in the analysis are in the range of 75 to 100 lb/hr, as shown in the table. As a context, if 25 percent of California waste tire crumb rubber production (about 8 million tires per year, * Insufficient technical information and data were found during the study to enable reliable cost analyses for other devulcanization technologies.
CalRecovery, 2003) were to be devulcanized at 10 plants, the processing rate would be about 2,000 lb/hr.

The data in Table 10 summarize the capital costs and operating and maintenance costs for the technologies analyzed. The data for the capital cost analysis include an allowance for engineering services for the construction of the facility. The information shows that the capital costs for the processes vary from about $92,000 to about $166,000.

**Table 10. Estimated Unit Costs for the Production of Devulcanized Rubber**

<table>
<thead>
<tr>
<th>Item</th>
<th>Mechanical</th>
<th>Chemical</th>
<th>Ultrasonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (lb/hr)</td>
<td>100</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Capital Cost ($)</td>
<td>92,000</td>
<td>166,000</td>
<td>163,000</td>
</tr>
<tr>
<td>O&amp;M Cost ($)</td>
<td>135,000</td>
<td>172,000</td>
<td>136,000</td>
</tr>
<tr>
<td>Amortized Capital and O&amp;M ($)</td>
<td>143,000</td>
<td>186,000</td>
<td>150,000</td>
</tr>
<tr>
<td>Amortized Unit Cost ($/lb)</td>
<td>0.7</td>
<td>1.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Interest rate: 6% per year  
Amortization period: 20 years  
Refer to Appendix A on page 67 for breakdown of cost estimates.

Similarly, the data in the table indicate that the operating and maintenance costs for facilities of this type range from about $135,000 to $172,000. The operating cost estimates include the cost of crumb rubber feedstock for each of the processes. Based on the relative small size of the facilities, members of the project team opted for including the costs of the rental of a building for processing in operating and maintenance costs. This eliminated the cost of building a structure.

As shown in Table 10, the estimated amortized costs for producing devulcanized rubber are: $1.0/lb for the ultrasonic process, $1.2/lb for the chemical process, and $0.7/lb for the mechanical process. The analysis used an interest rate of 6 percent per year and an amortization period of 20 years. Due to uncertainties represented by the lack of detailed technical data and operating history for the technologies, the accuracy of the cost estimates is +/- 30 percent. As mentioned earlier, these costs reflect production at low capacities.

Some reduction in unit cost would likely occur due to economies of larger scale production. However, estimating reduction in unit cost is difficult because of the lack of data relating to production costs to different levels of throughput capacity for particular devulcanization technologies.

For the size of operations considered in this analysis, labor costs are a substantial portion of the production costs. It is very difficult, however, to estimate the magnitude of any potential reductions in unit labor costs that might occur if processing capacities were increased substantially. All circumstances considered, any estimates of commercial production costs for devulcanization of waste tire rubber are highly speculative at best. The best estimate of the study team is that perhaps production costs could be reduced by 25 to 30 percent if processing capacities were increased by a factor of approximately 5 to 10. Selling prices for devulcanized rubber would also normally include markups for marketing and profit.

The revenue potential of devulcanized material is described in the following section.
Chapter 5. Market Analysis

Devulcanized Grades of Products

The commercial market for devulcanized rubber is at best limited. The market, especially for tire-derived devulcanization, is quite small. There are no industry or common product specifications and grade definitions. Accordingly, there is no consensus on the devulcanization product grades. The companies promoting and developing devulcanization programs use a mechanism that allows a degree of understanding of the material in question. The approach is to specify the devulcanized rubber first by particle size using crumb rubber mesh sizes, and second by the narrowest definition of the original rubber or application; for example, whole tire or buffing. This method of description is incomplete, and devulcanized rubber offerings under these definitions can vary significantly.

Factors Determining Product Characteristics

As described previously, a number of devulcanization process categories (chemical, ultrasonic, microwave, biological, and others), as well as separate processes within each category, are being marketed and/or developed. Presumably, each of these processes yields devulcanized products with unique characteristics and properties that match up differently as blending agents or substitutes for virgin rubber.

Process operating conditions such as temperature, residence time, and other process variables can change the devulcanized rubber characteristics. Thus, the particle size and rubber source product definition is a loose specification for devulcanized rubber that allows substantial differences in product properties from the original rubber, as well as those contributed by the individual devulcanized rubber processes and producers.

The devulcanization industry needs a standard classification method based on analytical results and measured properties. For example, a devulcanized rubber from tire treadstocks, containing natural rubber and SBR, could be analyzed for bound styrene. Such testing would indicate the proportion of SBR in the blend. Products could also be characterized by testing for the degree of devulcanization. As for properties, the rubber could be compounded using a standard recipe, and the tensile strength, modulus, elongation, and hardness could be measured by standard tests. Such test results, along with the source, crumb size, and process, would provide a method of classification, just as the different types of virgin rubber are classified.

The market for devulcanized rubber, particularly the portion derived from crumb tire rubber, remains in a conceptual or early stage of development. The primary devulcanization topics in literature are academic research developments. Other papers on devulcanization were presented to the Rubber Division of the American Chemical Society in 2003.

A few North American companies have been characterized as having devulcanization capability. These include American Rubber Technologies, Inc. (chemical), CCG/PARMA of Canada (chemical), GoodRubber de Mexico SA DE CV (microwave), LandStar Rubber (chemical), TRC Industries, Inc. (thermal/mechanical), and Ultramer, Inc. (ultrasound) (Recycle Research Institute, 2002).

Industry presentations and website content by American Rubber Technologies, LandStar Rubber, and Ultramer in 2004 include the results of comparative testing of virgin rubber with blends of devulcanized rubber. This is the first step in developing customer interest, requests for samples, product qualification, and sales.
Devulcanized rubber is divided into two primary classifications. The first class is a homogeneous devulcanization of a single rubber grade or formulation made of materials such as natural rubbers or synthetic rubbers (butadiene rubber, butyl, EPDM, nitrile, polyisoprene, and styrene-butadiene rubber [SBR]). These materials typically originate as home scrap or recovered manufacturing scrap from rubber producers or fabricators.

The second class is recycled tire crumb rubber that is a non-uniform material composed of a generally ill-defined mixture of dozens of rubber types and hundreds of tire formulations. Certainly, most devulcanized tire rubber producers eliminate trace amounts of steel, fiber, and other contaminants. For some devulcanized tire rubber products, the normal derived tire impurities could also be present. A devulcanized single rubber type has the potential of being reused by blending it into virgin stock of its original application or a wider specification product using the same rubber grade and/or formulation.

This creates at least two problems in practice. The first is that the devulcanized rubber is not turned back to virgin material with common properties. Depending on the process used, process conditions, the material, and the blending level of the devulcanized rubber, most properties will be reduced by a few percent to more than two-thirds of those of the virgin material. In situations where the devulcanized rubber properties are within 10 percent of the original rubber material, blending would seem to be an attractive opportunity that offers the potential of adding a low-cost recycled substitute.

The operative word in blending devulcanized rubber with virgin rubber is potential. Commercial realities come into play. The costs savings cannot always be realized because of transportation costs, the available scrap, or policies of the buyer. The buyer may think the potential or actual liabilities are too high. The best operating model for devulcanizers of single rubber formulation is a dedicated devulcanization line (or long run) of specific rubber. Smaller volumes of single formulations require incurring extra costs for downtime and lost product caused by the cleanout between runs.

Yet another compatibility issue is present for manufacturers of rubber. The scrap rubber available for devulcanization could possibly undergo formulation with fillers, colorants, antioxidants, and a variety of other rubber chemicals to impart certain final product characteristics.

Table 11 represents the breakout of materials in finished tires. Carbon black accounts for 28 percent of the weight and fillers, fibers, and chemicals account for another 16 to 17 percent. When using a devulcanized rubber, the manufacturer has to change its formulation to account for whatever additives, colorants, and fillers remain in the devulcanized rubber. The devulcanized rubber itself and some of its additives and fillers—such as carbon black—presumably add value. These fillers take the place of new additives and fillers that would otherwise be necessary.

The possibility of mixing unidentified non-rubber materials in the devulcanized rubber may be harmful to critical applications such as tires. Other uncertainties are the performance state and concentration of these other constituents that could have been modified in the postconsumer processing of the tire and rubber.

A related issue is the degree to which protective antioxidants and antiozonants break down or lose effectiveness during the life of the tire or other product. Testing and qualification are required to determine whether devulcanized rubber is technically and commercially attractive for the rubber buyer.
Table 11. Composition of Tires

<table>
<thead>
<tr>
<th>Passenger Tire</th>
<th>Constituents</th>
<th>Common Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>14%</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>27%</td>
<td>SBR, butadiene rubber</td>
</tr>
<tr>
<td>Carbon black</td>
<td>28%</td>
<td>Carbon black</td>
</tr>
<tr>
<td>Steel</td>
<td>14%–15%</td>
<td>Steel</td>
</tr>
<tr>
<td>Fabric, fillers, accelerators, antiozonants, etc.</td>
<td>16%–17%</td>
<td>Polyester, nylon, aromatic oil, coumarine resin, silica, bonding agent, stearic acid, antioxidant, processing chemicals, sulfur, zinc oxide</td>
</tr>
<tr>
<td>Average weight</td>
<td></td>
<td>New 25 lbs, Scrap 20 lbs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Truck Tire</th>
<th>Constituents</th>
<th>Common Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>27%</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>Synthetic rubber</td>
<td>14%</td>
<td>Synthetic rubber</td>
</tr>
<tr>
<td>Carbon black</td>
<td>28%</td>
<td>Carbon black</td>
</tr>
<tr>
<td>Steel</td>
<td>14%–15%</td>
<td>Steel</td>
</tr>
<tr>
<td>Fabric, fillers, accelerators, antiozonants, etc.</td>
<td>16%–17%</td>
<td>Polyester, nylon, aromatic oil, stearic acid, antioxidant, wax, processing chemicals, sulfur, zinc oxide</td>
</tr>
<tr>
<td>Average weight</td>
<td></td>
<td>New 120 lbs, Scrap 100 lbs</td>
</tr>
</tbody>
</table>


Market Situation

Only a few companies devulcanize single formulation rubber by tolling, captive conversion, or merchant scrap recovery from manufacturing. The production of devulcanized rubber from home manufacturing scrap ranges from 100 to 200 million pounds annually, which represents about 1 to 2 percent of total U.S. rubber consumption. The largest volume devulcanization activity supports the domestic tire and rubber companies.

Examples of devulcanized rubber are butyl, EPDM, fluorosilicone, natural, nitrile, SBR, and silicone. The group of home scrap reprocessors is not devulcanizing tire rubber with its mix of rubbers, fillers, and additives. Devulcanized rubber supplies only 15 to 20 percent of the rubber manufactured scrap market. The reasons for the limitation of recycled content are primarily difficulty of creating manufactured product of uniform quality and difficulty of reprocessing certain rubber formulations.

TRC Industries uses a proprietary steam/mechanical devulcanization process. TRC claims the devulcanized material will retain all of its original physical properties and characteristics. The degree of devulcanization typically is in the 70 to 80 percent range and is occasionally 100 percent. Heavy carbon-blacked rubber is the hardest to devulcanize, and silica, or other mineral-filled EDPM, is the easiest. Reincorporation of the devulcanized rubber is typically in the 20 to 40 percent range.

Devulcanized single-product rubber applications are wide ranging. The reclaimed product may be reintroduced into the same end product or one with more tolerant performance characteristics for the devulcanized rubber. Examples of applications using devulcanized rubber are tire bladders,
seat spring covers, mounts, various molded goods, matting, and foam crack sealer. While many of these devulcanization operations of manufacturing scrap are tolling or captive processing, value of the scrap is priced effectively at a discount to virgin rubber in the 20 to 50 percent range. The reprocessing of home scrap requires a location in proximity to a large volume scrap generator.

Significant growth for devulcanized single rubbers depends on continuing process development of the reclaiming operation as the manufacturers strive to reduce operational losses. The supply stream from existing scrap applications will over time decline as scrap from these operations is reduced by manufacturing improvements. Increasing the volume of single rubber scrap for devulcanization processing requires adding new sources of rubber for reuse and developing ways to process them.

Companies developing the market for devulcanized tire rubber would first use more uniform types of rubber or tire component. These include buffings (tire tread or other portion of the tire free of metal or fiber; usually removed in preparation for retreading), peels (tire separations; usually the portion of the tire retread that has separated and been left on the highway), or truck tire sections with a high, natural-rubber content.

Using a whole tire mixture of rubbers introduces especially wide devulcanization product specifications and performance variations. Whole tire devulcanized rubber is at the low end of supply quality for each market application. Despite ongoing research and business promotion of devulcanized rubber, industry observers note slow sales of devulcanized tire rubber. Feeding an inconsistent supply of devulcanized rubber is less interesting for the buyer than a guaranteed, stable supply. This may be one of the larger market restraints on the success of waste tire devulcanization.

Replacement treads for some vehicle tires are made of undevulcanized crumb rubber (American Rubber Technologies, 2004). Devulcanized rubber seems to have advantages in bonding, strength, and tread integrity above the properties of crumb rubber, which acts only as a “rubber”-like filler. The unknown factor is cost, which could prevent devulcanized rubber from being used in many retread rubber applications.

Regardless of the actual level of commercial success for devulcanized tire rubber, no industry grade definitions are available. Developers of devulcanized tire rubber described their products in terms of crumb rubber mesh sizes and the narrowest form of use for the original rubber that might apply, such as buffings or whole tire. Purchasing guidance is provided on the devulcanized tire rubber, but not a uniform specification. The lack of a standard specification creates uncertainty for the buyer.

The type of devulcanization process, and process conditions, will cause variations in devulcanized tire rubber products. Other factors causing variation include composition of the mixture of scrap tires or tire components processed, and quality control of the devulcanization process. The quality of a single type of devulcanized rubber scrap will also have inherent variation introduced by the devulcanizing process and operating conditions.

### Devulcanized Rubber Product Characteristics

No data are available comparing devulcanization processes or the offerings of one company to another. The available data in the public domain is predominantly in research and development, with available commercial data doubling as sales literature for promoting devulcanized rubber. The physical property data presented in Table 12 are referenced by source. Comparing devulcanized rubber properties leads into the next section in this report, “Devulcanized Rubber Prices.”
Table 12. Percent Change from Virgin with Selected Devulcanization Rubber Formulations

<table>
<thead>
<tr>
<th>Test Rubber Compounds (grade) Parts or %</th>
<th>% Devulc. or (Ground) Mat'l.</th>
<th>Hardness Shore</th>
<th>Tear Strength</th>
<th>Tensile Strength</th>
<th>100% Modulus</th>
<th>300% Modulus</th>
<th>Elongation to Break</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STI-K Polymers DeLinka</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR w/devulc NR</td>
<td>30</td>
<td></td>
<td>-5.9%</td>
<td>8.3%</td>
<td>-8.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR (1520) w/devulc SBR</td>
<td>30</td>
<td></td>
<td>-7.7%</td>
<td>-4.4%</td>
<td>-3.6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kyoto University</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Truck tire (93 NR+ 7 BR)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>84 NR+ 6 BR + 20 devulc</td>
<td>18</td>
<td>8.1%</td>
<td>-2.3%</td>
<td>2.6%</td>
<td>0.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>74 NR+ 6 BR + 40 devulc</td>
<td>33</td>
<td>12.9%</td>
<td>-11.9%</td>
<td>28.2%</td>
<td>-17.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65 NR + 5 BR + 60 devulc</td>
<td>46</td>
<td>11.3%</td>
<td>-19.1%</td>
<td>23.1%</td>
<td>-13.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LandStar/Guangzhou RI</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>100 SIR 10 + 50 devulc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIR vs. Case 1</td>
<td>33</td>
<td>4.3%</td>
<td>-23.7%</td>
<td>6.7%</td>
<td>-6.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIR vs. Case 2</td>
<td>33</td>
<td>6.5%</td>
<td>-23.0%</td>
<td>11.5%</td>
<td>-8.6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tread Tire Compound</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 NR + 30 SR + 20 CIS-BR +40 AMR</td>
<td>28.6</td>
<td>6.7%</td>
<td>-17.3%</td>
<td>-3.0%</td>
<td>-18.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Light Duty Truck Tire Compound</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>30 NR + 70 SR + 0 CIS-BR + 40 AMR</td>
<td>28.6</td>
<td>1.6%</td>
<td>-10.9%</td>
<td>-13.9%</td>
<td>-6.7%</td>
<td></td>
<td></td>
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<tr>
<td>Retread Tire Compound</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>65 NR + 35 SR + 40 AMR</td>
<td>28.6</td>
<td>6.3%</td>
<td>-8.6%</td>
<td>-10.3%</td>
<td>-16.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ultrasonic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>University of Akron</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Versus Akrochem SBR (1848)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR w/devulc SBR</td>
<td>10</td>
<td></td>
<td>-55.5%</td>
<td>6.8%</td>
<td>-30.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR w/whole Tire Reclaim</td>
<td>10</td>
<td></td>
<td>-19.7%</td>
<td>2.7%</td>
<td>-15.4%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Test Rubber Compounds (grade) Parts or %

<table>
<thead>
<tr>
<th>Test Rubber Compounds (grade)</th>
<th>% Devulc. or (Ground) Mat'l.</th>
<th>Hardness Shore</th>
<th>Tear Strength</th>
<th>Tensile Strength</th>
<th>100% Modulus</th>
<th>300% Modulus</th>
<th>Elongation to Break</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR w/30 Mesh Buffings</td>
<td>10</td>
<td>-40.4%</td>
<td>5.4%</td>
<td>-38.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural Rubber and SBR versus devulc</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Base 100% NR (SMR CV60) &amp; 0% SBR (23.5% bound styrene, and Firestone Duraden 706)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Add 25% SBR, 75% NR</td>
<td>0</td>
<td>-42.2%</td>
<td>6.3%</td>
<td>-10.4%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Devulc SBR replaces SBR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25% devulc SBR, 75% NR</td>
<td>25</td>
<td>-69.2%</td>
<td>0.0%</td>
<td>-36.7%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% devulc SBR, 50% NR</td>
<td>50</td>
<td>-10.7%</td>
<td>-5.6%</td>
<td>-17.9%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% devulc SBR, 25% NR</td>
<td>75</td>
<td>-24.0%</td>
<td>-10.0%</td>
<td>-15.3%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR versus devulc SBR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% devulc SBR</td>
<td>100</td>
<td>0.0%</td>
<td>-9.5%</td>
<td>-10.0%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*b Kyoto Chemical Research Institute, 2002.
*d Boron, et al., 1996.
*e Hong & Isayev, 2002 (pp. 160–168).

The devulcanized rubber properties displayed are not necessarily optimized for a specific end use. Formulators will likely be able to incorporate devulcanized rubber along with other formulation components to achieve a higher level of final product performance. Key product performance variables are level of contamination, number of rubber types in the rubber mixtures, and additives used by the formulations. The effect of additives was discussed previously under “Product Characteristics.” The number of types of rubber in waste tires is one of the most important factors affecting quality of devulcanized waste tire rubber. Optimizing a devulcanization process is very difficult when more than one type of rubber is involved.

**Blend Rates**

According to one developer of a devulcanization process, about 3 to 10 percent of the final product can be blended into virgin material before performance properties are affected (Rubberworks International, 2004). Variations of a few percent are reported by developers of devulcanization when they vary process run conditions (Howlett, 1999). Run-to-run variations are...
Another firm that is developing devulcanized rubber placed the breakpoint for noticeable performance change at 10 percent, reasoning that customers typically allow a 10 percent variation in product from the purchasing specifications (Thomas, 2004).

The descriptions of properties for a common grade of virgin rubber from two producers vary by 7 to 20 percent (Boron et al., 1996; International Specialty Products, 2004). With this much variation in the marketplace, devulcanized rubber is expected to find technical acceptance increasing. This will happen as the devulcanized product property variance from virgin rubber falls from above 20 percent to less than 5 percent.

**Performance Properties**

The key point of Table 12 is that devulcanized rubber is not the same as virgin rubber. Thus, the extent of variation and the specific characteristics will be important determinants in the acceptance and value of devulcanized rubber versus virgin rubber. The data points of Table 12 demonstrate that devulcanized single rubber products have a much lower degree of degradation than multiple rubber mixtures with devulcanized rubber. Virgin single-grade SBR—or natural rubber replacement with devulcanized material shown by the STI-K and the University of Akron datasets—has, at worst, a reduction of 10 percent in tensile strength, modulus, or elongation.

Based on the results shown in Table 12, the properties of the single rubber compounds with devulcanized material are within normal grade tolerances. These single rubber compounds seem likely to have some market application, if not restrained by cost. The performance properties of multiple compound formulations—when replaced by devulcanized tire or single rubber grade—are lowered, with at least one property dropping by 15 percent or more.

The Kyoto University tests show that progressively increased devulcanized material in the formulations resulted in a steadily poorer match with virgin rubber. University of Akron data indicate weakening properties with increasing additions of devulcanized rubber. While not uniform with each step of increased concentration of devulcanized SBR, devulcanized rubber consistently performed at a level below that of virgin SBR.

In some cases, the addition of devulcanized rubber causes a major reduction in performance of some properties, along with improvements in one or two properties (hardness and modulus). Because the modulus is the measure of deformation—that is, tension (stretching), compression (crushing), flexing (bending), or torsion (twisting)—a higher reading means a stiffer product that may or may not be desirable. Similarly, the increase in hardness could be an improvement or detraction, depending on the application. Because each use has its own measures of desired performance, generalizations about acceptability are not appropriate. This is extremely important. Increase in modulus and/or hardness is quite often accompanied by decrease in strength and elongation, quite possibly making the rubber unsuitable for use in the normal applications of that type of rubber.

**Development Status**

Rubber devulcanization processes have been in development for more than 60 years (Baker, 2003). The research goals continue to seek processes that offer a better combination of the cost of devulcanizing the rubber and properties compared to virgin material. The processes in Table 12 are a sample of many development programs that are reportedly still in consideration or active. STI-K Polymer offered the De-Link chemical process that was first introduced into the United States about 1995.

This company has apparently closed its office in Washington D.C., but it remains listed on [www.recycle.net/](http://www.recycle.net/). American Rubber Technologies (ART) is reportedly licensed to the De-Link
process. ART employs the brand name ReVived Rubber® for its devulcanized rubber. ART adopted the process in 1997, producing partially devulcanized output. ART claims that devulcanized particle sizes that are twice as large as crumb rubber work as well or better. ART continues to promote ReVived Rubber®; however, it may have reduced its devulcanized rubber sales effort. CCG/Parma has offered the STI-K Polymer process in Canada and reportedly has the capability to make devulcanized rubber as well.

Kyoto Chemical Research Institute at Kyoto University is actively reporting research findings on its supercritical CO₂ devulcanization process. A commercial partner was not identified.

LandStar Rubber licensed the Guangzhou R I chemical devulcanized process in 1999. This company has emphasized devulcanized rubber products as it grew its tire recycling business by acquisition and more recently as it scaled back operations. The LandStar company name was changed by adding the word “rubber” to reflect its focus on devulcanized rubber. The company is now reportedly protected in a bankruptcy proceeding.

University of Akron Professor A.I. Isayev is one the founders of modern rubber devulcanization. His team appears to be the most active of the research teams, based upon many papers reporting results for more than a decade. The focus of the University of Akron research is ultrasonic devulcanization. Ultramer, Inc., a subsidiary of NFM/Welding Engineers, Inc., is participating in the development of this devulcanization process; however, development efforts appear to have lessened recently.

Several California companies, such as Redwood Rubber LLC, Tires2Oil, POLYMERight, and Champion Rubber Products, have been researching and developing devulcanization technologies at various levels of effort.

The apparently limited commercial success of these processes is not highly encouraging for the probable future prospects of marketing devulcanized rubber. Devulcanizing waste tires may be a technology with a bright future, but no success stories on this process are currently available.

**Devulcanized Rubber Prices**

The devulcanized rubber market is not developed enough to have established prices. Even the few devulcanizers that are reclaiming manufacturing scrap in large volume view each supply agreement as a special case. The manufacturing customers have differing purchasing specifications, liability concerns, environmental drivers (recycling can be a positive public relations boost), disposal costs, and product mixes that are able to adsorb devulcanized rubber as “off spec” virgin. The pricing issue is further confused by the internal pricing of captive devulcanizing operations.

**Substitute Pricing**

The virgin natural and synthetic rubber prices are ultimately driven by the volatile supply and demand effects of the agricultural crop, natural rubber, and energy prices. The synthetics are petrochemical-based materials. Devulcanized rubber competes with virgin rubbers. Thus, its market price is influenced by natural and synthetic rubber. Figure G illustrates the natural rubber volatility.

The natural rubber price trend line (spot price for ribbed smoked sheets, Grade No. 1, New York) from 1980 to 2003 had an average annual rate of decline at 0.5 percent/year. However, during this same period, the natural rubber price experienced four declines and five peaks. These fluctuations averaged 15 to 18 percent, respectively, beneath and above the trend line. The fluctuations in the relative prices of natural and synthetic rubbers do affect consumption. When natural rubber has a
price spike such as that of 1995 to 1996, rubber product producers will change their compounds to use as much synthetic rubber as they can without sacrificing product performance. Likewise, when natural rubber prices are low, such as in 1999 to 2001, natural rubber consumers will use more product.

**Figure G. Natural Rubber Prices Show Volatility**

Table 13 shows that rubber prices have traded in a narrow range in the period from 1999 to 2002. The prices of virgin rubber and crumb rubber begin to bracket the expected price for devulcanized rubber. The synthetic rubbers, SBR and butadiene rubber, are both major elastomers used in tires.

To simplify the estimate, unit imports values are used as a proxy for the market price of the virgin rubber. The actual market price of large buyers and sellers is very difficult to estimate without inside knowledge. The unit value for large shipments can be a reasonable representation of the market price for a high level evaluation. SBR and butadiene rubber have price spikes with market shortages. Nevertheless, the annual import values for SBR for the period of 1999 to 2002 were within 8 percent of the 44.8 ¢/lb average over the seven years. Butadiene rubber annual import unit values were within 15 percent of the 41.9 ¢/lb average.
Table 13. Price and Unit Values (¢/lb)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Natural Rubber</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSR 20(^a)</td>
<td>30.3</td>
<td>27.5</td>
<td>31.7</td>
<td>27.2</td>
</tr>
<tr>
<td>RSS 1(^b)</td>
<td>33.3</td>
<td>30.2</td>
<td>31.9</td>
<td>29.8</td>
</tr>
<tr>
<td><strong>Synthetic Rubber</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBR(^c)</td>
<td>47.2</td>
<td>47.3</td>
<td>44.2</td>
<td>41.5</td>
</tr>
<tr>
<td>Butadiene Rubber(^d)</td>
<td>39.6</td>
<td>45.5</td>
<td>40.8</td>
<td>36.4</td>
</tr>
<tr>
<td><strong>Crumb Rubber, Average(^e)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Mesh</td>
<td>13.3</td>
<td>12.7</td>
<td>12.4</td>
<td>12.1</td>
</tr>
<tr>
<td>20 Mesh</td>
<td>14.9</td>
<td>14.9</td>
<td>15.2</td>
<td>14.7</td>
</tr>
<tr>
<td>30 Mesh</td>
<td>17.3</td>
<td>17.3</td>
<td>17.8</td>
<td>17.5</td>
</tr>
<tr>
<td>40 Mesh</td>
<td>21.0</td>
<td>21.0</td>
<td>22.0</td>
<td>20.6</td>
</tr>
<tr>
<td>80 Mesh</td>
<td>31.0</td>
<td>31.0</td>
<td>30.8</td>
<td>29.2</td>
</tr>
</tbody>
</table>


\(^e\) Recycle Research Institute, 2002.

Recycle Discount

Recycled materials have no common pricing rules. These markets are driven by the overall supply and demand for a specific material or substitute, with very wide price swings possible. The practice of determining value for recycled plastic and fiber, as well as devulcanized manufacturing scrap rubber, suggests a range of discounts from the virgin material. Manufacturing scrap of fibers and plastics can sometimes be reused directly or reused in the same application with reprocessing.

The value of the recycled fibers and plastics can vary substantially, with discounts of 20 to 50 percent or more off the virgin material price. Compared to single compound or tire rubber processing, plastic and fiber recycled materials are only slightly degraded by the recycling process. Accordingly, except in special cases, discounts from virgin material of at least 20 to 50 percent would be considered reasonable for devulcanized tire rubber. With tightness or weakness in the market, the discounts off the price of virgin rubber can shift throughout a wider range.

Market Value

Single composition rubber devulcanization will follow its own market dynamics, establishing an appropriate unique product discount. Most single devulcanized rubber transactions are expected to be discounted in the 20 to 50 percent range. The United States unit import value is a proxy for the market price of natural rubber, SBR, and butadiene rubber.
Devulcanized tire rubber has a cost relationship with its raw material, crumb rubber. Crumb rubber prices have remained fairly steady because its cost structure is based on the low to negative value of surplus tires. The surplus tire situation and valuation of waste tires are not expected to dramatically change in the foreseeable future.

Crumb tire rubber (20 to 80 mesh) is the main raw material for devulcanized tire rubber. Crumb rubber will act as the price foundation, with an appropriate upcharge for the process of devulcanizing rubber. From 1996 to 2002, the average price for mesh 20 to 80 crumb rubber grew at an annual average of less than 1 percent, with little year-to-year variation.

The high and low crumb prices of 80 mesh varied from 7 to 31¢/lb in 2002. This spread has narrowed significantly during the past four years, probably reflecting an increased ability of crumb rubber producers to make the small mesh sizes. The average 20 to 40 mesh prices have been particularly flat during the past four years (Sunthonpagasit & Hickman, 2003). Crumb rubber prices were reported to be flat from 1994 to 2000 because of oversupply of crumb rubber and other factors.

The following demonstration case illustrates the price relationship of virgin rubber to crumb rubber and creates a range of expected prices for devulcanized tire rubber. A discount for using a recycled product is applied to the virgin rubber price and becomes the high expected value for devulcanized tire rubber. The low expected value for devulcanized tire rubber is based on the cost of crumb rubber and the devulcanization process costs. Prices between the high and low expected values establish the most likely range for devulcanized tire rubber prices.

Table 14 presents values that will be the basis for estimating the foundation level for devulcanized rubber pricing based on crumb rubber and the ceiling for devulcanized rubber based on a discount off virgin rubber prices. The actual floor for successful devulcanization operations is the crumb rubber price plus a markup for the reclaiming operation.

**Table 14. Bracketing of the Expected Devulcanized Rubber Price (¢/lb)**

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Tire tread rubber price (50% NR + 30% SBR + 20% BR)</td>
<td>38.0</td>
<td>37.7</td>
<td>37.3</td>
<td>34.0</td>
</tr>
<tr>
<td>Less 20% discount from virgin</td>
<td>30.4</td>
<td>30.2</td>
<td>29.8</td>
<td>27.2</td>
</tr>
<tr>
<td>Less 50% discount from virgin</td>
<td>19.0</td>
<td>18.9</td>
<td>18.7</td>
<td>17.0</td>
</tr>
<tr>
<td>Average crumb rubber price + devulcanization upgrade (+10 ¢/lb)</td>
<td>33.1</td>
<td>33.1</td>
<td>33.5</td>
<td>32.4</td>
</tr>
</tbody>
</table>

Based on Table 13.
A cost basis for devulcanized tire rubber can be approximated by taking the crumb rubber price and adding an estimate for commercial-scale devulcanized rubber processing. For this particular analysis, assume that the cost of devulcanization is in the vicinity of 10¢/lb. This optimistic figure represents a five- to tenfold improvement over the cost estimate derived in the previous section. Under this assumption devulcanized rubber is competitive if the average of the 20 to 40 mesh crumb rubber was taken for 2002 at 23¢/lb. Adding the assumed 10¢/lb for additional processing creates an estimated cost for devulcanized tire rubber of 33¢/lb in 2002.

As shown by the data in Table 14, the applicable potential margin for devulcanized tire rubber would likely squeeze producers. The following demonstration case calculates the value of a type of devulcanized tire rubber made partially of virgin rubbers. The tire tread formulation use for this case is 50 percent natural rubber, 30 percent SBR, and 20 percent butadiene rubber (the same ratio as used by LandStar in comparing its devulcanized rubber to virgin rubber).

To be truly competitive, the selling price of devulcanized rubber would need to be at or below the ceiling prices established by the 20 to 50 percent discount off the weighted average price of rubber in the tire tread formulation. In 2002, a 20 percent discount on the virgin rubber price yields a ceiling price for devulcanized tire rubber of 30¢/lb. This 30¢/lb ceiling price is below the minimum estimated production cost of 33¢/lb that was computed earlier.

With different cases and assumptions, the devulcanized tire rubber might fall into a range likely to offer commercial potential. Applications that are well matched to properties of devulcanized rubber would lower the expected recycling discount. If crumb rubber and/or devulcanization processing had a lower cost—for example, below average crumb rubber costs—its prospects look more promising. The reported high to low price range in 2002 for crumb rubber mesh sizes from 20 to 80 are 7¢ to 16¢/lb, and the low to average range is 3¢ to 9¢/lb. The variation reflects quality, distance to market, and end use differences.

The tire tread example discussed here is built on many assumptions. The best way to determine the acceptance of devulcanized rubber and its selling price is to test devulcanized tire rubber in the marketplace. Only a business development effort can pinpoint a set of costs and expected value based on product properties for devulcanization material. Potential customers can verify these costs in turn.

The above example leads to speculation about why devulcanized tire rubber has not made a greater impact. Selling crumb rubber may be more attractive than the potential benefits resulting from the extra processing of devulcanization. The crumb rubber markets are now better defined, but the missionary work necessary to develop devulcanization applications is another drain on company resources. Tire recycler/crumb rubber producers are generally very lean organizations. Devoting resources to a long-term effort necessary to build devulcanization sales is relatively expensive, especially if the anticipated return is modest or negative.

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* In all cases for devulcanized rubber value, credit for non-rubber constituents is assumed to be valued at the same price as the rubber. A detailed investigation could refine the estimate in this study to adjust the value of the rubber by the price and weight of non-rubber compounds. The actual value impact of carbon black, fillers, and rubber chemicals will depend on usefulness of these chemicals in each application of the devulcanized rubber. For situations where any or all of these non-rubber ingredients are not required, the buyer might not offer any value or assign a negative value. In most situations, the pricing of the devulcanized rubber could be further adjusted by using concentrations of significant chemicals and fillers that make up the product. Dozens of grades of carbon black could be commingled in devulcanized rubber. Carbon black, the other major material present in crumb rubber, has sold in the range of 35¢ to 50¢/lb, in approximately the same range as that of virgin rubber. The price of stearic acid is usually below that of the virgin rubber. Zinc oxide sells at a significantly higher price.
This simplified analysis has ignored distinctions created by different devulcanized rubber processes presumed to have unique properties with special pricing needs. Each process could conceivably have its own cost structure, reflecting the tradeoff between product properties and market prices.

Therefore, each different production process will probably have different market coverage and competitive strength. ART quoted a price of 30¢/lb for its fine grade and 37¢/lb for its super-fine grade. In the tire tread example, this fine grade is approximately at the 20 percent discount level. The quoted price for super-fine devulcanized rubber is only a penny a pound below the composition virgin rubber tire tread price, which will probably be a tough sell. Buyers under the right conditions might consider devulcanized rubber at a discount less steep than 20 percent.

The commercial market for vulcanized rubber includes a wide variety of rubber compounds and formulations being used in thousands of different applications. Whatever the market condition, rubber purchasing specifications may very well be a good match for devulcanized tire rubber in some niches. But, finding these special circumstance market niches could be challenging. Thus, the long-term opportunities for devulcanized rubber remain unclear. Companies engaged in developing devulcanized tire rubber have not yet reported large-scale commercial success, leaving a pessimistic outlook.

**The Demand for Devulcanization**

**Single Composition Devulcanized Rubber**

Single compound home scrap devulcanization is currently almost a captive market. The few participants are located in Ohio, Texas, and the southeast United States. The companies are captive suppliers or are selling (tolling) back to their raw material suppliers. Thus, the market is not fully open to competition. These devulcanizers have a large volume scrap which can be processed close to its source—an unusual situation.

The existing available market is growing at less than the underlying pace of the industry. The amount of scrap generated by rubber companies is probably declining as management of their operations improves. Because only 15 to 20 percent of the scrap is being reprocessed, considerable high-side potential exists for the single compound devulcanization industry. This potential will be available if these businesses can expand the use of devulcanized rubber into a new and better process technology.

A potentially large single-composition devulcanized rubber market will exist for the foreseeable future as long as the devulcanization technologies continue to improve. The 100 million pound-plus market will grow at least as fast as the rubber industry (less than 3 percent annually) and is likely to significantly outpace the industry with technology and product innovations.

**Devulcanized Tire Rubber**

Determining the future demand for devulcanized tire rubber is more difficult, since the present products and markets are so ill defined. After years of development, devulcanized tire rubber is still seeking a market. The reasons may be economic, coupled with the difficulty of doing long-term market development with a base in the recycled rubber business.

The devulcanized tire market is divided between partially and fully devulcanized processes. Neither partially or fully devulcanized tire rubber has a significant established market. A portion of the crumb rubber used for asphalt paving operations is devulcanized. Caltrain has a provisional specification for paving material to incorporate crumb rubber. While most crumb rubber being used in asphalt is not devulcanized, a very high-end asphalt product consumes relatively large
amounts of crumb rubber that is “reclaimed” in the process. This crumb rubber application is ignored when looking at the demand of devulcanized rubber.

No devulcanized tire rubber applications were identified. Devulcanized rubber should, under the right conditions, replace crumb rubber in applications where it is more compatible with vulcanized rubber. Compared to virgin material, devulcanized rubber may offer a discount price for the cost-conscience buyer.

The devulcanized tire rubber is expected to find a market in molded goods, binders for plastics, and applications needing a better surface finish. Examples of product areas are footwear soles, rubber sheeting, car mats, tire carcass, and inner liner compounds. Others include tread and sidewalls of tires, flaps, belts and hoses, other automotive molded parts, other manufacturing high-quality molded parts, gaskets, extruded profiles, rubber strips, and caster wheels.

Companies such as Ford and Kumho have each set 10 percent goals for recycled material in their tire formulations. Devulcanized rubber has an obvious compatibility advantage over crumb rubber, which is merely a filler. No development program using devulcanized rubber in tires was found. Therefore, establishing a successful program in the commercial sphere is probably at least three to four years in the future if program development begins immediately.

Development delays are created by lags in the preparation for automotive model years. Ford and Bridgestone, as well as the other automotive and rubber tire companies, are very likely to be methodical in looking at uses for new material. They know the risk of mistakes such as the Ford Explorer tire failures that hurt both Ford and Bridgestone financially and organizationally.

Tire devulcanizers are not well equipped to start a recycled rubber campaign aimed at capturing a major share of the rubber needs of tire companies. Such an effort would be both expensive in time and capital resources for the size of their businesses. Should the United States institute a 10 percent devulcanized rubber requirement for U.S.-manufactured tires, the demand for devulcanized rubber would exceed 500 million pounds annually. This is more than half the present North American market for all crumb rubber.

This potential demand is so large that even the major rubber or auto companies would have to move slowly into its implementation. Recycling tire rubbers into new tires remains an interesting market. However, this is a very difficult path for individual devulcanizers. They are much too small, with too few resources.

California

California has a well-developed growing market for rubber. The state is the home to one of the largest regional business activities for rubber products in the United States, as is shown in Table 15. The 1997 California sales share of the U.S. total manufactured rubber products, tires and treads, and other rubber products was 4 percent, 3 percent, and 5 percent, respectively. Sales of all rubber products manufactured in California totaled $1.4 billion. This represents a major rubber market. California is the largest crumb rubber market in North America, by far. California had about 17 percent of the crumb rubber production of the United States and Canada, despite a significant dip in 2002. With this large volume of crumb rubber in the state, it could, under the right circumstances, lead California to be a major force in the development of devulcanized rubber.
Table 15. 1997 Role of California in the United States Rubber Product Manufacturing Sector

<table>
<thead>
<tr>
<th>Type</th>
<th>Area</th>
<th>Establishments</th>
<th>Sales $000</th>
<th>Payroll $000</th>
<th>Employees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Tire Rubber</td>
<td>United States</td>
<td>1,898</td>
<td>19,016,832</td>
<td>3,812,770</td>
<td>130,164</td>
</tr>
<tr>
<td>Products</td>
<td>California</td>
<td>221</td>
<td>997,516</td>
<td>214,000</td>
<td>8,253</td>
</tr>
<tr>
<td></td>
<td>California %</td>
<td>11.6%</td>
<td>5.2%</td>
<td>5.6%</td>
<td>6.3%</td>
</tr>
<tr>
<td>Tire and Retread</td>
<td>United States</td>
<td>911</td>
<td>15,699,140</td>
<td>2,962,564</td>
<td>72,189</td>
</tr>
<tr>
<td></td>
<td>California</td>
<td>78</td>
<td>415,452</td>
<td>63,328</td>
<td>1,855</td>
</tr>
<tr>
<td></td>
<td>California %</td>
<td>8.6%</td>
<td>2.6%</td>
<td>2.1%</td>
<td>2.6%</td>
</tr>
<tr>
<td>All Rubber Products</td>
<td>United States</td>
<td>2,809</td>
<td>34,715,972</td>
<td>6,775,334</td>
<td>202,353</td>
</tr>
<tr>
<td></td>
<td>California</td>
<td>299</td>
<td>1,412,968</td>
<td>277,328</td>
<td>10,108</td>
</tr>
<tr>
<td></td>
<td>California %</td>
<td>10.6%</td>
<td>4.1%</td>
<td>4.1%</td>
<td>5.0%</td>
</tr>
</tbody>
</table>


The role of devulcanized rubber in the future for California is unclear, as it is elsewhere. The market analysis of the U.S. situation is uncertain because the base case economics require the development of new, undefined markets with below-average cost and/or less discount than is typical in the rubber and plastics industry for recycled material.

The California market potential for devulcanized rubber, particularly tire rubber, has advantages over most other North American locations. California has a major share of crumb rubber production, which is the starting material for devulcanized rubber. The state also has a major rubber products industry that could become a devulcanized rubber consumer. What appears to be lacking in the marketplace are applications that can make the best of the properties of devulcanized rubber while still benefiting customers with discounts off of virgin rubber prices. The identification of these applications will take some creative thinking to match devulcanized rubber strengths with unmet market needs.
Chapter 6. Environmental Analysis

**Introduction**

Little information is available in the literature on the environmental effects associated with waste tire devulcanization technologies. The lack of information apparently exists because business developers and researchers have concentrated their efforts primarily on technology improvements and achieving satisfactory properties for devulcanized rubber. Since reported data are lacking from actual devulcanization systems, an estimation of emission rates and a detailed environmental analysis are not possible.

However, using data and information from some other types of tire manufacturing processes (for example, extrusion of rubber) and the characteristics of vehicle tires, the CalRecovery team performed a qualitative analysis. The main purposes of the analysis are to describe the potential environmental impacts of waste tire devulcanization systems, the types of environmental regulations that might or do apply, and the types of environmental control systems that might be required for commercial-scale operations.

The environmental analysis described subsequently is limited to chemical and ultrasonic devulcanization processes because technical information is sufficient for a qualitative evaluation. The need for, and extent of, environmental control is a strong function of uncontrolled concentrations and/or mass flow rates of harmful emissions. The analysis assumes that control of emissions would be required. This condition is invoked in the analysis in order to illustrate the types of potential environmental emissions and potential means of controlling them if such control would be required. The waste tire devulcanization operations identified in the study were primarily small-scale processing operations. These operations may fall below regulatory thresholds for allowable emissions.

The analysis below describes potential environmental impacts of waste tire devulcanization and methods of controlling them. The methods described are meant to be illustrative of those that might be chosen and used; other methods of control might also feasible.

**Analysis**

**Chemical**

Chemical devulcanization processes are usually batch processes that involve mixing crumb rubber with chemical reactants at a specific temperature and pressure. Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A block flow diagram of a generic chemical devulcanization process is illustrated in Figure H, showing the raw material feed is crumb rubber.

The typical constituents of the crumb feedstock generally would consist of those listed in Table 16. The crumb rubber is mixed with one or more devulcanization agents. Chemical agents identified as devulcanization agents are listed in Table 17. During processing in the batch reactor, vapors are released that must be collected and treated before release to the ambient atmosphere. Typical types of vapors that might be emitted from a batch reactor are listed in Table 18.

The chemicals that would be vented from the batch reactor are dependent on the characteristics of the waste tire feedstock and on the chemical agent(s) used in devulcanizing the crumb rubber. For example, if disulfides are used in the process, they could result in formation of hydrogen sulfide ($\text{H}_2\text{S}$) or methyl or other mercaptans ($\text{RSH}$).
Table 16. Tire Raw Materials

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Antiozonants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber (polyisoprene)</td>
<td>2,2,4-trimethyl-1,2-dihydroquinoline (polymer)</td>
</tr>
<tr>
<td>Styrene-Butadiene Rubber (SBR)</td>
<td>n,n-(1,3-dimethylbutyl)-p-phenylenediamine</td>
</tr>
<tr>
<td>cis-Polybutadiene copolymer</td>
<td>paraffinic wax</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vulcanizing Agents</th>
<th>Antioxidants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>Alkylphenols</td>
</tr>
<tr>
<td>Tetra-methyl thiurame sulfide</td>
<td>Resorcinol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Accelerators</th>
<th>Retarders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylguanidine</td>
<td>n-Cyclohexylthiophthalimide</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td></td>
</tr>
<tr>
<td>n-Cyclohexyl-2-benzothiazolylsulfenamide</td>
<td></td>
</tr>
<tr>
<td>2-(n-Morpholinyl)-mercaptobenzothiazole</td>
<td></td>
</tr>
<tr>
<td>Hexamethylenetetramine</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activators</th>
<th>Plasticizers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide</td>
<td>Aliphatic oil</td>
</tr>
<tr>
<td>Zinc carbonate</td>
<td>Aromatic oil</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Naphthenic oil</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Extenders</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica gel</td>
<td>Di-(2-ethylhexyl)-phthalate</td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
</tr>
</tbody>
</table>
Table 17. Chemical Agents Used in Chemical Tire Devulcanization Processes

<table>
<thead>
<tr>
<th>Chemical Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triphenyl phosphine</td>
</tr>
<tr>
<td>Sodium di-n-butyl phosphite</td>
</tr>
<tr>
<td>Thiol-amine reagents (specifically propane-thiol/piperidine, dithiothreitol, and hexane-1-thiol)</td>
</tr>
<tr>
<td>Lithium aluminum hydride</td>
</tr>
<tr>
<td>Phenyl lithium</td>
</tr>
<tr>
<td>Methyl iodide</td>
</tr>
<tr>
<td>Hydroxide with quaternary ammonium chloride as a catalyst</td>
</tr>
<tr>
<td>Orthodichlorobenzene</td>
</tr>
<tr>
<td>Diphenyldisulphide</td>
</tr>
<tr>
<td>Diallyl disulfide</td>
</tr>
<tr>
<td>Toluene, naphtha, benzene, and/or cyclohexane, etc. in the presence of sodium</td>
</tr>
<tr>
<td>Diamly disulfide</td>
</tr>
<tr>
<td>Dibenzyl disulfide</td>
</tr>
<tr>
<td>Diphenyl disulfide</td>
</tr>
<tr>
<td>Bis(alkoxy aryl) disulfides</td>
</tr>
<tr>
<td>Butyl mercaptan and thiopenols</td>
</tr>
<tr>
<td>Xylene thiols</td>
</tr>
<tr>
<td>Phenol sulfides and disulfides</td>
</tr>
<tr>
<td>Alkyl phenol sulfides (for SBR)</td>
</tr>
<tr>
<td>N,N-dialkyl aryl amine sulfides (for SBR in neutral or alkaline solutions)</td>
</tr>
</tbody>
</table>
Table 18. Potential Types of Chemical Compounds Emitted by Chemical and Ultrasonic Devulcanization Technologies

<table>
<thead>
<tr>
<th>Compound</th>
<th>Probable Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>Toluene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Heptane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>4-Vinylcyclohexene</td>
<td>Polymers: Natural Rubber (polyisoprene), styrene-butadiene rubber (SBR), cis-Polybutadiene</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Octane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Styrene</td>
<td>Polymers: styrene-butadiene rubber (SBR)</td>
</tr>
<tr>
<td>Nonane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>1,4-Cyclohexadiene-1-isopropyl-4-methyl</td>
<td>Polymers: Natural Rubber (polyisoprene)</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Cyclohexene-1-methyl-3-(1-methylvinyl)</td>
<td>Polymers: Natural Rubber (polyisoprene)</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>Polymers: styrene-butadiene rubber (SBR)</td>
</tr>
<tr>
<td>1-isopropyl-4-methylcyclohexane (trans)</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>1-isopropyl-4-methylcyclohexane (cis)</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>1-isopropyl-3-methylcyclohexane</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>Decane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Tri-isobutylene</td>
<td>Polymers: styrene-butadiene rubber (SBR) &amp; cis-Polybutadiene; Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>Cyclohexene-5-methyl-3-(1-methylvinyl)</td>
<td>Polymers: Natural Rubber (polyisoprene)</td>
</tr>
<tr>
<td>Indane</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>1-Isopropyl-4-methylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Cyclohexene-1-methyl-4-(1-methylvinyl)</td>
<td>Polymers: Natural Rubber (polyisoprene)</td>
</tr>
<tr>
<td>1-Isopropyl-2-methylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Dimethylstyrene</td>
<td>Polymers: styrene-butadiene rubber (SBR)</td>
</tr>
<tr>
<td>Undecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Tetramethylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>1,2,3,4-Tetrahydronaphthalene</td>
<td>Plasticizers: Naphthemic oil</td>
</tr>
<tr>
<td>1,3-Di-isopropyl benzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>1,4-Di-isopropyl benzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>2-Isopropyl-6-methylphenol</td>
<td>Antioxidents: Alkylphenols</td>
</tr>
<tr>
<td>Compound</td>
<td>Probable Source</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>---------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Cyclohexylisothiocyanate</td>
<td>Retarders: n-Cyclohexyl-thiophthalimide</td>
</tr>
<tr>
<td>Cyclooctadecatriene</td>
<td>Polymers: cis-Polybutadiene</td>
</tr>
<tr>
<td>Dodecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Tridecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Tetraisobutylene</td>
<td>Polymers: styrene-butadiene rubber (SBR) &amp; cis-Polybutadiene; Plasticizers: Napthemic oil</td>
</tr>
<tr>
<td>p-ter-Butylstyrene</td>
<td>Polymers: styrene-butadiene rubber (SBR)</td>
</tr>
<tr>
<td>Dimethylpropylhexahydronaphthalene</td>
<td>Plasticizers: Napthemic oil</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Nonylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>2,6-Di-ter-butyl-p-quinone</td>
<td>Antioxidents: 2,6-Diterbutyl-hydroquinone</td>
</tr>
<tr>
<td>Pentadecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>1,6-dimethyl-4-isopropyl-1,2,3,4-tetrahydronaphthalene</td>
<td>Plasticizers: Napthemic oil</td>
</tr>
<tr>
<td>Decylbenzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Di-ter-butylthiophene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Diethyl phthalate</td>
<td>Plasticizers: Di-(2-ethylhexyl)-phthalate</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>1,2-Di-tolylethane</td>
<td>Polymers: styrene-butadiene rubber (SBR)</td>
</tr>
<tr>
<td>Heptadecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>2,6-Di-ter-butyl-4-ethylphenol</td>
<td>Antioxidents: Alkylphenols</td>
</tr>
<tr>
<td>Octadecane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>1-Phenylhexaphthalene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Di-iso-butyl phthalate</td>
<td>Plasticizers: Di-(2-ethylhexyl)-phthalate</td>
</tr>
<tr>
<td>Tridecylic benzene</td>
<td>Plasticizers: Aromatic oil</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>Plasticizers: Di-(2-ethylhexyl)-phthalate</td>
</tr>
<tr>
<td>Eicosane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Heneicosane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Docosane</td>
<td>Plasticizers: Aliphatic oil</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl) phthalate</td>
<td>Plasticizers: Di-(2-ethylhexyl)-phthalate</td>
</tr>
</tbody>
</table>

* Information based on types of emissions from the vulcanization area of a tire retreading operation and from a tire retreading extrusion operation.

If the chemical agent orthodichlorobenzene is used, chlorinated hydrocarbons could potentially be released in the form of air emissions. Methyl iodide is volatile, and if used as a devulcanization agent, it could be vaporized. Since tire manufacturing utilizes zinc oxide and zinc carbonate, chemical devulcanization might also produce airborne metal particulates.

Once the batch is fully processed, the reactor is vented. The vent gases are treated prior to release to the atmosphere. The vapors cannot be treated by vapor phase carbon because these chemicals will plate out and blind the carbon, making it ineffective. Instead, the vapor from the batch
reactor needs to be thermally oxidized. At the high exit temperatures, typically as high as 2000°F (1100°C), the thermal oxidizer vent gases need to be cooled in a quench tower to approximately 300°F (150°C). Then, to remove any metals or other particulate, the vent gases are piped to a baghouse.

Because of the high thermal oxidizer temperatures, methyl mercaptans (RSH) or hydrogen sulfide (H₂S) from the crumb rubber is oxidized to sulfur dioxide (SO₂). Therefore, downstream of the baghouse, a scrubber is required to remove sulfur dioxide (SO₂), as shown in Figure H. Scrubbed vent gases are then released to the atmosphere.

In addition to the scrubber vent gases described above, liquid waste is generated from the crubber. This liquid stream contains sodium sulfate (Na₂SO₄). This liquid waste can be disposed in receiving waters such as a river, stream, or bay. However, discharging to receiving waters will require a significant amount of treatment equipment and a permit.

Obtaining the necessary National Pollutant Discharge Elimination System (NPDES) permit is often difficult. NPDES permits are typically costly and require a significant amount of paperwork to be submitted to the Regional Water Boards. The cost and effort to obtain an NPDES permit is considerable, and the time required to receive an approved NPDES permit is lengthy.

If the facility is located near a sanitary sewer, the publicly-owned treatment works (POTW) can conduct treatment of the effluent water. Using the POTW eliminates the need to buy, install, and operate water treatment equipment. Furthermore, it is much simpler to obtain a POTW permit than an NPDES permit because the paperwork, application fee, and time required to obtain the permit is significantly less.

In addition to an application fee, POTWs will assess a usage fee. The fee will be based on the volume of effluent water discharged to their sanitary district and on the difficulty that wastewater treatment will create. Furthermore, the local POTW may not have the capacity and the capability to handle the quantity and composition of chemicals present in the liquid waste.

As seen in Figure H, the devulcanized rubber is moved from the batch reactor to a separator by a heated extruder. Liquid that drips off the devulcanized rubber is removed in the separator and eliminated by feeding it to the same thermal oxidizer as the vent gases from the batch reactor. After the liquid has dripped off the devulcanized rubber in the separator, any remaining moisture is removed in the dryer. Fired dryers are typically fueled by natural gas burners. Dryer vent gases are piped to the common thermal oxidizer.

Based on the concentration of solids in the scrubber effluent, processing the scrubber effluent through a filter press to dewater the solids may be necessary and cost-effective. Filter-pressed dewatered solids are called “filter cake.” Filter cake might require disposal in a hazardous waste site. Even though the waste disposal site may accept the scrubber effluent water, the economics may favor installation and use of a filter press. This is necessary to dewater the solids due to the high cost of disposal of liquid waste.

**Ultrasonic**

Devulcanization by ultrasonic methods may be a continuous process (see Figure I). As the figure illustrates, crumb rubber is loaded into a hopper and is subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and soften the rubber.
As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy. The resulting combination of ultrasonic energy, along with the heat, pressure, and mechanical mastication, is sufficient to achieve varying degrees of devulcanization. The exposure time to the ultrasonic energy is only seconds. Essentially all of the rubber entering the process is discharged from the extruder in a semi-solid product stream. Process losses would be primarily emissions of fine particulate or of gases, if any, resulting from the mechanical and thermal applications occurring during devulcanization.

Since the typical operating temperature of an ultrasonic devulcanization reactor is about 230°F (110°C), less vapor emission would be expected than from chemical devulcanization. Furthermore, since no chemicals are added to break the sulfur bonds that caused vulcanization to occur, there would likely be lower air emissions. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried. Tire raw materials for this process are listed in Table 16.

Typical types of gaseous compounds that could be released from an ultrasonic devulcanization reactor are listed in Table 18. Vented vapors would need to be treated by one of two methods. One method would be to use a small thermal oxidizer. The design of the thermal oxidizer, baghouse, and scrubber would be similar to that described previously for chemical devulcanization. However, the physical size of the oxidizer would be smaller, and the baghouse and scrubber would be larger.

A second method to treat the vent gases exiting the ultrasonic devulcanization reactor would be use of vapor phase carbon. In this method, due to the lower operating temperatures of the ultrasonic process, vent gas exiting the ultrasonic zone would have to be heated above the dew point temperature. If this elevation in temperature is not accomplished, the vent gases could condense on the surface of the carbon and thus blind the bed. In other words, adsorption sites on the surface of the carbon would be ineffective, and vent gases would exit the carbon bed untreated.
If vapor phase carbon were to be used, the capital cost would be less than that of a thermal oxidizer. However, carbon is not very efficient. Weight loading can be approximately 10 weight percent—in other words, adsorbing ten pounds of vent gas contaminants for every 100 pounds of carbon used. Use of carbon will have a relatively high operating cost. Also, the disposal of spent carbon can be very expensive. This is especially true if the spent carbon requires disposal at a hazardous waste disposal site. Even if the carbon is regenerated on-site, adsorption efficiency decreases after each regeneration. Typically, carbon can only be regenerated ten times. For illustration purposes, Figure I indicates the use of vapor phase carbon.

Devulcanized rubber exiting the ultrasonic processing zone has to be cooled. A common method of reducing the rubber temperature is a cooling bath. The volume of cooling water used would be significant. Cooling water may become contaminated from the process; this effluent water leaving the cooling bath has to be treated. As discussed in the chemical treatment system, a POTW permit would be preferred to obtaining an NPDES permit. If an air cooler such as fin fans is used in lieu of water in the cooling bath, the volume of effluent liquid would be reduced.

Another alternative would be to use a closed-loop cooling system, where the cooling water is cooled and returned to the process for reuse. If there is a buildup of contaminants, a small slip-stream could be taken off and treated in a POTW, greatly reducing the amount of effluent that would otherwise require treatment.

**Air Emission Regulations**

Regulations controlling air emissions have been written by multiple organizations. The United States Environmental Protection Agency (U.S. EPA) established Title V regulations that apply if the emission rate is for a large facility. Title V emissions are based on Hazardous Air Pollutants (HAP), the federal designation for toxic compounds. U.S. EPA also has regulations governing emission of Volatile Organic Compounds (VOC).

In addition to Federal Regulations set by U.S. EPA, air emission regulations are established by the California Air Resources Board (ARB). ARB has developed a list of chemicals identified as Toxic Air Contaminants (TAC). A copy of the list is included as Appendix B. If a chemical is not listed as a TAC, it can still be listed by ARB as an air toxic under the Air Toxic “Hot Spots” Information Act list of substances. In California, air emission regulations established by local agencies are typically the most stringent. For purposes of this analysis, the regulations of the Bay Area Air Quality Management District (BAAQMD) were reviewed for applicability to devulcanization processes. None of the three agencies appear to have regulations written specifically for waste tire devulcanization.

**BAAQMD Regulations**

In general, based on the type of gaseous compounds listed in Table 18, a permit would be required for a waste tire devulcanization facility. Regulation 2, Rule 1, section 121.1 allows an exemption from needing a permit for grinding the tires to make crumb rubber, provided that organic emissions from the coolant, lubricants, or cutting oil are 5 tons per year or less. Regulation 2, Rule 1, section 121.10 provides an exemption from needing a permit for the curing of rubber products. The use of mold release products or lubricants is not exempt unless the VOC contents of these materials are less than 10 pounds per year.

BAAQMD categorizes air emissions into six classes of pollutants:

1. Precursor Organic Compounds (POC). This is basically the same as the U.S. EPA VOCs.
2. Non-Precursor Organic Compounds (NPOC). All organics will fall into class 1 or 2.
3. Nitrous oxides (NOx).
4. Carbon monoxide (CO).
5. Particulate matter smaller than 10 micron (PM$_{10}$).
6. Sulfur dioxide (SO$_2$).

Regulation 2, Rule 1, section 103 requires that any class of pollutant not exceed 10 pounds on a single day. In addition, the facility cannot exceed 5 tons per year of any class of pollutant. A large emission rate can trigger the need to complete a federal Title V permit, in addition to BAAQMD permits. A Title V permit is required if the facility emits more than 100 tons per year of all six of these classes; or, if the emission rate exceeds 10 tons per year of a single hazardous air pollutant (not all pollutants are HAPs); or, if emission rate exceeds 25 tons per year of just HAPs.

Regulation 2, Rule 1, Table 316 (see Appendix C on page 77) lists trigger levels that cannot be exceeded for specific chemicals.

Regulation 8, Rule 2, section 301 states that it is illegal to discharge into the atmosphere an emission containing more than 15 pounds per day and containing a concentration of more than 300 parts per million total carbon on a dry basis.

If POCs are greater than 10 pounds per day, BAAQMD requires that equipment be in place to treat air emissions. Depending on the type of emission, it could be an electrostatic mist precipitator and a baghouse to control particulate and visible emissions. Scrubbers and thermal oxidizers are commonly used to control organic concentrations in vent gases.
Chapter 7. Barriers

The study has identified a number of potential barriers to developing an economically competitive waste tire devulcanization technology. The barriers are described below under specific subject headings.

**Technical Needs**

Devulcanization of specific types of rubber and/or waste tire rubber has a long history. However, only recently have limited technical data been reported in the available literature. Usually when reported, the tested properties of devulcanized rubber compose an incomplete list. This is especially true in the interpretation of how the devulcanized product would perform during compounding, in the manufactured end product, or both. Few studies provide detailed descriptions and characteristics of the waste tire feedstock that would be required to evaluate the effect of feedstock properties on system operation and on end product performance.

Clearly, the need for testing of waste tire devulcanization technologies is substantial. These tests should be based on a variety of waste tire feedstocks in order to identify the technical barriers to the technologies (and, therefore, resulting cost barriers). Circumstantial and anecdotal evidence indicates significant technical and economic barriers to devulcanization of waste tire rubber.

If such testing studies are to be productive, they must measure a comprehensive list of material properties, including percent rubber devulcanized (using accepted test methods wherever possible). The tests must fully describe feedstock and system operating conditions. Finally, the tests must relate process operating conditions (including energy required) to properties of devulcanized material and to those of a manufactured end product.

Equipment design parameters must be reported for the various devulcanization processes. These parameters are necessary to provide a basis for determining the capital equipment costs needed for the complete economic analysis required to determine unit prices; for example, $/lb. The parameters are also necessary to determine the technical feasibility of producing a high-quality devulcanized product.

**The Cost of Devulcanization**

At present, the economic cost of devulcanization technology is a critical barrier to developing and commercializing the process. The price spread between the selling price of crumb rubber and the price of virgin rubber is substantially less than current estimates of devulcanization cost. Crumb rubber is the raw material for the devulcanizing process.

Further aggravating the problem is the expected discount sales price of devulcanized rubber. The properties of devulcanized rubber will probably never equal those of virgin rubber. Based on current estimates, the processing cost must be reduced by 80 to 90 percent (to 10 to 20 percent of current estimates) before the process could be operated profitably. This represents a substantial reduction in the estimated processing cost.

Based on the results of the cost analysis, research and development should be directed toward reducing the cost of devulcanization processes or toward developing lower-cost processes. If the processing cost cannot be substantially reduced, improving the properties of devulcanized waste tire rubber is of limited benefit. This applies also to reducing the cost of existing devulcanization processes and to developing new types of technologies.
The Mixture of Rubber Types Present in a Tire

Because a tire is not a homogeneous product with respect to the type of rubber used, any ground rubber becomes a mixture of all the types of rubber and the compounds in the tire. For example, the sidewalls of a radial tire are predominantly natural rubber. The tread is a compound with SBR and either natural rubber or polybutadiene, and the inner liner is mostly polyisobutylene. Whitewalls are EPDM, and other specialized parts are other types of rubber or special compounds of more than one type.

When a tire is size reduced, the ground rubber becomes a mixture of all types of materials with different properties. Optimizing devulcanization processes is difficult when materials of disparate properties go into the feedstock for the process. Thus, the properties of the resultant devulcanized product are compromised.

Two possible areas of research could be focused on this problem. The first would examine how a tire could be reclaimed in a process that would isolate the different types of rubber. For example, by grinding off the tread, that rubber could be devulcanized separately, with the devulcanized product blended into new tread rubber.

A second option would be to process truck tires separately and then blend this devulcanized rubber back into natural rubber compounds. This would be possible since truck tires contain a much higher proportion of natural rubber. Finally, a third option would be to find applications (most likely non-tire) where the mixture derived from ground tires would have properties adequate for that application. The best way to find such applications would be to compare the measured properties of rubber devulcanized from ground whole tires with the properties required for different types of rubber products. The goal would be to find a match.

Gaining Acceptance in High-Value Markets

Because devulcanization technologies require a feedstock in particulate form, the cost of devulcanization (and, therefore, its product) must include the price of the crumb rubber feedstock. Consequently, devulcanized products cannot compete on price for products manufactured with crumb rubber. Devulcanized waste tire rubber can only be realistically used in high-value applications where crumb rubber cannot be used due to property requirements. This means that the properties of devulcanized waste tire rubber must be sufficiently close to those of virgin rubber so that it can be blended with virgin rubber without substantially reducing the properties of the final compound.

For example, if the devulcanized rubber has a modulus equal to 90 percent of that of virgin rubber, blending it into virgin rubber at a 10 percent rate would probably reduce the modulus of the compound by approximately 1 percent. Before acceptance for use in vehicle tires—where failures could potentially lead to deaths, injuries, and legal action—use of devulcanized tire rubber would have to be subjected to extensive testing. Other markets require high-quality rubber, but the liability risks are not as great as those of the new tire market.

Research and development work should be focused on two areas. First, efforts should continue to bring the properties of the devulcanized material as close as possible to that of virgin rubber. Second, researchers should conduct comprehensive studies of compounding to better quantify the properties of blends containing devulcanized waste tire rubber and virgin rubber.

Market research is also needed in this area to determine requirements for gaining acceptability in tire applications. Second, researchers need to identify non-tire applications where devulcanized rubber has the best chance of finding acceptability.
**The Environmental Effects of the Process**

The estimates of processing costs developed in this study do not include the costs of pollution control. Chapter 6 of this report, “Environmental Analysis,” lists the types of emissions that could be expected. The difficulty of permitting such a process and the cost of compliance with environmental regulations may comprise a significant barrier to the implementation of this technology.

Conceivably, pollution control costs could add 10 to 30 percent to the cost of devulcanization. The difficulty of permitting—and the cost—would be a function of the type of devulcanization technology, the processing rates, and other factors. In general, the expectation is that the cost of environmental control systems for chemical devulcanization systems would be greater than that for ultrasonic or mechanical processes.

Potential research and development efforts on environmental control would include quantifying the environmental releases of various chemical compounds from the process and developing cost-effective means of using or recovering these compounds or their derivatives.
Chapter 8. Conclusions and Recommendations

The key conclusions and recommendations of the study are presented below, under four general headings.

Research and Development

Approximately 25 potential technology researchers and developers have been identified throughout the world and North America, including 3 in California. Apparently, only a very small number of devulcanization systems are now operating. These are primarily small-capacity systems, devulcanizing single types of natural or synthetic rubber (as opposed to devulcanizing rubber from waste tires) or both.

The definition of “devulcanization” varies in the literature. This compromises the ability to identify devulcanization processes, to interpret the performance of devulcanization technologies, and to determine the feasibility of devulcanizing waste tire rubber.

Particle size can play an important role in the effectiveness and feasibility of devulcanization processes. A number of devulcanization processes require a finely sized particle distribution, while others can tolerate or use a coarser particle size. In the process of producing very finely sized rubber, the distinction between or among individual processes of devulcanization, surface devulcanization, and size reduction becomes narrow or blurred. Many of the descriptions of devulcanization technologies are unclear about the relationship between feedstock particle size distribution and performance of particular devulcanization technologies and their devulcanized products.

The composition of rubber and additives that are used in rubber compounds in the manufacture of vulcanized rubber can and do have a dramatic effect on the properties of materials manufactured from devulcanized rubber. Apparently, the inferior properties of some poorly (inadequately) devulcanized rubber can be compensated for by the addition of chemicals and the adjustment of operating conditions, among other remedies. In many cases in the literature, this situation is not addressed or discussed. Consequently, comparing devulcanization technologies is difficult. From most of the literature descriptions of the processes, what happens to the sulfur and other vulcanization chemicals during the various processes is unclear.

Technical

Based on the information collected in the study, CalRecovery believes that the only method of achieving bulk devulcanization, as opposed to surface devulcanization, rests with ultrasonic or microwave devulcanization methods. Of these two methods of energy application, ultrasound appears to have substantially more research and development history. An important observation is that microwave technology is not an effective or efficient way to devulcanize non-polar rubber types, which collectively compose the vast majority of the mass of rubber in waste tires.

Because of the ability to internally devulcanize cured rubber, ultrasonically devulcanized waste tire rubber may have more desirable marketing characteristics than those of surface-devulcanizing processes under similar conditions of cost and yield. The latter processes (surface devulcanizing) include mechanical, chemical, and biological processes. However, test data and applications for ultrasonically devulcanized waste tire rubber are lacking in the industry, along with process cost documentation.
Market

At the present time, the processing cost of the various types of devulcanization process is greater than the difference between the price of crumb rubber (the raw material) and the likely selling price. This price would be at a discount from the price of virgin rubber. The processing cost is the single largest factor limiting the market for devulcanized rubber, so the most potentially productive areas of research are the reduction of processing cost and the development of substantially lower-cost processes. To be viable under current market conditions, the processing cost of devulcanization would have to be reduced by an estimated 50 to 90 percent.

The devulcanized rubber market is most fully developed for single product materials made from manufacturing scrap that are reclaimed for reuse in the same process or in a broader specification application. The reprocessing of single rubbers depends upon being located near a large-volume rubber products company with enough scrap and enough rubber applications to justify the devulcanization step.

Devulcanization of waste tire rubber, despite considerable research and developmental effort, is still in an early growth stage. Devulcanization lacks adequate test data and data interpretation, and it has poorly defined end product specifications without adequately justified and defined applications and uses. Research funds appear to be most available for studying devulcanization of single rubber types, as opposed to studying rubber types with complex mixtures such as those present in waste tires.

Devulcanization typically reduces the resulting rubber product properties and value compared to virgin material. Devulcanized waste tire rubber would normally be expected to sell at a steep discount to virgin rubber, unless special circumstances prevail.

Devulcanized tire rubber yields a product that is effectively a mixture of rubbers, fillers, and chemical additives that create barriers to its reuse as a blending material. In applications already using crumb rubber, devulcanized rubber can have advantages if the process combines a vulcanized rubber or other compatible material to create an integrated structure. The structure must have much better properties than those imparted by the filler role that crumb rubber frequently serves.

While the market prospects are currently limited for devulcanized rubber because of economics, California has both a large supply of crumb rubber and markets for raw materials supporting its large rubber products industry. Creative thinking may offer ways to better match devulcanized tire rubber with potential applications that fit its product profile closely. A better fit would offer a fair value (less substantial discount) for the devulcanized rubber, while still giving the buyer the incentive of a discount off virgin rubber prices.

The devulcanization industry needs a classification method for devulcanized tire rubber based on analytical results and measured properties. The measured properties should include those that characterize the performance of the devulcanized material during the process of compounding as well as the performance of the end product itself.

Potential Future Efforts

If waste tire devulcanization is to succeed in the marketplace, it needs proven applications and a competitive price. Consequently, if the CIWMB is to pursue devulcanization as a method of waste tire management and recycling, program efforts would best be devoted to reducing processing cost and proving viable product applications. In this pursuit, researchers and developers of devulcanization processes should be required to perform comprehensive testing. These tests should evaluate the characteristics of waste tire feedstocks and their resultant effect on
process and end product performance. Equally important is the identification of specific, viable markets and the uses of devulcanized waste tire rubber. Finally, the test data should include documentation of production and marketing costs and the prices users offer for the devulcanized rubber.
### Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BR</td>
<td>Butadiene rubber</td>
</tr>
<tr>
<td>C-C</td>
<td>Carbon-carbon</td>
</tr>
<tr>
<td>C-S</td>
<td>Carbon-sulfur</td>
</tr>
<tr>
<td>EPDM</td>
<td>Ethylene propylene diene monomer</td>
</tr>
<tr>
<td>GRT</td>
<td>Ground rubber tire, or ground tire rubber</td>
</tr>
<tr>
<td>NR</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>phr</td>
<td>Parts per hundred</td>
</tr>
<tr>
<td>RRM</td>
<td>Renewable resource material</td>
</tr>
<tr>
<td>SBR</td>
<td>Styrene-butadiene rubber</td>
</tr>
<tr>
<td>S-S</td>
<td>Sulfur-sulfur</td>
</tr>
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Appendix A
Support for Cost of Waste Tire Devulcanization Technologies
Support for Cost of Waste Tire Devulcanization Technologies

<table>
<thead>
<tr>
<th>Capital</th>
<th>Mechanical</th>
<th>Chemical</th>
<th>Ultrasonic</th>
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</thead>
<tbody>
<tr>
<td>Equipment</td>
<td>77,141</td>
<td>138,075</td>
<td>135,870</td>
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<tr>
<td>Engineering</td>
<td>14,828</td>
<td>27,615</td>
<td>27,174</td>
</tr>
<tr>
<td>Totals</td>
<td>91,969</td>
<td>165,690</td>
<td>163,044</td>
</tr>
</tbody>
</table>

Operations

<p>| | | | |</p>
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<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Labor</td>
<td>79,560</td>
<td>79,560</td>
<td>79,560</td>
</tr>
<tr>
<td>Utilities</td>
<td>6,379</td>
<td>8,393</td>
<td>13,171</td>
</tr>
<tr>
<td>Feedstocks(^a)</td>
<td>24,960</td>
<td>55,224</td>
<td>19,344</td>
</tr>
<tr>
<td>Rent (building)</td>
<td>24,000</td>
<td>28,800</td>
<td>24,000</td>
</tr>
<tr>
<td>Totals</td>
<td>134,899</td>
<td>171,977</td>
<td>136,075</td>
</tr>
</tbody>
</table>

\(^a\) Includes crumb rubber feedstock and chemicals, if any.

Financial Assumptions:

- Capital amortization:
  - Interest rate: 6% per annum
  - Amortization period: 20 years
- Labor:
  - Technician: $27/hr, including overhead; 1 FTE
  - Maintenance: $22.5/hr, including overhead; 0.5 FTE
- Electricity: $0.12/kWh
- Chemicals: $0.06/lb tire rubber processed
- Crumb rubber: $0.21, $0.12, and $0.124/lb for Chemical, Mechanical, and Ultrasonic technologies, respectively
- Building rental: $1/ft\(^2\)/mo
Appendix B
Toxic Air Contaminant List
Toxic Air Contaminant List Quick Reference Format

December 1999

I. Substances identified as Toxic Air Contaminants by the Air Resources Board, pursuant to the provisions of AB 1807** and AB 2728** (includes all Hazardous Air Pollutants listed in the Federal Clean Air Act Amendments of 1990).

Information within the square brackets refers to the corresponding subcategory on the Substances By Category version of the list.

Acetaldehyde [IIa]
Acetamide [IIa]
Acetonitrile [IVa]
Acetophenone [IVa]
2-Acetylaminofluorene [V]

☐ Acrolein [IIa]
Acrylamide [IIa]
Acrylic acid [IIa]
Acrylonitrile [IIa]
Allyl chloride [IIa]
4-Aminobiphenyl [V]
Aniline [IIa]
o-Anisidine [IVa]
Antimony compounds (Note 4) [IIa]

☐ * Inorganic Arsenic and Arsenic compounds (Note 4) [IIa] (inorganic including arsine)
* Asbestos [IIa]
[asbestiform varieties of serpentine (chrysotile) riebeckite (crocidolite), cummingtonite-grunerite(amosite), tremolite, actinolite, and anthophyllite]
* Benzene (including benzene from gasoline) [IIa]
Benzidine [V]
Benzotrichloride [V]
Benzyl chloride [IIa]
Beryllium Compounds (Note 4) [IIa]
Biphenyl [IVa]
Bis(2-ethylhexyl)phthalate (DEHP) [IIa]
Bis(chloromethyl)ether [IIa]
Bromoform [V]

☐ * 1,3-Butadiene [IIa]

* Cadmium and cadmium compounds (Note 4)[IIa] (metallic cadmium and cadmium compounds)
Calcium cyanamide [V]
Caprolactam [V]

☐ Captan [VI]

☐ Carbaryl [VI]
Carbon disulfide [IIa]
* Carbon tetrachloride (Tetrachloromethane) [IIa]
Carbonyl sulfide [IVa]
Catechol [IVa]
Chloramben [V]
Chlordane [V]
* Chlorinated dibenzo-\(p\)-dioxins and dibenzofurans (Note 5) [IIa] 2,3,7,8-Tetrachlorodibenzo-\(p\)-dioxin (TCDD) [IIa]

☐ Chlorine [IIa]
Chloroacetic acid [IVa]
2-Chloroacetophenone [V]
Chlorobenzene [IIa]
Chlorobenzilate [IVa]
* Chloroform [IIa]
Chloromethyl methyl ether [V]
Chloroprene [IVa]

☐ Chromium and Compounds (Note 4) [IIa]
* Chromium VI (Hexavalent chromium) [IIa]
Cobalt Compounds (Note 4) [IIa]
Coke Oven Emissions [V]

☐ Cresols/Cresylic acid (isomers and mixture) [IIa]
m-Cresol [VI]
o-Cresol [V]
p-Cresol [V]
Cumene [IVa]

☐ Cyanide compounds (Note 4&11) [IIa]

☐ 2,4-D, salts and esters [VI]
DDE (p,p-Dichlorodiphenyldichloroethylene) [V]
Diazomethane [V]
Dibenzofuran [IVa]
1,2-Dibromo-3-chloropropane (DBCP) [V]
Dibutylphthalate [IVa]

☐ 1,4-Dichlorobenzene (p-Dichlorobenzene) [IIa]
3,3-Dichlorobenzidine [IIa]
Dichloroethyl ether (Bis(2-chloroethyl) ether) [V]

☐ 1,3-Dichloropropene (Telone)[IVa]

☐ Dichlorvos (DDVP) [VI]
Diethanolamine (Note 6) [IIa]
N,N-Diethyl aniline (N,N-Dimethylaniline) [V]
Diethyl sulfate [V]
3,3-Dimethoxybenzidine [V]
4-Dimethyl aminoazobenzene [V]
3,3-Dimethyl benzidine (o-Tolidine) [V]
Dimethyl carbamoyl chloride [V]
Dimethyl formamide [IIa]
1,1-Dimethyl hydrazine [IVa]
Dimethyl phthalate [IVa]

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Dimethyl sulfate [IVa]
4,6-Dinitro-o-cresol, and salts [V]
2,4-Dinitrophenol [V]
2,4-Dinitrotoluene [V]
1,4-Dioxane (1,4-Diethyleneoxide) [IIa]
1,2-Diphenylhydrazine [V]
Epichlorohydrin (1-Chloro-2,3-epoxypropane) [IIa]
1,2-Epoxybutane [IIa]
Ethyl acrylate [IVa]
Ethyl benzene [IIa]
Ethyl carbamate (Urethane) [IIa]
Ethyl chloride (Chloroethane) [IIa]
* Ethylene dibromide (1,2-Dibromoethane) [IIa]
* Ethylene dichloride (1,2-Dichloroethane) [IIa]
Ethylene glycol [IIa]
Ethylene imine (Aziridine) [V]

* Ethylene oxide (1,2-Epoxyethane) [IIa]
Ethylene thiourea [IIa]
Ethylidene dichloride (1,1-Dichloroethane) [IIa]
Fine mineral fibers (Note 13) [IVa]

* Formaldehyde [IIa]
Glycol ethers (Note 7) [IIa]
Heptachlor [V]
Hexachlorobenzene [IIa]
Hexachlorobutadiene [V]
Hexachlorocyclopentadiene [V]
Hexachloroethane [IIa]
Hexamethylene-1,6-diisocyanate [IIa]
Hexamethylphosphoramide [V]
Hexane [IIa]
Hydrazine [IIa]

Hydrochloric acid [IIa]
Hydrogen fluoride (Hydrofluoric acid) [IIa]
Hydroquinone [IVa]
Isophorone [IIa]

* Inorganic Lead and Inorganic lead compounds (includes elemental lead) (Note 4 & 8) [IIa]
Lead and compounds (Note 4) [IIa] (does not include elemental lead)

Lindane [IIa]
Maleic anhydride [IIa]

Manganese and compounds (Note 4) [IIa]
Mercury and compounds (Note 4) [IIa]

Methanol [IIa]

Methoxychlor [VI]
Methyl bromide (Bromomethane) [IIa]
Methyl chloride (Chloromethane) [IVa]
Methyl chloroform (1,1,1-Trichloroethane) [IIa]
Methyl ethyl ketone (2-Butanone) [IIa]
Methyl hydrazine [IVa]
Methyl iodide (Iodomethane) [V]
Methyl isobutyl ketone
Methyl isocyanate [V]
Methyl methacrylate [IIa]
Methyl tertiary butyl ether (MTBE) [IIa][IIIa]
4,4-Methylene bis (2-chloroaniline) [IIa]
* Methylene chloride (Dichloromethane) [IIa]
4,4-Methyleneedianiline [IIa]
Methylene diphenyl diisocyanate (MDI) [IIa]
Naphthalene [IIa]
* Nickel and compounds (Note 4) [IIa] (metallic nickel & inorganic nickel compounds)
Nitrobenzene [IIa]
4-Nitrobiphenyl [V]
4-Nitrophenol [V]
2-Nitropropane [IIa]
N-Nitroso-N-methylurea [V]
N-Nitrosodimethylamine [IIa]
N-Nitrosomorpholine [IIa]
Parathion [V]
* Particulate emissions from diesel-fueled engines [IIa]
  □ Pentachloronitrobenzene (Quintozene) [IVa]
  □ Pentachlorophenol [IIa]
  * Perchloroethylene (Tetrachloroethylene) [I]
Phenol [IIa]
p-Phenylenediamine [IVa]
Phosgene [IIa]
Phosphine [IIa]
  □ Phosphorus [IIa]
Phthalic anhydride [IIa]
Polychlorinated biphenyls (PCBs) [IIa]
Polycyclic organic matter (POM) (Note 9) [IIa][IIIa][IVa] Benzo[a]pyrene (Note 10) [IIa]
1,3 Propane sultone [IIa]
 beta-Propiolactone [V]
Propionaldehyde [IVa]
  □ Propoxur (Baygon) [VI]
Propylene dichloride (1,2-Dichloropropane) [IVa]
  □ Propylene oxide [IIa]
1,2-Propylenimine (2-Methyl aziridine) [IVa]
Quinoline [V]
Quinone [V]
Radionuclides (including radon) (Note 12) [IVa]
Selenium and compounds (Note 4) [IIa]
Styrene [IIa] [IIIa]
Styrene oxide [IIa]
1,1,2,2-Tetrachloroethane [IIa]
Titanium tetrachloride [IVa]
Toluene [IIa]
2,4-Toluene diamine (2,4-Diaminotoluene) [V]
Toluene-2,4- diisocyanate [IIa]
o-Toluidine [V]
Toxaphene (Chlorinated camphene) [V]
1,2,4-Trichlorobenzene [IVa]
1,1,2-Trichloroethane [IIa]
* Trichloroethylene [IIa]
2,4,5-Trichlorophenol [V]
2,4,6-Trichlorophenol [IIa]
Triethyamine [IIa]
Trifluralin [VI]
2,2,4-Trimethylpentane [IVa]
Vinyl acetate [IIa]
Vinyl bromide [V]
* Vinyl chloride [IIa]
Vinylidene chloride (1,1-Dichloroethylene) [IIa]
Xylenes (isomers and mixture) [IIa]
m-Xylene [IIa]
o-Xylene [IIa]
p-Xylene [IIa]

II. Substances NOT identified as Toxic Air Contaminants, known to be emitted from stationary source facilities, which are being evaluated for entry into Category I. Factors considered in this evaluation include carcinogenic and noncarcinogenic health effects, emissions and exposure in California. Aluminum and Compounds (Note 4) [IVb]

Ammonia [IIb]
Ammonium nitrate [IVb]
Ammonium sulfate [IVb]
Barium and Compounds (Note 4) [IVb]
Benzoyl chloride [IVb]
Bis(2-ethylhexyl)adipate [IVb]
Bromine and compounds (inorganic) (Note 4) [IVb]
Butyl acrylate [IVb]

n-Butyl alcohol [IVb]
sec-Butyl alcohol [IVb]
tert-Butyl alcohol [IVb]
Butyl benzyl phthalate [IVb]
Carbon black and Carbon black extracts [IVb]
Chlorinated fluorocarbons [IVb]

☐ Chlorine dioxide [IIb]
☐ Chlorophenols [IVb]

☐ Chloropicrin [IIb]
☐ Copper and Compounds (Note 4)[IIb]
☐ Creosotes [IIb]
  Crystalline silica [IIIb]
  Cumene hydroperoxide [IVb]
  Cyclohexane [IVb]
  Decabromodiphenyl oxide [IVb]
  Dialkylnitrosamines [IVb]
  Diaminotoluene (mixed isomers) [IVb]
  Dicofol [IVb]
  Environmental Tobacco Smoke (Note 14) [IVb]

☐ Ethylene [IIb]
☐ Gasoline vapors [IVb]
☐ Glutaraldehyde [IVb]
  Hexachlorocyclohexanes [IIb]
  Hydrogen sulfide [IIb]

☐ Isopropyl alcohol [IIIb]
  4,4'-Isopropylidenediphenol [IVb]
  Michler’s ketone [IIb]
  Molybdenum trioxide [IVb]
  Nitric acid [IIb]
  Nitrilotriacetic acid [IVb]
  Peracetic acid [IVb]

☐ 2-Phenylphenol [IVb]
☐ Phosphoric acid [IIb]
  Propene [IVb]

☐ Silver and Compounds (Note 4) [IIb]
☐ Sodium hydroxide [IIb]
☐ Sulfuric acid [IIb]
  Terephthalic acid [IVb]
  Thiourea [IVb]

☐ 1,2,4-Trimethylbenzene [IVb]
☐ Zinc and Compounds (Note 4) [IIb]

Footnotes

* Substances which have already been identified by the Air Resources Board as Toxic Air Contaminants through a comprehensive AB 1807 risk assessment and which have health values developed by the Office of Environmental Health Hazard Assessment and approved by the Scientific Review Panel. A full risk assessment report is available.

To be listed as a Toxic Air Contaminant, these substances will go through a comprehensive AB 1807 risk assessment. These substances are active ingredients in pesticides in California. For further information regarding the pesticidal uses of these compounds, please contact the Department of Pesticide Regulation.

Note 4: For all listings above which contain the word “compounds” and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical’s infrastructure.

Note 5: Chlorinated dibenzo-p-dioxins and dibenzofurans: The cancer potency value for 2,3,7,8-tetrachlorodibenzo-p-dioxin was determined for the identification of chlorinated dioxins and dibenzofurans as toxic air contaminants in 1986. At that time, the Board identified dibenzo-p-dioxins and dibenzofurans chlorinated in the 2,3,7, and 8 positions and containing 4,5,6, or 7 chlorine atoms as toxic air contaminants. Since 1986, International Toxicity Equivalency Factors (ITEFs) have been developed which are used to evaluate the cancer risk due to exposure to samples containing mixtures of chlorinated dibenzo-p-dioxins and dibenzofurans. ITEFs are numerical factors that express the toxicity of an individual chlorinated dibenzo-p-dioxin or dibenzofuran relative to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin. ITEFs are listed for 16 chlorinated dibenzo-p-dioxins and dibenzofurans.

Note 6: Diethanolamine: There is a 1997 draft report by the National Toxicology Program that shows evidence of carcinogenic activity in mice. (This may result in a change of the cancer classification.)

Note 7: Glycol ethers: Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol

\[(R(OCH\_CH\_2)\_n \_OR')\ where\ 2\ 2\ n\]

\[n = 1, 2, 3\]

\[R = \text{alkyl or aryl groups}\]

\[R = \text{R,H, or groups which, when removed, yield glycol ethers with the structure; } R(OCH\_CH\_2)\_OH.\]

Polymers are excluded from the glycol category. 2 n

Note 8: Inorganic Lead: Due to information on non-cancer health effects showing no identified threshold, no Reference Exposure Level has been developed. However, guidelines for assessing noncancer health impacts are currently being developed by ARB staff.

Note 9: Polycyclic organic matter: Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C.

Note 10: Benzo[a]pyrene: Potency Equivalency Factors (PEF) have been developed for 24 polycyclic aromatic hydrocarbons (PAHs). Using benzo[a]pyrene as a reference compound, a weighting scheme for PAHs was developed in the 1994 Air Resources Board document entitled, *Benzo[a]pyrene as a Toxic Air Contaminant*. When a specific potency value is developed for a chemical, it should be used in place of the PEF.

Note 11: Cyanide compounds: X’CN where X=H’ or any other group where a formal dissociation may occur. For example, K-CN or Ca(CN)2.

Note 12: Radionuclides: A type of atom which spontaneously undergoes radioactive decay.

Note 13: Fine mineral fibers: Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

Note 14: Environmental tobacco smoke: An AB 1807-type of health assessment for Environmental Tobacco Smoke was conducted by the Office of Environmental Health Hazard Assessment (OEHHA) and was approved by the Scientific Review Panel on June 19, 1997. The Air Resources Board accepted the report from OEHHA on October 23, 1997 and then forwarded to the Department of Health Services’ Tobacco Control Program for appropriate action.
Appendix C
Toxic Air Contaminant Trigger Levels
Toxic Air Contaminant Trigger Levels
Table 2-1-316, Bay Area Air Quality Management District, August 1, 2001

* This is a chemical compound group. If a CAS number is listed, it represents only a single chemical within the chemical class (for metallic compounds, the CAS number of the elemental form is listed; for other compounds, the CAS number of a predominant compound in the group is given).

n/a—No CAS number is available for this compound or compound group.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS Number</th>
<th>Trigger Level (lb/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>75070</td>
<td>7.2E+01</td>
</tr>
<tr>
<td>Acetamide</td>
<td>603505</td>
<td>9.7E+00</td>
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<td>Acrolein</td>
<td>107028</td>
<td>3.9E+00</td>
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<td>Acrylamide</td>
<td>79061</td>
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<td>Acrylonitrile</td>
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<tr>
<td>Allyl chloride</td>
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<td>Aminoanthraquinone, 2</td>
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<td>2.1E+01</td>
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<tr>
<td>Ammonia</td>
<td>7664417</td>
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<tr>
<td>Aniline</td>
<td>62533</td>
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<tr>
<td>Arsenic and arsenic compounds (inorganic)</td>
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<td>Asbestos</td>
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<td>Benzene</td>
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<td>Benzidine (and its salts)</td>
<td>92875*</td>
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<td>Benzyl chloride (see chlorotoluenes)</td>
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<td>Beryllium and beryllium compounds</td>
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<tr>
<td>Bis(2-chloro-ethyl)ether</td>
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<td>Bis(chloro-methyl)ether</td>
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<td>Bromine and bromine compounds (inorganic)</td>
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<td>Butadiene, 1,3-</td>
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<td>Compound</td>
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<td>Trigger Level (lb/year)</td>
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<tr>
<td>Butyl alcohol, tert-</td>
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<td>1.4E+05</td>
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<tr>
<td>Cadmium and cadmium compounds</td>
<td>7440439*</td>
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<td>Carbon disulfide</td>
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<td>Carbon tetrachloride</td>
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<td>Chlorinated dibenzodioxins and dibenzofurans (TCDD equivalent)</td>
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<td>Chlorinated paraffins</td>
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<td>Chloroform</td>
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<td>Chloro-o-phenylenediamine, 4-</td>
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<td>Chlorotoluenes</td>
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<td>Chromium (hexavalent) and chromium (hexavalent) compounds</td>
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<td>Copper and copper compounds</td>
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<td>Cresol</td>
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<td>Cupferron</td>
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<td>Diaminoanisole,</td>
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<td>Dibromo-3-chloropropane, 1,2- (DBCP)</td>
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<td><strong>Compound</strong></td>
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<td><strong>Trigger Level (lb/year)</strong></td>
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<td>Dichlorobenzidine, 3,3'-</td>
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<td>Dichloroethylene, 1,1- (see vinylidene chloride)</td>
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<td>Diesel exhaust particulate matter</td>
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<td>Ethylene thiourea</td>
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<td>Freons (see Chlorofluorocarbons)</td>
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<td>Glutaraldehyde</td>
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<td><strong>Glycol Ethers:</strong></td>
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<td>ethylene glycol monoethyl ether</td>
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<td>2-Ethoxyethyl acetate (cellosolve acetate; ethylene glycol monoethyl ether)</td>
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<td><strong>Isocyanates:</strong></td>
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<td>Toluene diisocyanates</td>
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<td>Isophorone</td>
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<td>Isopropyl alcohol</td>
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<td>Lead, inorganic, and lead</td>
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<td>Compound</td>
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<td>Trigger Level (lb/year)</td>
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<td>compounds (inorganic)</td>
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<td>Methyl bromide</td>
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<td>Methyl chloroform (1,1,1-TCA)</td>
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<td>Methyl mercury</td>
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<td>Methyl methacrylate</td>
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<td>Naphthalene</td>
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<td>Nickel and nickel compounds</td>
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<td>Nitrosodiethylamine, N-</td>
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Bowers, B., D. Barber, and R. Allinger, “Profile of Silicone Reclaim,” presented at the 130th Meeting of the American Chemical Society Rubber Division, Atlanta, Ga., Paper #81, Fall 1986.

<www.lub.lu.se/cgi-bin/show_diss.pl/tec_653.html> (September 2003).


Knorr, K., “Reclaimed Rubber: Are Our Technical Abilities at the End?” presented at 148th Meeting of the American Chemical Society Rubber Division Meeting, Cleveland, Ohio, Paper #5, Fall 1995.


Background Information


Ultrasonic


Incineration

From Wikipedia, the free encyclopedia
For other forms of waste plant that produces energy, see waste-to-energy.
"Incinerator" redirects here. For the fictional character, see Incinerator (Transformers).
"Incinerate" redirects here. For the Sonic Youth song, see Incinerate (song). For the Dew-Scented album, see Incinerate (album).

The Spittelau incineration plant in Vienna, designed by Friedensreich Hundertwasser.
SYSAV incineration plant in Malmö, Sweden capable of handling 25 metric tons (28 short tons) per hour household waste. To the left of the main stack, a new identical oven line is under construction (March 2007).

**Incineration** is a waste treatment process that involves the combustion of organic substances contained in waste materials.[1] Incineration and other high temperature waste treatment systems are described as "thermal treatment". Incineration of waste materials converts the waste into ash, flue gas, and heat. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. In some cases, the heat generated by incineration can be used to generate electric power.

Incineration with energy recovery is one of several waste-to-energy (WtE) technologies such as gasification, Plasma arc gasification, pyrolysis and anaerobic digestion. Incineration may also be implemented without energy and materials recovery.

In several countries, there are still concerns from experts and local communities about the environmental impact of incinerators (see arguments against incineration).

In some countries, incinerators built just a few decades ago often did not include a materials separation to remove hazardous, bulky or recyclable materials before combustion. These facilities tended to risk the health of the plant workers and the local environment due to inadequate levels of gas cleaning and combustion process control. Most of these facilities did not generate electricity.
Incinerators reduce the solid mass of the original waste by 80–85% and the volume (already compressed somewhat in garbage trucks) by 95-96%, depending on composition and degree of recovery of materials such as metals from the ash for recycling.[2] This means that while incineration does not completely replace landfilling, it significantly reduces the necessary volume for disposal. Garbage trucks often reduce the volume of waste in a built-in compressor before delivery to the incinerator. Alternatively, at landfills, the volume of the uncompressed garbage can be reduced by approximately 70%[citation needed] by using a stationary steel compressor, albeit with a significant energy cost. In many countries, simpler waste compaction is a common practice for compaction at landfills.

Incineration has particularly strong benefits for the treatment of certain waste types in niche areas such as clinical wastes and certain hazardous wastes where pathogens and toxins can be destroyed by high temperatures. Examples include chemical multi-product plants with diverse toxic or very toxic wastewater streams, which cannot be routed to a conventional wastewater treatment plant.

Waste combustion is particularly popular in countries such as Japan where land is a scarce resource. Denmark and Sweden have been leaders in using the energy generated from incineration for more than a century, in localised combined heat and power facilities supporting district heating schemes.[3] In 2005, waste incineration produced 4.8% of the electricity consumption and 13.7% of the total domestic heat consumption in Denmark.[4] A number of other European countries rely heavily on incineration for handling municipal waste, in particular Luxembourg, the Netherlands, Germany and France.[2]

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  - 2.7 Specialized incineration
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### History

The first incinerators for waste disposal were built in Nottingham by Manlove, Alliott & Co. Ltd. in 1874 to a design patented by Albert Fryer. They were originally known as destructors.\(^5\)

### Technology

An incinerator is a furnace for burning waste. Modern incinerators include pollution mitigation equipment such as flue gas cleaning. There are various types of incinerator plant design: moving grate, fixed grate, rotary-kiln, and fluidised bed.

### Burn pile

The burn pile, or burn pit is one of the simplest and earliest forms of waste disposal, essentially consisting of a mound of combustible materials piled on bare ground and set on fire. Indiscriminate piles of household waste are strongly discouraged and may be illegal in urban areas, but are permitted in certain rural situations such as clearing forested land for farming, where the stumps are uprooted and burned.\(^6\) Rural burn piles of organic yard waste are also sometimes permitted, though not asphalt shingles, plastics, or other petroleum products.\(^6\)
Burn piles can and have spread uncontrolled fires, for example if wind blows burning material off the pile into surrounding combustible grasses or onto buildings. As interior structures of the pile are consumed, the pile can shift and collapse, spreading the burn area. Even in a situation of no wind, small lightweight ignited embers can lift off the pile via convection, and waft through the air into grasses or onto buildings, igniting them.

**[edit] Burn barrel**

The burn barrel is a somewhat more controlled form of private waste incineration, containing the burning material inside a metal barrel, with a metal grating over the exhaust. The barrel prevents the spread of burning material in windy conditions, and as the combustibles are reduced they can only settle down into the barrel. The exhaust grating helps to prevent the spread of burning embers. Typically steel 55-US-gallon (210 L) drums are used as burn barrels, with air vent holes cut or drilled around the base for air intake. Over time the very high heat of incineration causes the metal to oxidize and rust, and eventually the barrel itself is consumed by the heat and must be replaced.

Private burning of dry cellulose/paper products is generally clean-burning, producing no visible smoke, but the large amount of plastics in household waste can cause private burning to create a public nuisance and health hazard, generating acrid odors and fumes that make eyes burn and water. The temperatures in a burn barrel are not regulated, and usually do not reach high enough or for long enough time to completely break down chemicals such as dioxin in plastics and other waste chemicals. Therefore plastics and other petroleum products must be separated and sent to commercial waste disposal facilities.

In The United States, private rural incineration is typically permitted so long as it is not a nuisance to others, does not pose a risk of fire such as in dry conditions, and the fire is clean-burning, producing no visible smoke. However, many states, such as New York, Minnesota, and Wisconsin, have laws against private burn barrels due to EPA findings that one household burning their own waste can release more dioxins and furans annually than a modern incinerator processing 1,000 tons per day. People intending to burn waste may be required to contact a state agency in advance to check current fire risk and conditions, and to alert officials of the controlled fire that will occur.

**[edit] Moving grate**
Control room of a typical moving grate incinerator overseeing two boiler lines

The typical incineration plant for municipal solid waste is a moving grate incinerator. The moving grate enables the movement of waste through the combustion chamber to be optimised to allow a more efficient and complete combustion. A single moving grate boiler can handle up to 35 metric tons (39 short tons) of waste per hour, and can operate 8,000 hours per year with only one scheduled stop for inspection and maintenance of about one month's duration.[10] Moving grate incinerators are sometimes referred to as Municipal Solid Waste Incinerators (MSWIs).

The waste is introduced by a waste crane through the "throat" at one end of the grate, from where it moves down over the descending grate to the ash pit in the other end. Here the ash is removed through a water lock.

Municipal solid waste in the furnace of a moving grate incinerator capable of handling 15 metric tons (17 short tons) of waste per hour. The holes in the grate elements supplying the primary combustion air are visible.

Part of the combustion air (primary combustion air) is supplied through the grate from below. This air flow also has the purpose of cooling the grate itself. Cooling is important for the mechanical strength of the grate, and many moving grates are also water cooled internally.
Secondary combustion air is supplied into the boiler at high speed through nozzles over the grate. It facilitates complete combustion of the flue gases by introducing turbulence for better mixing and by ensuring a surplus of oxygen. In multiple/stepped hearth incinerators, the secondary combustion air is introduced in a separate chamber downstream the primary combustion chamber.

According to the European Waste Incineration Directive, incineration plants must be designed to ensure that the flue gases reach a temperature of at least 850 °C (1,560 °F) for 2 seconds in order to ensure proper breakdown of toxic organic substances. In order to comply with this at all times, it is required to install backup auxiliary burners (often fueled by oil), which are fired into the boiler in case the heating value of the waste becomes too low to reach this temperature alone.

The flue gases are then cooled in the superheaters, where the heat is transferred to steam, heating the steam to typically 400 °C (752 °F) at a pressure of 40 bars (580 psi) for the electricity generation in the turbine. At this point, the flue gas has a temperature of around 200 °C (392 °F), and is passed to the flue gas cleaning system.

In Scandinavia scheduled maintenance is always performed during summer, where the demand for district heating is low. Often incineration plants consist of several separate 'boiler lines' (boilers and flue gas treatment plants), so that waste can continue to be received at one boiler line while the others are subject to revision.

[edit] Fixed grate

The older and simpler kind of incinerator was a brick-lined cell with a fixed metal grate over a lower ash pit, with one opening in the top or side for loading and another opening in the side for removing incombustible solids called clinkers. Many small incinerators formerly found in apartment houses have now been replaced by waste compactors.

[edit] Rotary-kiln

The rotary-kiln incinerator[1] is used by municipalities and by large industrial plants. This design of incinerator has 2 chambers: a primary chamber and secondary chamber. The primary chamber in a rotary kiln incinerator consist of an inclined refractory lined cylindrical tube. Movement of the cylinder on its axis facilitates movement of waste. In the primary chamber, there is conversion of solid fraction to gases, through volatilization, destructive distillation and partial combustion reactions. The secondary chamber is necessary to complete gas phase combustion reactions.

The clinkers spill out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases may be combusted in an "afterburner".[2]

[edit] Fluidized bed
A strong airflow is forced through a sandbed. The air seeps through the sand until a point is reached where the sand particles separate to let the air through and mixing and churning occurs, thus a fluidised bed is created and fuel and waste can now be introduced.

The sand with the pre-treated waste and/or fuel is kept suspended on pumped air currents and takes on a fluid-like character. The bed is thereby violently mixed and agitated keeping small inert particles and air in a fluid-like state. This allows all of the mass of waste, fuel and sand to be fully circulated through the furnace.

**[edit] Specialized incineration**

Furniture factory sawdust incinerators need much attention as these have to handle resin powder and many flammable substances. Controlled combustion, burn back prevention systems are essential as dust when suspended resembles the fire catch phenomenon of any liquid petroleum gas.

**[edit] Use of heat**

The heat produced by an incinerator can be used to generate steam which may then be used to drive a turbine in order to produce electricity. The typical amount of net energy that can be produced per tonne municipal waste is about 2/3 MWh of electricity and 2 MWh of district heating. Thus, incinerating about 600 metric tons (660 short tons) per day of waste will produce about 400 MWh of electrical energy per day (17 MW of electrical power continuously for 24 hours) and 1200 MWh of district heating energy each day.

**[edit] Pollution**

Incineration has a number of outputs such as the ash and the emission to the atmosphere of flue gas. Before the flue gas cleaning system, the flue gases may contain significant amounts of particulate matter, heavy metals, dioxins, furans, sulfur dioxide, and hydrochloric acid.

In a study from 1994, Delaware Solid Waste Authority found that, for same amount of produced energy, incineration plants emitted fewer particles, hydrocarbons and less SO2, HCl, CO and NOx than coal-fired power plants, but more than natural gas fired power plants. According to Germany's Ministry of the Environment, waste incinerators reduce the amount of some atmospheric pollutants by substituting power produced by coal-fired plants with power from waste-fired plants.

**[edit] Gaseous emissions**

**[edit] Dioxin and furans**

The most publicized concerns from environmentalists about the incineration of municipal solid wastes (MSW) involve the fear that it produces significant amounts of dioxin and furan emissions. Dioxins and furans are considered by many to be serious health hazards.
In 2005, The Ministry of the Environment of Germany, where there were 66 incinerators at that time, estimated that "...whereas in 1990 one third of all dioxin emissions in Germany came from incineration plants, for the year 2000 the figure was less than 1 %. Chimneys and tiled stoves in private households alone discharge approximately 20 times more dioxin into the environment than incineration plants."[14]

According to the United States Environmental Protection Agency, incineration plants are no longer significant sources of dioxins and furans. In 1987, before the governmental regulations required the use of emission controls, there was a total of 10,000 grams (350 oz) of dioxin emissions from US incinerators. Today, the total emissions from the 87 plants are 10 grams (0.35 oz) annually, a reduction of 99.9 %.

Backyard barrel burning of household and garden wastes, still allowed in some rural areas, generates 580 grams (20 oz) of dioxins annually. Studies conducted by the US-EPA[16] demonstrate that the emissions from just one family using a burn barrel produced more emissions than an incineration plant disposing of 200 metric tons (220 short tons) of waste per day by 1997 and five times that by 2007 due to increased chemicals in household trash and decreased emissions by municipal incinerators using better technology[citation needed].

Dioxin cracking methods and limitations

Generally, the breakdown of dioxin requires exposure of the molecular ring to a sufficiently high temperature so as to trigger thermal breakdown of the strong molecular bonds holding it together. Small pieces of fly ash may be somewhat thick, and too brief an exposure to high temperature may only degrade dioxin on the surface of the ash. For a large volume air chamber, too brief an exposure may also result in only some of the exhaust gases reaching the full breakdown temperature. For this reason there is also a time element to the temperature exposure to ensure heating completely through the thickness of the fly ash and the volume of waste gases.

There are trade-offs between increasing either the temperature or exposure time. Generally where the molecular breakdown temperature is higher, the exposure time for heating can be shorter, but excessively high temperatures can also cause wear and damage to other parts of the incineration equipment. Likewise the breakdown temperature can be lowered to some degree but then the exhaust gases would require a greater lingering period of perhaps several minutes, which would require large/long treatment chambers that take up a great deal of treatment plant space.

A side effect of breaking the strong molecular bonds of dioxin is the potential for breaking the bonds of nitrogen gas (N\textsubscript{2}) and oxygen gas (O\textsubscript{2}) in the supply air. As the exhaust flow cools, these highly reactive detached atoms spontaneously reform bonds into reactive oxides such as NO\textsubscript{x} in the flue gas, which can result in smog formation and acid rain if they were released directly into the local environment. These reactive oxides must be further neutralized with selective catalytic reduction (SCR) or selective non-catalytic reduction (see below).

Dioxin cracking in practice
The temperatures needed to break down dioxin are typically not reached when burning of plastics outdoors in a burn barrel or garbage pit, causing high dioxin emissions as mentioned above. While plastic does usually burn in an open-air fire, the dioxins remain after combustion and either float off into the atmosphere, or may remain in the ash where it can be leached down into groundwater when rain falls on the ash pile.

Modern municipal incinerator designs include a high temperature zone, where the flue gas is ensured to sustain a temperature above 850 °C (1,560 °F) for at least 2 seconds before it is cooled down. They are equipped with auxiliary heaters to ensure this at all times. These are often fueled by oil, and normally only active for a very small fraction of the time.

For very small municipal incinerators, the required temperature for thermal breakdown of dioxin may be reached using a high-temperature electrical heating element, plus a selective catalytic reduction stage.

[edit] CO2

As for other complete combustion processes, nearly all of the carbon content in the waste is emitted as CO2 to the atmosphere. MSW contains approximately the same mass fraction of carbon as CO2 itself (27%), so incineration of 1 ton of MSW produces approximately 1 ton of CO2.

If the waste was landfilled, 1 ton of MSW would produce approximately 62 cubic metres (2,200 cu ft) methane via the anaerobic decomposition of the biodegradable part of the waste. Since the global warming potential of methane is 21 and the weight of 62 cubic meters of methane at 25 degrees Celsius is 40.7 kg, this is equivalent to 0.854 ton of CO2, which is less than the 1 ton of CO2 which would have been produced by incineration. In some countries, large amounts of landfill gas are collected, but still the global warming potential of the landfill gas emitted to atmosphere in the US in 1999 was approximately 32 % higher than the amount of CO2 that would have been emitted by incineration.[17]

In addition, nearly all biodegradable waste has biological origin. This material has been formed by plants using atmospheric CO2 typically within the last growing season. If these plants are regrown the CO2 emitted from their combustion will be taken out from the atmosphere once more.

Such considerations are the main reason why several countries administrate incineration of the biodegradable part of waste as renewable energy.[18] The rest – mainly plastics and other oil and gas derived products – is generally treated as non-renewables.

Different results for the CO2 footprint of incineration can be reached with different assumptions. Local conditions (such as limited local district heating demand, no fossil fuel generated electricity to replace or high levels of aluminum in the waste stream) can decrease the CO2 benefits of incineration. The methodology and other assumptions may also influence the results significantly. For example the methane emissions from landfills occurring at a later date may be neglected or given less weight, or biodegradable waste may not be considered CO2 neutral. A
study by Eunomia Research and Consulting in 2008 on potential waste treatment technologies in London demonstrated that by applying several of these (according to the authors) unusual assumptions the average existing incineration plants performed poorly for CO₂ balance compared to the theoretical potential of other emerging waste treatment technologies.[19]

[edit] Other emissions

Other gaseous emissions in the flue gas from incinerator furnaces include sulfur dioxide, hydrochloric acid, heavy metals and fine particles.

The steam content in the flue may produce visible fume from the stack, which can be perceived as a visual pollution. It may be avoided by decreasing the steam content by flue gas condensation and reheating, or by increasing the flue gas exit temperature well above its dew point. Flue gas condensation allows the latent heat of vaporization of the water to be recovered, subsequently increasing the thermal efficiency of the plant.

[edit] Flue gas cleaning

The quantity of pollutants in the flue gas from incineration plants is reduced by several processes.

Particulate is collected by particle filtration, most often electrostatic precipitators (ESP) and/or baghouse filters. The latter are generally very efficient for collecting fine particles. In an investigation by the Ministry of the Environment of Denmark in 2006, the average particulate emissions per energy content of incinerated waste from 16 Danish incinerators were below 2.02 g/GJ (grams per energy content of the incinerated waste). Detailed measurements of fine particles with sizes below 2.5 micrometres (PM₂.₅) were performed on three of the incinerators: One incinerator equipped with an ESP for particle filtration emitted 5.3 g/GJ fine particles, while two incinerators equipped with baghouse filters emitted 0.002 and 0.013 g/GJ PM₂.₅. For ultra fine particles (PM₁.₀), the numbers were 4.889 g/GJ PM₁.₀ from the ESP plant, while emissions of 0.000 and 0.008 g/GJ PM₁.₀ were measured from the plants equipped with baghouse filters.[20][21]

Acid gas scrubbers are used to remove hydrochloric acid, nitric acid, hydrofluoric acid, mercury, lead and other heavy metals. Basic scrubbers remove sulfur dioxide, forming gypsum by reaction with lime.[22]

Waste water from scrubbers must subsequently pass through a waste water treatment plant.

Sulfur dioxide may also be removed by dry desulfurisation by injection limestone slurry into the flue gas before the particle filtration.

NOₓ is either reduced by catalytic reduction with ammonia in a catalytic converter (selective catalytic reduction, SCR) or by a high temperature reaction with ammonia in the furnace (selective non-catalytic reduction, SNCR). Urea may be substituted for ammonia as the reducing reagent but must be supplied earlier in the process so that it can hydrolyze into ammonia.
Substitution of urea can reduce costs and potential hazards associated with storage of anhydrous ammonia.

Heavy metals are often adsorbed on injected active carbon powder, which is collected by the particle filtration.

**[edit] Solid outputs**

Operation of an incinerator aboard an aircraft carrier

Incineration produces fly ash and bottom ash just as is the case when coal is combusted. The total amount of ash produced by municipal solid waste incineration ranges from 4 to 10 % by volume and 15-20 % by weight of the original quantity of waste, and the fly ash amounts to about 10-20 % of the total ash. The fly ash, by far, constitutes more of a potential health hazard than does the bottom ash because the fly ash often contain high concentrations of heavy metals such as lead, cadmium, copper and zinc as well as small amounts of dioxins and furans. The bottom ash seldom contain significant levels of heavy metals. In testing over the past decade, no ash from an incineration plant in the USA has ever been determined to be a hazardous waste. At present although some historic samples tested by the incinerator operators' group would meet the being ecotoxic criteria at present the EA say "we have agreed" to regard incinerator bottom ash as "non-hazardous" until the testing programme is complete.

**[edit] Other pollution issues**

Odor pollution can be a problem with old-style incinerators, but odors and dust are extremely well controlled in newer incineration plants. They receive and store the waste in an enclosed area with a negative pressure with the airflow being routed through the boiler which prevents unpleasant odors from escaping into the atmosphere. However, not all plants are implemented this way, resulting in inconveniences in the locality.

An issue that affects community relationships is the increased road traffic of waste collection vehicles to transport municipal waste to the incinerator. Due to this reason, most incinerators are located in industrial areas. This problem can be avoided to an extent through the transport of waste by rail from transfer stations.

**[edit] Debate**

Use of incinerators for waste management is controversial. The debate over incinerators typically involves business interests (representing both waste generators and incinerator firms), government regulators, environmental activists and local citizens who must weigh the economic appeal of local industrial activity with their concerns over health and environmental risk.
People and organizations professionally involved in this issue include the U.S. Environmental Protection Agency and a great many local and national air quality regulatory agencies worldwide.

**Arguments for incineration**

Kehrichtverbrennungsanlage Zürcher Oberland (KEZO) in Hinwil, Switzerland

- The concerns over the health effects of dioxin and furan emissions have been significantly lessened by advances in emission control designs and very stringent new governmental regulations that have resulted in large reductions in the amount of dioxins and furans emissions.\(^{[14]}\)
- The U.K. Health Protection Agency concluded in 2009 that "Modern, well managed incinerators make only a small contribution to local concentrations of air pollutants. It is possible that such small additions could have an impact on health but such effects, if they exist, are likely to be very small and not detectable."\(^{[25]}\)
- Incineration plants can generate electricity and heat that can substitute power plants powered by other fuels at the regional electric and district heating grid, and steam supply for industrial customers. Incinerators and other waste-to-energy plants generate at least partially biomass-based renewable energy that offsets greenhouse gas pollution from coal-, oil- and gas-fired power plants.\(^{[29]}\) The E.U. considers energy generated from biogenic waste (waste with biological origin) by incinerators as non-fossil renewable energy under its emissions caps. These greenhouse gas reductions are in addition to those generated by the avoidance of landfill methane.
- The bottom ash residue remaining after combustion has been shown to be a non-hazardous solid waste that can be safely put into landfills or recycled as construction aggregate. Samples are tested for ecotoxic metals.\(^{[27]}\)
- In densely populated areas, finding space for additional landfills is becoming increasingly difficult.
The Maishima waste treatment center in Osaka, designed by Friedensreich Hundertwasser, uses heat for power generation.

Fine particles can be efficiently removed from the flue gases with baghouse filters. Even though approximately 40 % of the incinerated waste in Denmark was incinerated at plants with no baghouse filters, estimates based on measurements by the Danish Environmental Research Institute showed that incinators were only responsible for approximately 0.3 % of the total domestic emissions of particulate smaller than 2.5 micrometres ($PM_{2.5}$) to the atmosphere in 2006. [20][21]

- Incineration of municipal solid waste avoids the release of methane. Every ton of MSW incinerated, prevents about one ton of carbon dioxide equivalents from being released to the atmosphere. [17]
- Incineration of medical waste and sewage sludge produces an end product ash that is sterile and non-hazardous. [citation needed]
- Most municipalities that operate incineration facilities have higher recycling rates than neighboring cities and counties that do not send their waste to incinerators. [28] This is in part due to enhanced recovery of ceramic materials reused in construction, as well as ferrous and in some cases non-ferrous metals that can be recovered from combustion residue. [29] Metals recovered from ash would typically be difficult or impossible to recycle through conventional means, as the removal of attached combustible material through incineration provides an alternative to labor- or energy-intensive mechanical separation methods.
- Volume of combusted waste is reduced by approximately 90%, increasing the life of landfills. Ash from modern incinerators is vitrified at temperatures of 1,000 °C (1,830 °F) to 1,100 °C (2,010 °F), reducing the leachability and toxicity of residue. As a result, special landfills are generally no longer required for incinerator ash from municipal waste streams, and existing landfills can see their life dramatically increased by combusting waste, reducing the need for municipalities to site and construct new landfills. [30][31]

[edit] Arguments against incineration
Decommissioned Kwai Chung Incineration Plant from 1978. As of late February 2009, it has been demolished.

- The Scottish Protection Agency's (SEPA) comprehensive health effects research concluded "inconclusively" on health effects in Oct. 2009. The authors stress, that even though no conclusive evidence of non-occupational health effects from incinerators were found in the existing literature, "small but important effects might be virtually impossible to detect". The report highlights epidemiological deficiencies in previous UK health studies and suggests areas for future studies.\[32\] The U.K. Health Protection Agency produced a lesser summary in September 2009.\[25\] Many toxicologists criticise and dispute this report as not being comprehensive epidemiologically, thin on peer review and the effects of fine particle effects on health.\[citation needed]\[33\]\[34\]

- The highly toxic fly ash must be safely disposed of. This usually involves additional waste miles and the need for specialist toxic waste landfill elsewhere. If not done properly, it may cause concerns for local residents.\[33\]\[34\]

- Some people are still concerned about the health effects of dioxin and furan emissions into the atmosphere from old incinerators; especially during start up and shut down, or where filter bypass is required.

- Incinerators emit varying levels of heavy metals such as vanadium, manganese, chromium, nickel, arsenic, mercury, lead, and cadmium, which can be toxic at very minute levels.

- Incinerator Bottom Ash (IBA) has elevated levels of heavy metals with ecotoxicity concerns if not reused properly. Some people have the opinion that IBA reuse is still in its infancy and is still not considered to be a mature or desirable product, despite
additional engineering treatments. Concerns of IBA use in foam concrete have been expressed by the UK Health and Safety Executive in 2010 following several construction and demolition explosions. In its guidance document, IBA is currently banned from use by the UK Highway Authority in concrete work until these incidents have been investigated. [35]

- Alternative technologies are available or in development such as Mechanical Biological Treatment, Anaerobic Digestion (MBT/AD), Autoclaving or Mechanical Heat Treatment (MHT) using steam or plasma arc gasification (PGP), which is incineration using electrically produced extreme high temperatures, or combinations of these treatments. Erection of incinerators compete with the development and introduction of other emerging technologies. A UK government WRAP report, August 2008 found that in the UK median incinerator costs per ton were generally higher than those for MBT treatments by £18 per metric ton; and £27 per metric ton for most modern (post 2000) incinerators. [36][37]

- Building and operating waste processing plants such as incinerators requires long contract periods to recover initial investment costs, causing a long term lock-in. Incinerator lifetimes normally range 25–30 years. This was highlighted by Peter Jones, OBE, the Mayor of London's waste representative in April 2009. [35]

- Incinerators produce fine particles in the furnace. Even with modern particle filtering of the flue gases, a small part of this is emitted to the atmosphere. PM$_{2.5}$ is not separately regulated in the European Waste Incineration Directive, even though they are repeatedly correlated spatially to infant mortality in the UK (M.Ryan's ONS data based maps around the EfW/CHP waste incinerators at Edmonton, Coventry, Chineham, Kirklees and Sheffield). [39][40][41] Under WID there is no requirement to monitor stack top or downwind incinerator PM$_{2.5}$ levels. [42] Several European doctors associations (including cross discipline experts such as physicians, environmental chemists and toxicologists) in June 2008 representing over 33,000 doctors wrote a keynote statement directly to the European Parliament citing widespread concerns on incinerator particle emissions and the absence of specific fine and ultrafine particle size monitoring or in depth industry/government epidemiological studies of these minute and invisible incinerator particle size emissions. [43]

- Local communities are often opposed to the idea of locating waste processing plants such as incinerators in their vicinity (the Not In My Back Yard phenomenon). Studies in Andover, Massachusetts strongly correlated 10% property devaluations with close incinerator proximity. [44]

- Prevention, waste minimisation, reuse and recycling of waste should all be preferred to incineration according to the waste hierarchy. Supporters of zero waste consider incinerators and other waste treatment technologies as barriers to recycling and separation beyond particular levels, and that waste resources are sacrificed for energy production. [45][46][47]

- A 2008 Eunomia report found that under some circumstances and assumptions, incineration causes less CO$_2$ reduction than other emerging EfW and CHP technology combinations for treating residual mixed waste. [19] The authors found that CHP incinerator technology without waste recycling ranked 19 out of 24 combinations (where all alternatives to incineration were combined with advanced waste recycling plants);
being 228% less efficient than the ranked 1 Advanced MBT maturation technology; or 211% less efficient than plasma gasification/autoclaving combination ranked 2.

- Some incinerators are visually undesirable. In many countries they require a visually intrusive chimney stack.
- If reusable waste fractions are handled in waste processing plants such as incinerators in developing nations, it would cut out viable work for local economies. It is estimated that there are 1 million people making a livelihood off collecting waste.[48]

[edit] Trends in incinerator use

The history of municipal solid waste (MSW) incineration is linked intimately to the history of landfills and other waste treatment technology. The merits of incineration are inevitably judged in relation to the alternatives available. Since the 1970s, recycling and other prevention measures have changed the context for such judgements. Since the 1990s alternative waste treatment technologies have been maturing and becoming viable.

Incineration is a key process in the treatment of hazardous wastes and clinical wastes. It is often imperative that medical waste be subjected to the high temperatures of incineration to destroy pathogens and toxic contamination it contains.

[edit] Incineration in North America

The first incinerator in the U.S. was built in 1885 on Governors Island in New York.[49] In 1949, Robert C. Ross founded one of the first hazardous waste management companies in the U.S. He began Robert Ross Industrial Disposal because he saw an opportunity to meet the hazardous waste management needs of companies in northern Ohio. In 1958, the company built one of the first hazardous waste incinerators in the U.S.[50] The first full-scale, municipally operated incineration facility in the U.S. was the Arnold O. Chantland Resource Recovery Plant, built in 1975 and located in Ames, Iowa. This plant is still in operation and produces refuse-derived fuel that is sent to local power plants for fuel.[51] The first commercially successful incineration plant in the U.S. was built in Saugus, Massachusetts in October 1975 by Wheelabrator Technologies, and is still in operation today.[23]

There are several environmental or waste management corporations that transport ultimately to an incinerator or cement kiln treatment center. Currently (2009), there are three main businesses that incinerate waste: Clean Harbours, WTI-Heritage, and Ross Incineration Services. Clean Harbours has acquired many of the smaller, independently run facilities, accumulating 5–7 incinerators in the process across the U.S. WTI-Heritage has one incinerator, located in the southeastern corner of Ohio (across the Ohio River from West Virginia).

Several old generation incinerators have been closed; of the 186 MSW incinerators in 1990, only 89 remained by 2007, and of the 6200 medical waste incinerators in 1988, only 115 remained in 2003.[53] No new incinerators were built between 1996 and 2007. The main reasons for lack of activity have been:
• Economics. With the increase in the number of large inexpensive regional landfills and, up until recently, the relatively low price of electricity, incinerators were not able to compete for the 'fuel', i.e., waste in the U.S.
• Tax policies. Tax credits for plants producing electricity from waste were rescinded in the U.S. between 1990 and 2004.

There has been renewed interest in incineration and other waste-to-energy technologies in the U.S. and Canada. In the U.S., incineration was granted qualification for renewable energy production tax credits in 2004.[53] Projects to add capacity to existing plants are underway, and municipalities are once again evaluating the option of building incineration plants rather than continue landilling municipal wastes. However, many of these projects have faced continued political opposition in spite of renewed arguments for the greenhouse gas benefits of incineration and improved air pollution control and ash recycling.

[edit] Incineration in Europe

In Europe, with the ban on landilling untreated waste, scores of incinerators have been built in the last decade, with more under construction. Recently, a number of municipal governments have begun the process of contracting for the construction and operation of incinerators. In Europe, some of the electricity generated from waste is deemed to be from a 'Renewable Energy Source (RES)' and is thus eligible for tax credits if privately operated. Also, some incinerators in Europe are equipped with waste recovery, allowing the reuse of ferrous and non-ferrous materials found in landfills. A prominent example is the AEB Waste Fired Power Plant.[54][55]

[edit] Incineration in the United Kingdom

The technology employed in the UK waste management industry has been greatly lagging behind that of Europe due to the wide availability of landfills. The Landfill Directive set down by the European Union led to the Government of the United Kingdom imposing waste legislation including the landfill tax and Landfill Allowance Trading Scheme. This legislation is designed to reduce the release of greenhouse gases produced by landfills through the use of alternative methods of waste treatment. It is the UK Government's position that incineration will play an increasingly large role in the treatment of municipal waste and supply of energy in the UK.

In 2008, plans for potential incinerator locations exists for approximately 100 sites. These have been interactively mapped by UK NGO's.[56][57][58][59]

See the list of incinerators in the UK.

[edit] Small incinerator units
An example of a low capacity, mobile incinerator

Small scale incinerators exist for special purposes. For example, the small scale incinerators are aimed for hygienically safe destruction of medical waste in developing countries. Small incinerators can be quickly deployed to remote areas where an outbreak has occurred to dispose of infected animals quickly and without the risk of cross contamination. [citation needed]

[edit] In popular media

- There is an infamous scene in Toy Story 3, where the working of a moving-grate incinerator (and of a garbage shredder) is shown dramatically from the inside and almost kills the toys: Sheriff Woody and his friends, Buzz Lightyear, Jessie the Cowgirl, Bullseye the Horse, Hamm the Piggy Bank, Rex the Tyrannosaurus, Slinky Dog and the Potato Head couple.
- Incinerators make an appearance in SimCity 3000 in two varieties: a large, traditional combustion device that spews out a significant amount of air pollution, and a more modern device that converts the waste into energy to power the city with a bigger capacity to load the garbage, though still producing a lot of pollution.
- They also make an appearance in SimCity 4, but without the non-energy-from-waste variant.

[edit] See also

- Sustainable development portal
  - Cremation
  - Gasification
  - Incinerating toilet
  - Plasma Gasification
  - List of solid waste treatment technologies
  - Mobile incinerator
  - Pyrolysis
• Thermal treatment
• Waste Incineration Directive
• Waste management
• Waste-to-energy

[edit] References

6. ^ Wisconsin Department of Natural Resources NR 502.11.2 (a) and (d):
   Exemptions. The following woodburning facilities are exempt from licensing and all requirements of this section, although a burning permit from the department may still be required during certain times of the year in counties within a forest fire control area. These exempt facilities may not burn wet combustible rubbish, garbage, oily substances, asphalt, plastic or rubber products, unless these substances are exempt under s. NR 429.04.
   (a) Burning of trees, limbs, stumps, brush or weeds, except for yard waste, as a result of agricultural or silvicultural activities, if the burning is conducted on the property where the waste is generated.
   (d) Burning of yard waste and small quantities of dry combustible household rubbish, including paper, cardboard and clean untreated wood from a single family or household, on property where it is generated, unless prohibited by local ordinance.
11. ^ "HTT rotary kiln solid waste disposal system". HiTemp Technology.
19. Hogg, Dominic; Baddeley, Adam; Gibbs, Adrian; North, Jessica; Curry, Robin; Maguire, Cathy (January 2008). "Greenhouse Gas Balances of Waste Management Scenarios" (PDF). Eunomia.
27. Abbott, John; Coleman, Peter; Howlett, Lucy; Wheeler, Pat (October 2003). "Environmental and Health Risks Associated with the Use of Processed Incinerator Bottom Ash in Road Construction". BREWEB.
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42. van Steenis, Dick (31 January 2005). "Incinerators – are WMD's?". Country Doctor.
43. ^Nohamr.org[dead link]
47. ^ "Main EU Directives on Waste" (PDF). Friends of the Earth. Archived from the original on 7 October 2007.
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Kinetic modeling of pyrolysis of scrap tires

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ABSTRACT
The disposal of used tires is a major environmental problem. With increasing interest on recovery of wastes, pyrolysis is considered as an alternative process for recovering some of the value in scrap tires. An accurate kinetic model is required to predict product yields during thermal or catalytic pyrolysis of scrap tires. Pyrolysis products contain a variety of hydrocarbons over a wide boiling range. A common approach for kinetic modeling of such complex systems is lumping where each lump is defined by a boiling point range. Available experimental data for thermal and catalytic pyrolysis of scrap tires from the literature were used to evaluate two types of lumping models: discrete and continuous lumping models. The discrete model, the conversion of heavier to lighter lumps was described in terms of series and parallel first order reactions. In the continuous model, the normalized boiling point was used to describe the reactant mixture as a continuous mixture. An optimization procedure was implemented for estimation of the model parameters using experimental data reported in the literature. Model predictions with indicated that although the discrete model could reasonably predict the yields of different cuts in the products, predictions of the continuous model were very good, especially in thermal pyrolysis.

1. Introduction
Disposal of scrap tires is an environmental threat. It is estimated that 2.5 million tons per year are generated in the European Union, 2.5 million tons in North America and 1 million tons in Japan [1,2]. Landfills which were extensively used before are now banned in many countries. With increasing interest on recovery of wastes, alternative processes for tire recycling have been considered with the goal of recovering some of the value in the scrap tires. One of these processes is pyrolysis (heating to moderate temperatures in an oxygen-free atmosphere) where the volatile organics present in scrap tires are decomposed to gases and liquids which could be used as fuels or as a source for chemicals including benzene, toluene, xylene and limonene. The inorganic components, mainly steel and non-volatile carbon black, remain as a solid residue which is a suitable raw material for production of carbon black or active carbon. Process conditions can be optimized to maximize the yield of char, oil or hydrocarbon gases [3–8].

Several authors have studied the kinetics of tire pyrolysis by means of techniques based on thermal gravimetry (TG/DTG) [8–10]. Most of these studies have only considered the kinetics of rubber decomposition (devolatilization) without establishing the kinetic model for the formation of secondary products [11]. For the purposes of reactor design and process optimization, it is necessary to develop kinetic models that can accurately predict the product distributions under pyrolysis conditions. For feedstocks such as scrap tires containing complex hydrocarbon structures, due to the presence of a great variety of components, the development of such kinetic models is a challenging task. Because of great variety of structures in such mixtures, compound identification and quantification is very difficult, if not impossible. An alternative approach is to consider the mixture in terms of selected lumps that can be specified in terms of such properties as boiling range, molecular weight ranges, carbon numbers, solubility class fractions and other structural characteristics. Olazar et al. [11] have applied discrete lumping schemes for kinetic modeling of complex reactions for pyrolysis of waste tires involving series and parallel reactions based on carbon numbers. Continuous lumping [12–17] is an alternative approach that can be considered for kinetic modeling of thermal and catalytic processing of complex feedstocks.

In this work, experimental data reported in the literature [18,19] were used to develop appropriate kinetic models for thermal and catalytic pyrolysis of scrap tires using discrete and continuous lumping models. In the discrete lumping model, the boiling point distribution was used to describe the reactant and product mixtures in terms of selected boiling cuts (lumps) where conversion of heavier to lighter lumps was described in terms of
to the reactor to sweep the evolved gases through the reactor. The pyrolysis gases exiting the first reactor were passed to a secondary catalytic reactor containing about 100 g of zeolite. Operating temperatures of the catalytic reactor were 430, 500, 530 and 600 °C with nitrogen flow providing a gas residence time of approximately 30 s. Details of the equipments, sample preparation, and experimental procedures are given elsewhere [18].

The properties and distillation analysis of the tires used in the above studies are presented in Tables 1–4. Distillation cuts are

### Table 1

<table>
<thead>
<tr>
<th>Properties of scrap tires used for pyrolysis.</th>
<th>Thermal pyrolysis (Ref. [19])</th>
<th>Catalytic pyrolysis Ref. [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate analysis wt.%</td>
<td>Passenger car tire</td>
<td>Truck tire</td>
</tr>
<tr>
<td>Volatile content</td>
<td>58.2</td>
<td>66.1</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>21.3</td>
<td>27.5</td>
</tr>
<tr>
<td>Ash content</td>
<td>18.9</td>
<td>5</td>
</tr>
<tr>
<td>Moisture content</td>
<td>1.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

### Table 2

| Distillation analysis of scrap tires used in thermal pyrolysis (Ref. [19]). |
|-------------------------------|-------------------------------|
| Temperature, °C               | Cumulative wt.%               |
|                               | Passenger car tire | Truck tire |
| 343                           | IBP (initial boiling point)   | IBP         |
| 360                           | 5.56                         | 6.59        |
| 377                           | 11.20                        | 13.25       |
| 392                           | 16.91                        | 19.92       |
| 411                           | 22.65                        | 26.57       |
| 419.5                         | 25.53                        | 29.88       |
| 445                           | 34.15                        | 39.66       |
| 479                           | 45.47                        | 52.21       |
| 521.5                         | 59.05                        | 66.68       |

### Table 3

| Distillation analysis of scrap tires used in catalytic pyrolysis Ref. [18]. |
|-------------------------------|-------------------------------|
| Temperature, °C               | Cumulative wt.%               |
|                               | Passenger car tire |
| 343                           | IBP |
| 360                           | 7.21 |
| 377                           | 14.17 |
| 394                           | 20.90 |
| 402.5                         | 24.16 |
| 419.5                         | 30.52 |
| 436.5                         | 36.63 |
| 453.5                         | 42.49 |
| 470.5                         | 48.11 |

### Table 4

| Distillation cuts of scrap tires. |
|-------------------------------|-------------------------------|
| Distillation cuts wt.%         | Thermal pyrolysis | Catalytic pyrolysis |
|                               | Passenger car tire | Truck tire | Passenger car tire |
| 524 °C (cut A)                 | 40.2                     | 32.5        | 36.5                      |
| 343–524 °C (cut B)             | 59.8                     | 67.5        | 63.5                      |

### Table 5

| Boiling ranges of defined boiling cuts. |
|-------------------------------|-------------------------------|
| Distillation cut               | Boiling range                |
| A                              | 524 °C+                      |
| B                              | 343–524 °C                  |
| C                              | 177–343 °C                  |
| D                              | IBP–177 °C                  |
Table 6  
Overall product distribution from pyrolysis of scrap tires.

<table>
<thead>
<tr>
<th></th>
<th>Thermal pyrolysis (Ref. [18])</th>
<th>Catalytic pyrolysis (Ref. [17])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 550 °C</td>
<td>T = 800 °C</td>
</tr>
<tr>
<td></td>
<td>Passenger car tire</td>
<td>Truck tire</td>
</tr>
<tr>
<td>Gas</td>
<td>7.4</td>
<td>7.8</td>
</tr>
<tr>
<td>Oil</td>
<td>50.6</td>
<td>50.7</td>
</tr>
<tr>
<td>Solid</td>
<td>42</td>
<td>41.5</td>
</tr>
<tr>
<td>Coke</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 7  
Distillation analyses of products from pyrolysis of scrap tires.

<table>
<thead>
<tr>
<th>Cut, wt.%</th>
<th>Thermal pyrolysis (Ref. [18])</th>
<th>Catalytic pyrolysis (Ref. [17])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 550 °C</td>
<td>T = 800 °C</td>
</tr>
<tr>
<td></td>
<td>Passenger car tire</td>
<td>Truck tire</td>
</tr>
<tr>
<td>A</td>
<td>25.14</td>
<td>21.62</td>
</tr>
<tr>
<td>B</td>
<td>21.12</td>
<td>23.37</td>
</tr>
<tr>
<td>C</td>
<td>21.62</td>
<td>23.32</td>
</tr>
<tr>
<td>D</td>
<td>24.72</td>
<td>23.87</td>
</tr>
<tr>
<td>E</td>
<td>7.40</td>
<td>7.82</td>
</tr>
</tbody>
</table>

defined according to Table 5. Three kinds of materials were produced from pyrolysis including solids, liquids, and gas. The product distributions from the above studies are summarized in Tables 6 and 7 where cut E consists of the light hydrocarbon gases. Distillation cuts defined in Table 5 were used to describe the feed according to Table 4. The experimental product distributions given in Table 6 were also used along with the definition of each distillation cut to describe the pyrolysis products according to Table 7. Product distributions given in Table 7 were subsequently used in an optimization algorithm for determination of kinetic parameters.

3. Kinetic modeling

The kinetics of scrap tire pyrolysis was described in terms of discrete and continuous lumping models. In the discrete model, each lump was considered as a pseudo component. The main advantage of discrete models is that they result in a simple reaction network and require minimum computational effort. In the discrete model, the conversion of heavier lumps to lighter lumps was considered in terms of series and parallel reactions. In continuous models the reacting mixture is considered as a continuous lump where different properties such as boiling point or molecular weight can be used to describe the distribution of the components within the lump. Details of the kinetic models for discrete and continuous lumping models are given below.

3.1. Discrete lumping

Thermal pyrolysis data [19] were obtained from a semibatch reactor where a flow of nitrogen would continuously remove the gaseous products from the reactor. In the development of the discrete kinetic model it was assumed that the components in the lighter cuts C, D, and E resulting from pyrolysis of the heavier fractions do not further decompose as they are continuously removed from the reactor. The following first order reactions were considered:

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
B & \xrightarrow{k_2} C \\
B & \xrightarrow{k_3} D \\
B & \xrightarrow{k_4} E
\end{align*}
\]

The following equations give the concentration of each cut with reaction time:

\[
C_A = C_A e^{-k_1 t}
\]  
(2)

\[
C_B = \frac{k_1 C_A}{k - k_1} (e^{-k_1 t} - e^{-k t}) + C_B e^{-k t}
\]  
(3)

\[
C_C = \frac{k_3 C_A}{k - k_1} (1 - e^{-k_1 t}) - \frac{k_1 k_2 C_A}{k(k - k_1)} (1 - e^{-k t}) + \frac{k_3 C_B}{k} (1 - e^{-k t})
\]  
(4)

\[
C_D = \frac{k_3 C_A}{k - k_1} (1 - e^{-k_1 t}) - \frac{k_1 k_2 C_A}{k(k - k_1)} (1 - e^{-k t}) + \frac{k_3 C_B}{k} (1 - e^{-k t})
\]  
(5)

\[
C_E = \frac{k_3 C_A}{k - k_1} (1 - e^{-k_1 t}) - \frac{k_1 k_2 C_A}{k(k - k_1)} (1 - e^{-k t}) + \frac{k_3 C_B}{k} (1 - e^{-k t})
\]  
(6)

\[
k = k_2 + k_3 + k_4
\]  
(7)

where \(C_A\) and \(C_B\) are the mass concentration of lump \(J\) in the feed and products, respectively, and \(t\) is the reaction time.

Catalytic pyrolysis data [18] were obtained from two reactors connected in series. The first reactor containing no catalyst is similar to the reactor for thermal pyrolysis operating on a semibatch mode with continuous flow of nitrogen removing the gaseous pyrolysis products. The material leaving the first reactor would then flow over a bed of catalyst in the second reactor. The approach taken was to consider the reaction network given by Eq. (1) to account for thermal pyrolysis in the first reactor. The lighter cuts leaving the first reactor would subsequently decompose according to the following reactions:

\[
B \xrightarrow{k_1} C \xrightarrow{k_3} D \xrightarrow{k_4} E
\]  
(8)

It was assumed that the observed coke formation in the catalytic reactor was due to parallel reactions of the heavier cuts B and C entering the catalytic reactor. The governing equations for this
reactor based on plug flow assumption are given by:
\begin{align}
C_b(\tau) & = \frac{C_b(\tau - \Delta \tau)}{1 + (k_1 + k_2)\Delta \tau} \\
C_c(\tau) & = \frac{k_1 C_b(\tau) \Delta \tau + C_c(\tau - \Delta \tau)}{1 + (k_2 + k_3)\Delta \tau} \\
C_d(\tau) & = \frac{k_2 C_c(\tau) \Delta \tau + C_d(\tau - \Delta \tau)}{1 + (k_3)\Delta \tau} \\
C_e(\tau) & = k_3 \Delta \tau C_d(\tau) + C_e(\tau - \Delta \tau) \\
C_{Coke}(\tau) & = k_4 \Delta \tau C_d(\tau) + k_5 \Delta \tau C_c(\tau) + C_{Coke}(\tau - \Delta \tau)
\end{align}

where \( \tau \) is the residence time in the reactor.

All the rate constants were expressed in terms of an Arrhenius expression:
\[ k_i = A_i e^{-E_i/RT} \]

The optimum values of the Arrhenius parameters, for thermal and catalytic pyrolysis, were obtained by an optimization algorithm in which the objective function, Eq. (15) was formulated as the sum of the difference between predicted and experimental concentration of each lump in the products for all experiments. The optimization algorithm was a simple direct search algorithm by MATLAB.

\[ \text{objective function} = \sum_{i=1}^{M} \sum_{j=1}^{4} (C_{i,\text{experimental}} - C_{i,\text{model}})^2 \]

where \( C_{i,\text{experimental}} \) and \( C_{i,\text{predicted}} \) are the experimental and predicted concentration of lump \( i \) in the products, respectively, and \( M \) is the number of experimental runs.

### 3.2. Continuous lumping

The continuous lumping model used in this study was that proposed by Laxminarasimhan et al. [12] which is briefly described below. In this model the hydrocarbon components are represented by a single continuous mixture in terms of their true boiling point, TBP. The TBP curve is converted into a distribution function with the weight percent of any component as a function of the normalized boiling point, \( \theta \), which is defined as:
\[ \theta = \frac{TBP - TBP_h}{TBP_h - TBP_l} \]

where \( TBP_h \) and \( TBP_l \) represent the highest and the lowest boiling point of the components in the mixture, respectively. The proposed relationship [12] between the first order rate constants, \( k \), and \( \theta \) was of the following form:
\[ \frac{k}{k_{\text{max}}} = \theta^{1/\alpha} \]

where \( k_{\text{max}} \) which represents the rate constant for the component with the highest TBP, along with \( \alpha \) are model parameters. The mass balance for the component with reactivity of \( k \) is represented by:
\[ \frac{dC(k,t)}{dt} = -kC(k,t) + \int_{k}^{k_{\text{max}}} P(k,K)KC(K,t)D(K) \, dK \]

where \( C(k,t) \) is the concentration of the component with reactivity of \( k \) at time \( t \), \( P(k,K) \) is a yield distribution function for formation of the component with reactivity of \( k \) from cracking of component with reactivity of \( K \), and \( D(K) \) is the species type distribution function given by:
\[ D(k) = \frac{N_k}{k_{\text{max}}} k^{a_1} \]

where \( N \) is the total number of components in the mixture. The proposed form of the \( P(k,K) \) function [12] is as follows:
\[ P(k,K) = \frac{1}{2\sqrt{\pi}} \exp \left[ -\frac{(k/K)^{a_0} - 0.5}{a_1} \right]^2 - A + B \]

\[ A = \exp \left\{ -\frac{0.5}{a_1} \right\} \]

\[ B = \delta \left( \frac{1 - k}{K} \right) \]

\[ S_0 = \int_{0}^{K} \frac{1}{\sqrt{2\pi}} \exp \left[ -\frac{(k/K)^{a_0} - 0.5}{a_1} \right]^2 - A + B \, D(k) \, dk \]

Implementing the above model for thermal pyrolysis in a batch reactor would result in the following expression:
\[ \frac{C(k,t) - C(k,t - \delta t)}{\delta t} = -kC(k,t) \]

\[ + \int_{k}^{k_{\text{max}}} P(k,K)KC(K,t)D(K) \, dK \]

where \( C(k,t) \) is the concentration of the component with reactivity of \( k \) at time \( t \). The overall reaction time is divided in to 10 equal time steps, \( \delta t \). After each time step, Eq. (25) is first solved for the heaviest component, component \( N \), with corresponding reactivity, \( k_{\text{max}} \), which is only converted to lighter components during pyrolysis reactions:
\[ C(k_{\text{max}},t) = \frac{C(k_{\text{max}},t - \delta t)}{1 + k_{\text{max}} \delta t} \]

The calculation of the concentration of other components would then proceed from component \( N - 1 \) down. Trapezoidal rule was used for numerical integration and the value of \( N \) was chosen as 100 (i.e. 100 divisions on the \( \theta \) axis).

Because the reactor is semibatch and the products are withdrawn continuously, after each time step \( \delta t \), cuts \( C, D, \) and \( E \) are removed and their concentration in the remaining mixture is set to zero for the next time step. At the end of the reaction, the amounts of cuts \( C, D, \) and \( E \) removed from the reactor during previous time steps, are summed to give the overall yield of each of these lighter cuts.

The continuous model was extended for evaluation of experimental data from catalytic pyrolysis where an additional parallel reaction was included to account for coke formation as follows:

\[ \text{hydrocarbon compounds} \xrightarrow{k} \text{lower molecular weight hydrocarbon compounds} \]

\[ \text{hydrocarbon compounds} \xrightarrow{k_{\text{Coke}}} \text{Coke} \]
Furthermore, the following simple relationship was used to express the rate constant for coke formation reactions, \( k_{\text{Coke}} \), as a linear function of the normalized boiling point:

\[
k_{\text{Coke}} = \beta \theta + k_{\text{limin}}
\]

(28)

where \( \beta \) and \( k_{\text{limin}} \) are adjustable model parameters. Mass balance for cut \( i \) with corresponding reactivity \( k \) is given by:

\[
\frac{dC(k,t)}{dt} = -(k + k_{\text{Coke}})C(k,t) + \int_{k}^{k_{\text{max}}} P(k,K)KC(K,t)D(K)\,dK
\]

(29)

Implementing the catalytic pyrolysis in the plug flow design equation would result in the following expression:

\[
\frac{C(k,t) - C(k,\tau - \delta\tau)}{\delta\tau} = -(k + k_{\text{Coke}})C(k,\tau) + \int_{k}^{k_{\text{max}}} P(k,K)KC(K,t)D(K)\,dK
\]

(30)

where \( \tau \) is residence time of reactor. In a similar manner to that described for thermal pyrolysis, solution of Eq. (30) proceeds from the heaviest component with reactivity \( k_{\text{max}} \), Eq. (31), down to the lightest component.

\[
C(k_{\text{max}},\tau) = \frac{C(k_{\text{max}},\tau - \delta\tau)}{1 - (k_{\text{max}} + k_{\text{Coke}})\delta\tau}
\]

(31)

A direct search optimization method was used for the estimation of the model parameters where the objective function is given by:

\[
\text{objective function} = \sum_{i=1}^{5}(C_{\text{experimental}} - C_{\text{model}})^2
\]

(32)

The optimizations algorithm for estimation of the discrete and continuous model parameters consist of minimizing the objective functions as given by Eqs. (15) or (32). A pattern search tool program is used to minimize of the objective functions. Details of the algorithm are as follows:

1. Set iteration counter, \( i = 1 \).
2. Assign initial value for parameters.
3. Evaluate the product composition.
4. Evaluate objective function called OF.
5. Call pattern search tool a simulation of MATLAB to select other value for parameters.
6. \( i = i + 1 \).
7. Evaluate the product composition.
8. Evaluate objective function called OFN.
9. If OFN < OF, store parameter values as optimum and set OF = OFN.
10. Reduce the search region.
11. Go to step 5.
12. Stop.

**Table 8**

<table>
<thead>
<tr>
<th></th>
<th>Thermal pyrolysis</th>
<th>Catalytic pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_i, \text{h}^{-1} )</td>
<td>( E_i, \text{J/mol} )</td>
<td>( A_i, \text{h}^{-1} )</td>
</tr>
<tr>
<td>( k_1 )</td>
<td>1.21</td>
<td>5.90 ( \times 10^3 )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>8.57 ( \times 10^{-1} )</td>
<td>2.00 ( \times 10^3 )</td>
</tr>
<tr>
<td>( k_3 )</td>
<td>7.16 ( \times 10^{-1} )</td>
<td>0.00</td>
</tr>
<tr>
<td>( k_4 )</td>
<td>3.08 ( \times 10^{-1} )</td>
<td>2.91 ( \times 10^3 )</td>
</tr>
<tr>
<td>( k_5 )</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**4. Results and discussion**

The optimized Arrhenius parameters for the discrete model involving series and parallel reactions are presented in Table 8 for both thermal and catalytic pyrolysis. As indicated by Tables 6 and 7, the amount of hydrocarbon gases and lighter fractions produced from catalytic pyrolysis were significantly higher than those from thermal pyrolysis.

The optimized parameters of the discrete models were used to predict the weight percent of each boiling cut in the products.
from both thermal and catalytic pyrolysis. The predicted versus experimental weight percent of each cut in the products are presented in Figs. 1–6 which indicate that the proposed discrete models for both thermal and catalytic pyrolysis can reasonably predict the yields of various boiling cuts in the products. It should be noted that the catalytic pyrolysis was carried out in two reactors. The first reactor was operated thermally (without any catalyst) and the evolved gases from the first reactor were subsequently processed under catalytic pyrolysis conditions. The amount of solid reported in Table 6 is the residue in the first reactor and the feed to the second reactor did not contain any of the heavy cut A. Furthermore, the kinetic model for thermal pyrolysis was applied for the analysis of the first reactor.

The optimized model parameters for the continuous model are presented in Table 9 for each of the experiments reported. The optimized parameters from each experiment were used to predict the normalized TBP curve of the products. In the construction of the TBP curve for the feed, TBPL was taken as \( C_0 \), close to the normal boiling point of methane, and TBPH, in thermal and catalytic pyrolysis were taken as 700°C and 524°C, respectively. Furthermore, the distillation data reported in Tables 2 and 3 were used along with data extrapolation to the maximum boiling point for the construction of the TBP curve of the feed.

The normalized TBP curve for the feed and products from catalytic pyrolysis are presented in Fig. 7. The solid curve represents the TBP curve of the feed and the dashed lines represent the predicted TBP curves.

**Table 9**

Optimized parameters for the continuous model.

<table>
<thead>
<tr>
<th></th>
<th>Thermal pyrolysis</th>
<th>Catalytic pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Passenger car tire</td>
<td>Truck tire</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>( 2.13 \times 10^2 )</td>
<td>( 2.09 \times 10^2 )</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>( 1.22 \times 10^{-1} )</td>
<td>( 1.41 \times 10^{-1} )</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( 2.20 \times 10^2 )</td>
<td>( 2.10 \times 10^2 )</td>
</tr>
<tr>
<td>( \delta )</td>
<td>( 1.35 )</td>
<td>( 8.37 \times 10^{-1} )</td>
</tr>
<tr>
<td>( K_{max} )</td>
<td>( 1.11 )</td>
<td>( 1.02 )</td>
</tr>
<tr>
<td>( k_{min} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \beta )</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 6**

Optimized parameters for the continuous model.

<table>
<thead>
<tr>
<th></th>
<th>Thermal pyrolysis</th>
<th>Catalytic pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Passenger car tire</td>
<td>Truck tire</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( a_1 )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \delta )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( K_{max} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( k_{min} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \beta )</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
represent the curves for the products and are shifted to the left as lighter compounds are produced during the course of the reaction. The predicted normalized TBP curve of the products in the continuous model were used to determine the weight percent of each boiling cut in the products that are compared with experimental values in Figs. 8–13. Coke yields are expressed as concentration (g/cm³) in the product stream. With the exception of the yields of coke, agreements between experimental and predicted product yields were quite satisfactory. Experimental coke yields (Table 6) were somewhat questionable as they were nearly independent of reaction temperatures.

It should be pointed out that the predicted values for each experiment were obtained from the optimized parameters set for that specific experiment (Table 9). As indicated in Table 9, the optimized parameters were consistent from run to run for the case of thermal pyrolysis. For catalytic pyrolysis, however, there were variations in parameter estimates from one experiment to the other which could be related to the uncertainties in the reported experimental data.
5. Conclusions

From the experimental data reported in the literature, discrete and continuous lumping models were developed to predict the yields of different boiling point cuts in products of thermal and catalytic pyrolysis of scrap tires. The continuous model had only 5 adjustable parameters. For catalytic experiments where coke was also produced in small amounts, an additional 2 parameters were introduced to account for coke formation. Results indicated that although the discrete models could reasonably predict the weight percent of each cut in the products, the continuous model was superior.

References

PYROLYSIS AND COMBUSTION OF SCRAP TIRE


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Abstract

In this paper a literature review of both pyrolysis and combustion processes of scrap tires is presented. The work reports, the characteristics of materials, methods, effect of various process parameters, kinetic modelling applied to the pyrolysis and combustion of tires, characteristics of the products and emissions.

From the published works results that scrap tire rubber consists of about 60 wt.% volatile organics, 30 wt.% fixed carbon and 10 wt.% ash. Elemental analysis shows that tire rubber contains approximately 80 wt.% of C, 7 wt. of H, 0.4 wt.% of N, 1.5 wt.% of S, 3 wt.% of O and 8 wt.% of ash. Thermogravimetry analysis reveals that the pyrolysis of tire rubber at atmospheric pressure starts at a temperature around 250°C and finishes at a temperature of about 550°C. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. In general, by pyrolysing waste tire three fractions are obtained: solid residue (around 40 wt.%), liquid fraction (around 50 wt.%) and gas fraction (around 10 wt.%). The influence of the process conditions on the amount and characteristics of individual fractions was studied by the authors only partially. The general trend is an increase in yields of liquid and gas fractions as the temperature increases.

From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds containing a lot of aromatics. This liquid can be separated into light and higher fractions. The main components of pyrolysis gases reported by various authors are as: H2, H2S, CO, CO2, CH4, C2H4, C3H6 and other light hydrocarbons. The solid residue contains carbon black, and inorganic matter.

The results of kinetic modelling of scrap tire pyrolysis and combustion show large differences in the values of kinetic parameters obtained by different authors. As main pollutants from the combustion of waste tires are reported: SO2, NOx, CO and PAHs.

Key words: pyrolysis, combustion, waste tire, scrape rubber

1. Introduction

Only in the EU, USA and Japan around 6 million tones per year of scrap tires are produced. The huge quantity of waste tires presently produced in the world will certainly increase in the future as the associated automotive industries grow. The disposal of scrap tires becomes a serious environmental problem. The accumulation of discarded waste tires leads to environmental pollution. A large fraction of the scrap tires is simply dumped in sites where they represent hazards such as diseases and accidental fires. Rubbers are not biologically degradable, and this fact creates problems with their disposal. The impact of waste rubber on the environment can be minimized by recycling with material or energy recovery. However, during processing and moulding rubber materials are crosslinked, and therefore they cannot be simply again softened and remoulded by heating.

For many years landfill, was the main, practical means for dealing with the problem of waste tires. However, landfilling of tires is declining as a disposal option, since tires do not degrade easily in landfills, they are bulky, taking up valuable landfill space and preventing waste compaction. Open dumping may result in accidental fires with high pollution emissions. In the EU countries in 1990 the percentage of tires discarded in landfills was 62% of all produced waste tires in 2000 about 35% and in 2006 (as it results from the EU legislation) this percentage will decrease to 0%. Some countries including the Slovak Republic have already banned the use of discarded tires for landfilling.
A low percentage of scrap tires are recycled with material recovery and reused for second-quality rubber products (see methods of recycling in the next chapter). The problem is that waste tire generation rate is much more important than the amount of material required for these alternative uses. Because of their high calorific value, waste tires have been used as fuel in rotary cement kilns. However, this process can be acceptable from an environmental point of view only in the case of controlled combustion due to the toxic emissions produced during the tire combustion processes.

The high volatile carbon content and heating value (33-35 MJ/kg\(^1\)) make the scrap tires an excellent material for energy recovery. For this reason, both pyrolysis and combustion are currently receiving renewed attention. Pyrolysis offers an environmentally attractive method to decompose a wide range of wastes, including waste tires. In the pyrolysis process, the organic volatile matter of tires (around 60 wt\%) is decomposed to low molecular weight products, liquids or gases, which can be used as fuels or chemicals source. The non-volatile carbon black and the inorganic components (around 40 wt\%) remain as solid residues and can be recycled in other applications. Combustion of tires has been used also for generation of electrical energy. However, for minimizing emissions the conditions of the combustion process must be optimized.

In this paper a literature review of both pyrolysis and combustion processes of scrap tires is presented. All, the characteristics of materials, methods, effect of various process parameters, kinetic modelling applied to the pyrolysis and combustion of tires, characteristic of the products and emissions are reviewed.

2. Methods of recycling waste tires

The possible ways of recycling waste tires are as follows:

**Retreading and reusing of tires:**

In this process, the remaining tread is ground away from a tire to be remoulded and a new tread rubber strip is fused to the old carcass by vulcanization. The economic potential of the process is major advantage and the quality of the products is a disadvantage of retreading.

**Recycling by production of ground rubber for use in other applications:**

By mechanical or cryomechanical (cooling of rubber to a temperature ranging between –60 to –100°C) milling of tires the ground rubber of various sizes can be produced. These materials are used in other applications. For example: as component in asphalts, carpets, sport surfaces and children’s playgrounds. By the cryomechanical technology it is possible to obtain a very fine powder, which can be used as reinforcement in new rubber products. Retaining of some properties of rubber materials and the absence of direct air emissions are the major advantages, However, the high consumption of energy, liquid nitrogen in the cryomechanical process and the limited market for the products are the main disadvantages of the process.

**Reclaiming rubber raw materials:**

Many attempts have been made since 1910 for reclaiming of scrap rubber products. However, rubber products during the processing and moulding are crosslinked, and therefore they cannot be again softened or remoulded by heating. Reclaiming of scrap rubber products means the conversion of a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a two dimensional, soft, plastic, processable and vulcanizable polymer simulating many of the properties of virgin rubber. In this case reclaiming of scrap rubber is more complicated than reclaiming of thermoplastics. Various methods and processes for reclaiming waste rubber were developed. The most important of them are: the mechanical shearing process\(^2\), thermomechanical reclaiming\(^3\), reclaiming by use of various chemical agents\(^4\), microwave reclaiming\(^5\), ultrasonic reclaiming\(^6\), pyrolysis of waste rubber, reclaiming by renewable resource materials and reclaiming by biotechnological processes. A review of reclaiming waste rubber was published by Adhikari and Maiti\(^7\).

The main problem which reclaim producers face is the acceptability of reclaim by rubber industry as a raw material. This depends upon two major factors:
- The quality of reclaim products measured by their properties compared to the properties of virgin raw materials,
- The cost of reclaim compared to the cost of virgin rubber.

Recycling of scrape tires by reclaiming needs further research to obtain better quality of reclaim and a more cost-effective reclaiming process.
Pyrolysis:

Tire pyrolysis (thermal decomposition in an oxygen-free environment) is currently receiving renewed attention. Recycling of tires by pyrolysis offers an environmentally attractive method. The products of the tire pyrolysis process are: Solid char (30-40 wt%), liquid residue (40-60 wt%), and gases (5-20 wt%). (see chapter 6). The solid residue contains carbon black and the mineral matter initially present in the tire. This solid char may be used as reinforcement in the rubber industry, as activated carbon or as smokeless fuel. The liquid product consists of a very complex mixture of organic components. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock or a source of chemicals. The gaseous fraction is composed of non-condensable organics as, \( \text{H}_2, \text{H}_2\text{S}, \text{CO, CO}_2, \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6 \) etc. The gas fraction can be used as fuel in the pyrolyses process.

For growing economical efficiency and enlargement of markets for pyrolysis products, further research is needed in the field of process conditions, optimisation, and product characterisation and treatment.

Combustion

Incineration

Waste tires can be used directly as fuels in the incinerators. Due to their high heating value scrap tires are excellent materials for energy recovery. The use of tires directly as fuel in incinerators has the following advantages: Reduced power-production costs, maximum heat recovery, environmentally acceptable process. The disadvantages are: no material recovery, large capital investment, need for flue gas cleaning, \( \text{CO}_2 \) emission, high operating costs. Scrap tires are used also as fuel in cement kilns. More research works is needed for obtaining environmental impacts of this process, especially from the view of polycyclic aromatic hydrocarbon (PAH) emissions.

3. Characteristics and composition of scrap tires

Tires are composed of rubber compounds and textile or steel cords. Rubber compounds generally consist of elastomers (natural or synthetic rubber), carbon black, hydrocarbon oils, zinc oxide, sulphur and sulphur compounds and other chemicals such as stabilizers, anti-oxidants, anti-ozonants, etc. Table 1 shows the proximate analysis of scrap tires declared by various authors. The elemental analysis of waste tires found in the literature is presented in Table 2.

Tires consist of various types of rubber compounds with different compositions. Due analysing different rubber compounds, various authors report different results of elemental analysis, as shown in Table 2. For obtaining the average content of elements in tires each part of tire must be analysed.

Table 1: Proximate analysis of scrap tire rubber

<table>
<thead>
<tr>
<th>Author</th>
<th>Volatile (wt%)</th>
<th>Fixed carbon (wt%)</th>
<th>Moisture (wt%)</th>
<th>Ash (wt%)</th>
<th>Steel (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This paper</td>
<td>61.61</td>
<td>22.66</td>
<td>1.72</td>
<td>14.01</td>
<td>-</td>
</tr>
<tr>
<td>Rodrigues et al. [8]</td>
<td>58.8</td>
<td>27.7</td>
<td>-</td>
<td>3.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Jong Min Lee et al. [9]</td>
<td>67.3</td>
<td>28.5</td>
<td>0.5</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>Yu Min Chang et al. [10]</td>
<td>62.32</td>
<td>26.26</td>
<td>1.31</td>
<td>10.29</td>
<td>-</td>
</tr>
<tr>
<td>Gonazles et al. [11]</td>
<td>61.9</td>
<td>29.2</td>
<td>0.7</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td>Chen et al. [12]</td>
<td>93.73</td>
<td>-</td>
<td>0.54</td>
<td>5.3</td>
<td>-</td>
</tr>
<tr>
<td>Loresgoiti et al. [13]</td>
<td>59.3</td>
<td>27.6</td>
<td>-</td>
<td>3.5</td>
<td>9.6</td>
</tr>
<tr>
<td>Orr et al. [14]</td>
<td>68.7</td>
<td>23.3</td>
<td>0.4</td>
<td>7.6</td>
<td>-</td>
</tr>
<tr>
<td>Williams and Bottrill [15]</td>
<td>66.5</td>
<td>30.3</td>
<td>0.8</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>Atal and Levendis [16]</td>
<td>58.7</td>
<td>33.6</td>
<td>-</td>
<td>7.7</td>
<td>-</td>
</tr>
</tbody>
</table>

* - Based on reinforced tire with steel cords **- including fixed carbon
Table 2: Elemental analysis of scrap tire rubber

<table>
<thead>
<tr>
<th>Author</th>
<th>C (wt%)</th>
<th>H (wt%)</th>
<th>N (wt%)</th>
<th>S (wt%)</th>
<th>O (wt%)</th>
<th>Ashes (inorganic)</th>
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</thead>
<tbody>
<tr>
<td>This paper**</td>
<td>81.24</td>
<td>7.36</td>
<td>0.49</td>
<td>1.99</td>
<td>8.92</td>
<td>-</td>
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<tr>
<td>Rodrigues et al. [8] *</td>
<td>74.2</td>
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<td>0.3</td>
<td>1.5</td>
<td>4.7</td>
<td>13.5</td>
</tr>
<tr>
<td>Jong Min Lee et al. [9]</td>
<td>83.8</td>
<td>7.6</td>
<td>0.4</td>
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<td>3.7</td>
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<td>Yu Min Chang et al. [10]</td>
<td>74.4</td>
<td>6.96</td>
<td>0.21</td>
<td>1.6</td>
<td>5.02</td>
<td>10.21</td>
</tr>
<tr>
<td>Gonzales et al. [11]</td>
<td>86.7</td>
<td>8.1</td>
<td>0.4</td>
<td>1.4</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>Chen et al. [12]</td>
<td>81.16</td>
<td>7.22</td>
<td>0.47</td>
<td>1.64</td>
<td>2.07</td>
<td>7.44</td>
</tr>
<tr>
<td>Berrueco et al. [17]</td>
<td>88.5</td>
<td>6.6</td>
<td>0.4</td>
<td>1.6</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>Arion et al. [18]</td>
<td>73.8</td>
<td>5.3</td>
<td>0.44</td>
<td>1.71</td>
<td>0.11</td>
<td>17.8</td>
</tr>
<tr>
<td>Loresgoiti et al. [13] *</td>
<td>74.2</td>
<td>5.8</td>
<td>0.3</td>
<td>1.5</td>
<td>5.1</td>
<td>13.1</td>
</tr>
<tr>
<td>Williams and Bottrell [15]</td>
<td>85.8</td>
<td>8.0</td>
<td>0.4</td>
<td>1.0</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Lanoir et al. [19]</td>
<td>82.63</td>
<td>7.5</td>
<td>0.36</td>
<td>1.69</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Senneca et al. [20]</td>
<td>86.7</td>
<td>6.9</td>
<td>0.3</td>
<td>1.9</td>
<td>1.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Roy et al. [21]</td>
<td>86.6</td>
<td>8.1</td>
<td>0.5</td>
<td>0.8</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>Cunliffe and Williams [22]</td>
<td>86.4</td>
<td>8.0</td>
<td>0.5</td>
<td>1.7</td>
<td>3.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

* - Based on reinforced tire with steel cords  ** - Based on free of ash

4. Pyrolysis and combustion methods and equipment

4.1 Thermal decomposition of scrap tire

A number of experimental apparatus and laboratory scale plants for pyrolysis and combustion of scrap tires was presented by various authors. The behaviour of the thermal decomposition of rubber is generally studied by thermogravimetry analysis. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) are used as standard methods for studying thermal degradation of waste rubber samples. From the thermogravimetry analysis provided by various authors (for example: Leung and Wang [23], Yang et al. [24], Berrueco et al. [17]) results that more than one degradation temperature region during rubber pyrolysis is recorded.

Measurements provided in our laboratory sustain this fact (see Figure 2), however, it depends upon the composition of rubber compounds. The measured TG curves show two different mass loss regions over a temperature range of 250-550°C. Based on the evaporating characteristics of individual rubber components at the temperature ranging from 250 to 380°C, additives, oils and plasticizers are lost. At the temperature ranging 400-550 NR, SBR and BR are decomposed. A typical behaviour of sample mass loss during pyrolysis and char combustion measured by TG in our laboratory is shown in Figure 1.

The start and end temperatures of the pyrolysis process reported by various authors are compared with our measurements in Table 3.

Figure 1. A typical behaviour of mass loss of a scrap tire sample during pyrolysis and char combustion

Figure 2: Degradation temperature regions of scrap tire pyrolysis
Table 3: Start and end temperatures of pyrolysis of scrap tires

<table>
<thead>
<tr>
<th>Author</th>
<th>Start temperature of pyrolysis (°C)</th>
<th>End temperature of pyrolysis (°C)</th>
<th>Heating rate (°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This paper</td>
<td>250</td>
<td>550</td>
<td>5</td>
</tr>
<tr>
<td>Berrueco et al. [17]</td>
<td>200</td>
<td>500</td>
<td>15</td>
</tr>
<tr>
<td>Leung and Wang [23]</td>
<td>200</td>
<td>550</td>
<td>10</td>
</tr>
<tr>
<td>Chen et al. [12]</td>
<td>250</td>
<td>500</td>
<td>5</td>
</tr>
<tr>
<td>Senneca et al. [20]</td>
<td>200</td>
<td>450</td>
<td>5</td>
</tr>
<tr>
<td>Chen and Qian [25]</td>
<td>200</td>
<td>550</td>
<td>10</td>
</tr>
<tr>
<td>Conesa et al. [26]</td>
<td>250</td>
<td>500</td>
<td>5</td>
</tr>
</tbody>
</table>

4.2. Pyrolysis reactors

A number of studies has been done to investigate the pyrolysis of waste tires in both laboratory and industrial scale. Williams et al. [27] pyrolysed waste tires in a nitrogen atmosphere using a fixed-bed batch reactor at a temperature ranging from 300 to 720°C. This type reactor was also used by Berrueco et al. [17], Cunliffe and Williams [22] and others. Rodriguez et al. [8], Murena et al. [28] and Laresgoti et al. [13] employed for pyrolysing waste tires autoclaves. Kaminsky and Mennerich [29] pyrolysed waste tires in a fluidized bed reactor at a temperature ranging from 500 to 700°C. Roy et al. [21] used for the thermal decomposition of waste tires vacuum pyrolysis. Also plasma technology was employed by Tang and Huang [30] for pyrolysing waste tires.

4.3. Combustion technologies

Fluidized-bed combustion is one of the most appropriate processes for the treatment of waste tires. However, high operating costs and considerable feedstock preparation make this process relatively expensive. Fluidized-bed reactor for waste tire combustion was used by a number of authors [31] [32] [33].

Rotary kiln combustion enables combustion of tires in different sizes with relatively low operating costs. The requirement of a post-combustion chamber and particulate filtration, for controlling emissions are disadvantages of combustion in rotary kiln combustors. Waste tire utilisation in cement kilns brings economical benefits. However, environmental impact of this process calls for more research, especially from the view of emissions of polycyclic aromatic hydrocarbons. Carraso et al. [34], reports that energy recovery of scrap tires used by a cement kiln meets environmental standards. Giugliano et al. [35] determined the influence of shredded tires on the combustion process in a cement kiln.

Combustion in grate kilns is also used for waste tire combustion. The use of combustion in the grate kiln technology is justified economically, especially for large-sized plants.

5. Process conditions

5.1. Pyrolysis

Pyrolysis of waste tires leads to the production of a solid carbon residue (char), a condensable fraction (pyro-oil) and gases. The percentage of each phase is influenced by process conditions, such as temperature, pressure, heating rate, particle sizes, heat exchange system, catalysis etc. Williams et. al. [27] pyrolysing waste tire at a temperature between 300 and 720°C and heating rates 5 and 80°C min⁻¹ found that the maximum conversion of tire (see Table 4) occurred at a temperature of 600°C. Laresgoti et al. [13] found that the temperature does not significantly influence the char and gas yields over 500°C. However, temperature variations influence the gas composition. Rodriguez et. al. [8] pyrolysed cross-section samples (2-3 cm wide), representative of whole tire, at 300-700°C. They report that Tire-pyrolysis liquids are a complex mixture of hydrocarbons, which contains 0.4% of N and 1.2% of S. About 30% of such liquids is an easily distillable fraction with boiling points (70-210°C) and about 60% of liquids have boiling point range of 150-370°C.

Berrueco et al. [17], analysed the temperature influence on the global yields and the gas composition. They observed that the liquid yield increases with temperature from 400 to 500°C. However at temperatures higher than 500°C, this parameter remained almost constant. The gas yield showed a growth from 2.4 wt% at 400°C to 4.4 wt% at 700°C. A different distribution of scrap tire into yields (char, liquid and gas) was reported by Chang [10] (30-53 wt% gas, 28-42 wt% oil and 14-28 wt%...
char). Zabanioti and Stavropoulos\textsuperscript{[38]} pyrolysing scrap tire in a helium atmosphere in the temperature range 390-890°C and heating rates of 70-90°C min\textsuperscript{−1} found out that the char yield decreases with temperature reaching an asymptotic value of 20 wt.% of raw material, at about 830°C. The gas yield (condensable and non condensable) increases with temperature reaching an asymptotic value of 73 wt.% of raw material, at about 830°C. Barobboti et al.\textsuperscript{[39]} pyrolysed scrap tires in temperature range of 400-460°C, nitrogen flow rate of 0.2-0.5 m\textsuperscript{3}h\textsuperscript{−1} and particle size of 2-20 mm. As optimum conditions they present 430°C, 0.35 m\textsuperscript{3}h\textsuperscript{−1} and 10 mm, respectively. At this conditions the yield of char and liquid were 32.5 and 51.0 wt.%, respectively.

Lee et al.\textsuperscript{[9]} studied pyrolysis of waste tires with partial oxidation in a fluidized-bed reactor. They found that with increasing O\textsubscript{2} concentration, the gas yield increases from 22 to 43 % since CO\textsubscript{2} generation increases. Energy recovery is about 0.32 with O\textsubscript{2} concentrations up to, 6.5 %, thereafter, energy recovery is reduced to 0.24. Murena et al. carried out hydrogenative pyrolysis of waste tires for better saturation of the broken bonds. They declared that hydrogenative pyrolysis enables the use of the lowest reaction temperatures 390-430°C, the production of solid residue is minimized and the production of liquid phase is maximized. Roy et al.\textsuperscript{[40]} pyrolysed tire rubber at 500°C and a total pressure varying between 0.8 and 28.0 kPa. They found that the yields of gas, oil and pyrolytic carbon black changed little with the pyrolysis pressure. However, the oil composition and the carbon black characteristics depended considerably on the pyrolysis pressure.

The influence of some process conditions on char, liquid and gas yields presented by different authors is shown in Table 4.

Table 4: Influence of some process conditions on char, liquid and gas yields presented by different authors

<table>
<thead>
<tr>
<th>Author</th>
<th>Temperature (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Pressure kPa</th>
<th>Sample sizes</th>
<th>Solid (wt.%)</th>
<th>Liquid (wt.%)</th>
<th>Gas (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams et al.\textsuperscript{[27]}</td>
<td>300-720</td>
<td>5-50</td>
<td>101</td>
<td>-</td>
<td>35</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>Laresgoiti et al.\textsuperscript{[37]}</td>
<td>400-700</td>
<td>15</td>
<td>101</td>
<td>20-30 mm</td>
<td>43-53</td>
<td>28-40</td>
<td>7-9</td>
</tr>
<tr>
<td>Berrueco et al.\textsuperscript{[17]}</td>
<td>400-700</td>
<td>15</td>
<td>101</td>
<td>20 mm</td>
<td>47-63</td>
<td>30-43</td>
<td>2.4-4.4</td>
</tr>
<tr>
<td>González et al.\textsuperscript{[11]}</td>
<td>350-700</td>
<td>5-20</td>
<td>101</td>
<td>0.2-1.6 mm</td>
<td>37-40</td>
<td>55</td>
<td>4-11</td>
</tr>
<tr>
<td>Pakdel et al.\textsuperscript{[41]}</td>
<td>440-570</td>
<td>1.3-28</td>
<td>3.8 cm\textsuperscript{3}</td>
<td>30.6-53.4</td>
<td>50-60</td>
<td>3.2-11.9</td>
<td></td>
</tr>
<tr>
<td>Barbooti et al.\textsuperscript{[39]}</td>
<td>400-460</td>
<td>-</td>
<td>101</td>
<td>2-20 mm</td>
<td>32.5</td>
<td>51.0</td>
<td>16.6</td>
</tr>
<tr>
<td>Chang\textsuperscript{[10]}</td>
<td>200-600</td>
<td>101</td>
<td>20 mg</td>
<td>14-28</td>
<td>28-42</td>
<td>30-53</td>
<td></td>
</tr>
<tr>
<td>Cunliffe and Williams\textsuperscript{[22]}</td>
<td>450-60</td>
<td>-</td>
<td>101</td>
<td>-</td>
<td>37-38</td>
<td>53-58</td>
<td>5-9</td>
</tr>
<tr>
<td>Roy et al.\textsuperscript{[40]}</td>
<td>25-500</td>
<td>15</td>
<td>0.8-28</td>
<td>-</td>
<td>35-36</td>
<td>62</td>
<td>1-3</td>
</tr>
</tbody>
</table>

5.2. Combustion

Both combustion behaviour and emissions from the combustion process of waste tires are influenced by process conditions such as temperature, oxygen enrichment, particle sizes, reactor type, etc. Using thermogravimetry analysis Atal and Levendis\textsuperscript{[16]} observed that tire particles experienced an intense primary volatile combustion phase, followed by a phase of simultaneous secondary volatile combustion of less intensity and char combustion. They also found out that char burnout times were considerably shorter for tire particles than for coal. Mastral et al.\textsuperscript{[42]} using fluidized-bed combustion reported that both gas superficial velocity and partial pressure of oxygen exert influence upon the overall fixed carbon combustion efficiency. The efficiency increases slightly with the oxygen concentration and significantly if the gas superficial velocity decreases. They also burned waste tires in an atmospheric fluidized bed combustion plant with an airflow of 860 'l/h and 20% excess oxygen at three’ different combustion temperatures, (750, 850, and 950°C). They observed that the introduction of tires in the feeder increases the total PAH amount emitted with respect to coal emissions, with minimal variations at the combustion temperatures studied by them: thus, the higher the temperature, the lower the amount of emitted polycyclic aromatic hydrocarbons. Courtemanche et al.\textsuperscript{[43]} burned coal and waste tire crumb in an electrically heated drop-tube furnace at high particle heating rates (10\textsuperscript{4}-10\textsuperscript{5} K s\textsuperscript{−1}) and elevated gas temperatures (1300–1600 K). They found that combustion of coal generated four times more NO\textsubscript{x} than combustion of tire crumb, in proportion to their nitrogen content.
A complex study of process conditions such as temperature, O₂ concentration and particle sizes on combustion behaviour and pollutant emissions was not found in the literature. For disposal of waste tires by combustion with minimum environmental impact also for the prevention of fire hazards in tire landfills, more research in this area is required.

6. Characteristics and composition of the pyrolysis products

Use of pyrolysis as a method for recycling waste tire depends on the market for pyrolysis products. For this reason, characterization of pyrolysis products and possibilities of their application in other processes is very important. At present time, the main application for solid char is its use as active carbon, as reinforcement in rubber industry and as smokeless fuel. The liquid product is used as a fuel, or a source of chemicals, and the gas fraction as a fuel in the pyrolyses process.

6.1. Solid residue

The solid residue contains carbon black and the mineral matter initially present in the tire. Several studies have reported the production of chars and active carbon from waste tires [44], [45]. These active carbons have been used to adsorb phenols, basic dyes and metals, phenols, butane and natural gas. Active carbon from solid product of pyrolysis process is produced by activation with an activating gas at 800-1000°C. Carbon characteristics (especially specific area) are greatly influenced by the degree of the activation also by nature of activating agent (steam or CO₂) and process temperature. Based on the current technology and literature results tire char activation below 700°C looks impractical [44]. The particle size of the tire rubber was found to have influence on the porosity of the resultant carbon generated from steam activation [44].

Elemental analysis carried out by Zabaniotou et. al. [45] shows that pyrolysis char contains 71 wt.% of C, 13.3% wt. of O, 5.4 wt.% of Fe, 2.8 wt.% of S, 2.3 wt.% of Zn, 1.3 wt.% of Ca, and 0.3 wt.% of Al.

6.2. Pyrolysis liquid product

The liquid phase is the most important product of tire pyrolysis process. There are several papers in the literature devoted to the study of the characteristics of pyrolysis liquid products [8] [13] [15] [46] [47]. Gas chromatography/Mass spectroscopy (GC/MS) is the most often method used not only for analysing pyrolysis liquid product, but also for analysing the gas yield and products of char combustion. Laresgoiti et al. [13], present a detailed characterization of the all pyrolysis liquids obtained at 300, 400, 500, 600, and 700°C. All, the GC/MS analysis, elemental analysis, gross calorific values and distillation data were studied. They report that tire derived liquids are a complex mixture of C₆-C₂₄ organic compounds, containing a lot of aromatics (53.4–74.8%), some nitrogenated (2.47–3.5%) and some oxygenated compounds (2.29–4.85%). Their GCV (42 MJ kg⁻¹) is even higher than that specified for commercial heating oils, but the sulphur content (1–1.4%) is close to or slightly over the limit value. Significant quantities of valuable light hydrocarbons such as benzene, toluene, xylene, limonene, etc. were obtained. The concentration of these compounds increases with temperature up to 500°C and then decreases. There is also an important portion of polycyclic aromatics, such as naphthalenes, phenanthrenes, fluorenes, diphenyls, etc.; their concentration as well as that of total aromatics increase significantly with temperature.

Pakdel et. al. [41] reports that vacuum pyrolysis of used tires produces approximately 55 wt.% of pyrolysis oil. This oil typically contains 20-25 wt.% of naphtha fraction with a boiling point lower than 200°C. The naphtha fraction typically contains 20-25 wt. % dl- limonene. Williams and Taylor [48], found that the pyrolytic oil had molecular weight range from a nominal 50 to 1200.

6.3. Pyrolysis gases

The yield of the gas fraction obtained in different experimental systems shows important variations. For example: Berrueco et. al. [17] obtained the gas yield 2.4-4.4 wt.%, but Chang [10] 30-53 wt.%. Laresgoiti et al. [17], using an autoclave in a nitrogen atmosphere at temperatures between 400 and 700 C, found that the pyrolyzed gases consisted of CO, CO₂, H₂S and hydrocarbons such as CH₄, C₂H₆, C₃H₆ and C₄H₈, and their unsaturated derivatives. Berrueco et. al. [17] analysing pyrolysis gases by gas chromatography, found that the main gases produced by the pyrolysis process are H₂, CO, CO₂ and hydrocarbons: CH₄, C₂H₄, C₃H₆ and C₄H₈. Roy et al. [49] obtained gases by vacuum pyrolysis, mainly composed of H₂, CO, CO₂ and a few hydrocarbon gases. In general, main components of
pyrolysis gases was reported by various authors as: H\textsubscript{2}, H\textsubscript{2}S, CO, CO\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6} and other light hydrocarbons.

7. Pyrolysis and combustion kinetics

Several authors presented kinetic models for pyrolysis scrap tires\textsuperscript{[12][20][23][49][50]}. In general, these models are based on thermogravimetry data and Arrhenius equation and divide the decomposition of tires into two or more steps. The first order reaction based on the Arrhenius theory is commonly assumed by researchers in the kinetic analysis of data for tire decomposition:

\[
k = A \exp\left(\frac{-E}{RT}\right)
\]

In this equation \(k\) is the rate constant; \(A\) is the pre-exponential factor, \(E\) is the activation energy, \(R\) and \(T\) are the universal gas constant and absolute temperature, respectively. The rate of decomposition may be expressed by:

\[
\frac{d\alpha}{dt} = k(1 - \alpha)^n
\]

where \(\alpha\) is the fraction of reactant decomposed at time \(t\) and \(n\) is the order of reaction.

Some models published in the literature, which are the modification of the above given equations for tire pyrolysis under various conditions, together with experimental conditions and obtained kinetic parameters are given below:

**Leung and Wang\textsuperscript{[23]}**

Model:

\[
\frac{d\alpha_T}{dt} = \sum_{i=1}^{3} \frac{d\alpha_i}{dt} = \sum_{i=1}^{3} A_i \exp\left(\frac{-E_i}{RT}\right)(1 - \alpha)
\]

where

- \(\alpha_T\) (min\textsuperscript{-1}) - normalized mass loss rate,
- \(A\) - pre-exponential factor,
- \(E\) - activation energy,
- \(R\) - ideal gas constant,
- \(T\) - absolute temperature,
- \(t\) - time, index (i=1.2,3) - reaction.

**Experimental conditions:**
Temperature: 20-600°C, particle size: 0.355- 0.425 mm, heating rate: 10-60°C/min used mobile gas: N\textsubscript{2}. The kinetic parameters obtained are shown in the Table 5.

Table 5: Kinetic parameters obtained by Leung and Wang\textsuperscript{[23]}

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Activation energy, (E) (kJ/mol)</th>
<th>pre- exponential factor, (A)</th>
<th>Reaction order, (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower temperature</td>
<td>Higher temperature</td>
<td>Lower temperature</td>
</tr>
<tr>
<td>10</td>
<td>164.5</td>
<td>136.1</td>
<td>6.29 \times 10\textsuperscript{13}</td>
</tr>
<tr>
<td>30</td>
<td>180.9</td>
<td>133.6</td>
<td>1.32 \times 10\textsuperscript{14}</td>
</tr>
<tr>
<td>45</td>
<td>203.4</td>
<td>107.0</td>
<td>7.58 \times 10\textsuperscript{15}</td>
</tr>
<tr>
<td>60</td>
<td>218.7</td>
<td>99.1</td>
<td>1.13 \times 10\textsuperscript{17}</td>
</tr>
</tbody>
</table>

**Yang et. al\textsuperscript{[51]}**

Model:

\[
\frac{d\alpha}{dt} = A_i \exp\left(\frac{-E_i}{RT}\right)(1 - \alpha)^n
\]

where
a - mass fraction of the volatiles emitted at time \( t \), \( A \) - pre-exponential factor; \( E \) - activation energy; \( R \) - ideal gas constant \( T \) - absolute temperature, \( t \) - time index (i=1,2,3)- reaction.

**Experimental conditions:**
Temperature: 30-550°C, sample weight: 4-8 mg, heating rate: 1- 40°C/min. used mobile gas: \( \text{N}_2 \). The kinetic parameters obtained are shown in the Table 6.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Activation energy, ( E ) (kJ/mol)</th>
<th>pre- exponential factor, ( A )</th>
<th>Reaction order, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>SBR</td>
<td>NR</td>
<td>SBR</td>
</tr>
<tr>
<td>1</td>
<td>207</td>
<td>152</td>
<td>3.89 ( \times 10^{16} )</td>
</tr>
<tr>
<td>10</td>
<td>207</td>
<td>152</td>
<td>2.36 ( \times 10^{16} )</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
<td>139</td>
<td>-</td>
</tr>
</tbody>
</table>

Williams and Besler\(^{52}\):
Model:
\[
\frac{dw}{dt} = -k\left(W_0 - W_f\right) \tag{5}
\]
where
\( W \) is the weight of sample at time \( t \); \( W_0 \) is the weight of residue at the end of the reaction, and \( k \) represents the rate constant defined by Arrhenius equation

**Experimental conditions:**
Temperature: 720°C, Sample sizes: <1 mm, heating rate: 5°C/min. used mobile gas: \( \text{N}_2 \)
The kinetic parameters obtained are shown in the Table 7.

<table>
<thead>
<tr>
<th>Heating rate</th>
<th>Activation energy, ( E ) (kJ/mol)</th>
<th>pre- exponential factor, ( A )</th>
<th>Reaction order, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>Sample B</td>
<td>Sample A</td>
<td>Sample B</td>
</tr>
<tr>
<td>5</td>
<td>142.7</td>
<td>120.8</td>
<td>2.1 ( \times 10^{8} )</td>
</tr>
<tr>
<td>20</td>
<td>90.8</td>
<td>128.3, 137.7</td>
<td>2.6 ( \times 10^{8} )</td>
</tr>
<tr>
<td>40</td>
<td>70.4</td>
<td>66.1, 136.2</td>
<td>1.3 ( \times 10^{8} )</td>
</tr>
<tr>
<td>80</td>
<td>66.4</td>
<td>55.6</td>
<td>1.1 ( \times 10^{8} )</td>
</tr>
</tbody>
</table>

A relatively small number of works devoted to the kinetics of combustion was found. Conesa et al.\(^{50}\) modelled the combustion of tire rubber by dividing the decomposition process into pyrolysis and combustion steps. The pyrolysis step model assumes three independent organic fractions that are decomposed. For pyrolysis reactions the kinetic equation for the total mass loss is presented as:
\[
\frac{dw}{dt} = \sum k_0 \exp\left(\frac{-E_i}{RT}\right)w_0^n \tag{6}
\]
where \( w \) - mass fraction index \( i = 1,2,3 \) represents the fraction decomposed, \( k_i \) - pre-exponential factor; \( E \) - activation energy; \( R \) - ideal gas constant \( T \) - absolute temperature and \( t \) - time. For fourth carbonaceous fraction an n-order reaction, with dependence on the oxygen partial pressure is used:
\[
\frac{dw_i}{dt} = \sum k_{04} \exp\left(\frac{-E_i}{RT}\right)\frac{w_i^n}{p_{O_2}^m} \tag{7}
\]
The following parameters for this model were estimated by authors \[50\].

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_0)</td>
<td>(2.84 \times 10^8)</td>
<td>(2.64 \times 10^{14})</td>
<td>(4.15 \times 10^{14})</td>
<td>(3.79 \times 10^8)</td>
</tr>
<tr>
<td>(E) (kJ/mol)</td>
<td>83.6</td>
<td>245.6</td>
<td>201.7</td>
<td>223.2</td>
</tr>
<tr>
<td>(n)</td>
<td>2.445</td>
<td>3.905</td>
<td>1.456</td>
<td>0.692</td>
</tr>
<tr>
<td>(m)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.886</td>
</tr>
</tbody>
</table>

Leung and Wang\[23\] using the model described above (equation 3) for tire rubber char combustion determined following kinetic parameters:

<table>
<thead>
<tr>
<th>Sample size mesh</th>
<th>Temperature (°C)</th>
<th>Activation energy, (E) (kJ/mol)</th>
<th>pre-exponential factor, (A)</th>
<th>Reaction order, (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-16</td>
<td>45-610</td>
<td>145.4</td>
<td>(2.89 \times 10^8)</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>450-620</td>
<td>148.1</td>
<td>(3.84 \times 10^9)</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>450-620</td>
<td>161.2</td>
<td>(3.93 \times 10^9)</td>
<td>1</td>
</tr>
</tbody>
</table>

8. Emissions from the combustion of tires

For disposal of waste tires by combustion and energy recovery the characteristics of emissions are the main factor, which must be studied. The amount of toxic emissions like \(\text{SO}_2\), \(\text{NO}_x\), \(\text{CO}\) and PAHs is affected by the process conditions and the technology used. Though emission characteristics of waste tire combustion have been studied by a number of authors, more research in this field is required.

Levendis et al.\[53\] comparing combustion of coal and waste rubber found that \(\text{NO}_x\) emissions from tires is 3-4 times lower than those from coal, emissions of \(\text{SO}_2\) where comparable. CO and PAH emission yields from tire derived fuel were much higher than those from coal, but the relative amounts of individual PAH components were remarkable similar in the combustion effluent of the two fuels. Mastral, et al.\[42\] report that thus, the higher the temperature, the lower amount of emitted polycyclic aromatic hydrocarbons measured by fluidized-bed combustion of waste tires. Lemieux et al.\[54\] reviewed Emissions of organic air toxics from open burning of various types of wastes. From this review results that PAH emissions were highest when combustion of polymers was taking place. For this reason a post-combustion chamber and particulate filtration, for controlling emissions from the tire combustion is required. In addition, the conditions of the combustion process must be optimized.

9. Conclusion

In this paper the current status of research devoted to the pyrolysis and combustion of scrap tires is presented. From the published works results that scrap tire rubber consists of about 60 wt.% volatile organics, 30 wt.% fixed carbon and 10 wt. % ash. Elemental analysis shows that the tire rubber contains approximately 80 wt.% C, 7 wt. H, 0.4 wt.% N, 1.5 wt.% S, 3 wt.% O and 8 wt.% ash. From thermogravimetry analysis provided by various authors results that pyrolysis of tire rubber at atmospheric pressure starts at a temperature of about 250°C and finishes at a temperature of around 550°C. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. This fact also results from the thermogravimetric analysis made in our laboratory.

Several works have been devoted to the pyrolysis yield and their characteristics. However, pyrolysis yields and characteristics of the products obtained depend not only on the character of feed and operating conditions, but also on the specific characteristics of the system used. Therefore, results from different authors are different and difficult to compare. In general, three fractions are obtained. The solid residue (about 40 wt.%), liquid fraction (about 50 wt.%) and gas fraction (about 10 wt.%). Influence of the process conditions on the amount and characteristics of individual fractions was studied by the authors only partially. The general trend is an increase of yields to liquid and gas as the temperature increases.

From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds with a lot of aromatics. This liquid can be separated to light and higher fractions. The main components of pyrolysis gases reported by various authors are: \(\text{H}_2\), \(\text{H}_2\text{S}\), \(\text{CO}\), \(\text{CO}_2\), \(\text{CH}_4\), \(\text{C}_2\text{H}_4\), \(\text{C}_2\text{H}_6\) and other light hydrocarbons.

The results of kinetic modelling of scrap tire pyrolysis and combustion show large differences in the values of kinetic parameters obtained by different authors. However, these models generated good correlation between model and experimental data in the same work.
As main pollutants from the combustion of waste tires are reported: SO₂, NOₓ, CO and PAHs. However, emissions from both the direct combustion of the waste tire and the combustion of tire pyrolysis products need more studies.

There is a significant demand for optimization of pyrolysis process conditions, more intense study of the influence of various factors on the pyrolysis products yields and characteristics, and also influence of operating parameters on energy recovery in a pyrolysis plant.

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References
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Pyrolysis offers an environmentally and economically attractive method of waste tires transformation into useful products and energy. Pyrolysis also represents one of the most important steps during the waste tire gasification. In a pyrolysis reactor, solid fuel is decomposed into pyrolysis products obtained usually in all three phases: solid char, liquid oil, and gases. Distribution of material into the pyrolysis yields and composition of individual fractions depends not only on the composition of the feed material, but also on the pyrolysis technique and process conditions applied. Temperature, heating rate, hydrodynamic conditions; catalyst and particle size are the main factors affecting the amount and composition of the pyrolysis yields.

A Laboratory Set-Up with a Flow Reactor for Waste Tire Pyrolysis

Pyrolysis units enable observation of the influence of different factors on the quality and amount of pyrolysis products. The number of factors, influence of which can be studied is dependent on the type of the technology used. Generally, flow reactors enable observation of more parameters than batch reactors.

Different types of pyrolytic reactors have been presented in the literature. Batch reactors [1, 2] and fluidized bed reactors [3, 4] are the most often studied types of pyrolytic reactors. Batch reactors usually do not provide good heat or mass transfer conditions. Another disadvantage of this type of reactors is that they do not enable continual separation of volatile and solid phases, which results into worse quality of pyrolytic carbon black. Also the number of parameters that can be studied in batch reactors is quite limited. Fluidized bed reactors provide good heat and mass transfer conditions; however, continual separation of solid phase from the volatiles is still a problem. An alternative flow reactor for pyrolysing waste tires is presented in this work. A screw operated by an electric stepping motor under nitrogen flow and a temperature controlled tube furnace enable studying the influence of a number of parameters. Other advantages of this type of reactor are the very good heat and mass transfer conditions and the continuous removal of pyrolysis products, which result in better quality of the pyrolysis products.

Experimental set up

The experimental set up shown in Figure 1 aims at the maximization of the possibility of studying the influence of different factors on the pyrolysis process. The particles of solid material are fed into the system using a feeder. Then, the particles are passed through the reactor using a screw. The residence time of the particles in the reactor is controlled by the frequency cycle of the screw. The screw is moved by an electric stepping motor controlled by a controller and a PC.

The reactor (Fig. 2) is heated electrically by a tube furnace. The reactor temperature is controlled by a PID controller and software. Inert atmosphere in the reactor is achieved by nitrogen flowing through the reactor in the same direction as the solid material. The flow of nitrogen is measured by a flowmeter. Passing through the reactor, rubber particles are decomposed. A simple model of tire rubber decomposition could be based on the following scheme:

Tire rubber → Volatiles + Char
Secondary decomposition of high molecular compounds to compounds with low molecular weight follows.

Volatiles → Tars + Gases
Tars → Gases

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The volatiles are removed from the reactor at high temperature and they are led to a condenser. The solid residue is removed from the end of the reactor and collected in a jar. For laboratory tests, tire rubber without steel cords was used; however, when using tires with steel cords, steel material can be very easily removed from pyrolytic carbon black using a magnetic separator. Textile cords are decomposed under the same conditions as tire rubber. Samples of solid residue were taken for its characterization by thermogravimetric measurements, specific surface area, porosity and pore size distribution measurements, and ASTM standard tests for carbon black. The details of solid product characterization can be found in our previous work [5]. The volatile fraction, after partial condensation, was further cooled in a series of scrubber type coolers and then passed through an adsorber. Samples of gases were taken for measurement of their composition in a GC/MS. The liquid product was collected from the condensers for further characterization.

Ranges of operational parameters
Pyrolysis temperature, pressure, residence time of solid and gas phases, particle sizes, and inert gas flow rate are the most important operational parameters in tire pyrolysis. From the TG analysis of tire material results that the thermal decomposition of rubber vulcanizates starts at a temperature from the range of 200 and 250 °C and ends at temperatures between 500 and 550 °C (Fig. 3) [6, 7, 8]. At higher temperatures the residence time of the tire in the reactor can be reduced. At the same time, higher temperatures cause better decomposition of the pore structure of pyrolytic carbon black, which is an advantage for their use as reinforcement or adsorbents. However, pyrolysis at higher temperatures results in an increase of the gas to liquid ratio, energy consumption and requirement for higher quality of equipment materials. Usually, the pyrolysis temperature is chosen from the range of 550 to 700 °C. Effect of temperature on the conversion of waste tire pyrolysis was observed using the laboratory unit described above. As it is shown in Figure 4, at temperatures under 500 °C, tire pyrolysis is not completed. However, at temperatures above 500 °C, the residence time of 5 minutes was enough for the tire pyrolysis completion. The time needed for total conversion of the material in the reactor depends on the reactor temperature, particle sizes and heat and mass transfer conditions in the reactor.
The advantage of a screw type flow reactor is in its very good heat and mass transfer conditions. Tire particles with average size of 3 mm were pyrolyzed under isothermal conditions in the system described above. The residence time of only 3 min was set. Different pyrolysis temperatures, from 500 °C to 800 °C, were used. The obtained solid products were tested by thermogravimetric analysis using a simultaneous NETZCH STA 409 PC TG/DSC analyzer for the determination of the unreleased amount of volatiles. The reaction conversion was estimated by a comparison of TG curves of the solid product and used waste rubber. Figure 5 shows TG curves of pyrolytic chars obtained by tire pyrolysis at different temperatures. At 500 °C and residence time of 3 minutes (curve 1), the reaction was not finished. The reaction conversion in the pyrolytic reactor was under these conditions 93.5 %. However, at 600 °C, the reaction conversion was 98 % and at 800 °C it was 99.5 %. At the temperature of 550 °C, the conversion of 100 % was achieved in the residence time of only 5 min. Figure 6 shows the TG curve of the solid product produced under the mentioned conditions. The developed pyrolytic unit enables working at pressures of up to 100 kPa above the atmospheric. Usually the system works at a pressure slightly above the atmospheric to insure inert atmosphere in the reactor. The flow rate of inert gas influences the age of volatiles in the system. High flow rate of inert gas causes quick removal of the volatiles from the system. As a result, the time for their secondary pyrolysis is shorter. Based on these facts, high flow rates of inert gas result in higher liquid product to gas product ratio. But on the other side, high flow rates of inert gas cause also quick removal of volatiles from the condensation system. By increasing the flow rate of inert gas, the requirements for condensation system increased. Another disadvantage of high flow rate of inert gas is the high cost of the process and low energy value of the produced gas. As the optimal flow rate of inert gas, a value obtained at a pressure slightly above the atmospheric was selected. Particle size is another important parameter that can influence the amount and quality of pyrolytic products. By increasing the particle size, the time needed for the reaction to be completed increased. However, low values of \( \frac{d_P}{d_R} \) (\( d_P \) is equivalent diameter of particle and \( d_R \) is inner diameter of reactor) cause the residence time distribution deformation. Because of low values of heat transfer properties (thermal conductivity around 0.2 Wm\(^{-1}\)K\(^{-1}\), thermal diffusivity around 1.10\(^{-7}\) m\(^2\)/s [9]), rubber vulcanizates are classified as materials with low capability of heat transfer. Therefore, the slowest process in tire pyrolysis is the transfer of heat and the rate of decomposition reactions is limited by heat transfer. The system enables the use of particles with sizes from 0.1 to 10 mm. As the optimal value of \( \frac{d_P}{d_R} \), the value of 0.25 was estimated.

**Fields of application**

The laboratory pyrolysis unit developed in the frame of our research project enables the realization of a number of different applications directly or indirectly after the treatment of the pyrolysis products. The

![Figure 1: Effect of temperature on the conversion of waste tire. Residence time: 5 min., equivalent diameter: 3 mm](image1)

![Figure 3: TG curves of solid products obtained by pyrolysis of scrap tire at different temperatures: residence time: 3 min, 1- 500 °C, 2-600 °C, 3- 700 °C, 4- 800 °C](image3)

![Figure 5: TG curve of the solid product produced at 550 °C and residence time of 5 min](image5)
most important areas of its implementation are:

- Amount and composition of all pyrolysis products
- Influence of process conditions on the amount and quality of pyrolysis products
- Characterization of pyrolysis solid product; use of produced pyrolytic carbon black (CBp) for measurements of its specific surface area, pore structure and other characteristics; use of CBp in rubber compounds and measurement of mechanical properties of the prepared rubber compounds; further treatment of produced carbon black by their activation to active carbon and measurement of adsorption parameters.
- Characterization of pyrolytic gases; amount, composition, energy value
- Characterization of pyrolytic liquid product; amount, composition, physical characteristics, characterization as liquid fuel, distribution range of molecular weight.
- Measurement of kinetic parameters of the individual components release
- Experimental verification of the process mathematical model.

The unit provides also other possibilities, e.g.:

- Partial oxidation or gasification of scrap tire
- Connection of a secondary gas pyrolysis reactor (catalytic or non catalytic)
- Connection of other post pyrolytic treatment equipment

Examples of application

### Influence of process conditions on pyrolysis product yields

The unit was used for the determination of the influence of pyrolysis temperature and residence time of solid phase on the amount of individual pyrolysis yields. Figure 7 shows the influence of temperature. At temperatures below 600 °C, the thermal decomposition continues and the solid phase yield decreases with the increasing pyrolysis temperature. At temperatures above 550 °C, the yield of solid phase is practically constant. Increasing the pyrolysis temperature, the gas to liquid ratio of volatile fraction increases; this is caused by the secondary thermal decomposition of volatiles at higher temperatures. Generally, this type of reactor, at lower flow rates of inert gas, provides a high gas to liquid ratio. The reason is the relatively high residence time of the volatile fraction in the reactor. For lower gas to liquid ratios (production of more liquid), higher flow rates of inert gas have to be used.

Figure 8 shows the influence of the solid phase residence time on the pyrolys yields. At 600 °C, pyrolysis is completed at the residence time of around 100 seconds; this results from the behavior of the solid phase yield at different residence times. However, by increasing the residence time, the gas to liquid ratio increases rapidly.

### Influence of pyrolysis temperature on specific surface area of pyrolytic carbon black

Marketability of the residual char from the pyrolysis process is one of the most important factors for using pyrolysis as a method of waste tires recycling. This char, called also pyrolytic carbon black, can be used as reinforcement in new rubber products or as active carbon after its treatment. Using pyrolytic carbon black as reinforcement in new rubber products is conditioned by a number of quality parameters; the specific surface area being one of the most important parameters. The unit described above in combination with a device for measurement of the specific surface area (SORPOMATIC 1900, Fisons Instrument, Milano Italy) was applied in the characterization of pyrolytic carbon black produced at different pyrolysis temperatures. The measured values of the specific surface area for pyrolytic carbon blacks are compared with those of commercial carbon blacks in Table 1.

At temperatures below 550 °C, the pore structure of rubber material is still developing and specific surface area is increasing with temperature; but at higher temperatures, the change in the values of the specific surface area is negligible. Pyrolytic carbon black obtained in the unit described in this article has a specific surface area comparable with the surface area of commercial carbon black N330. However, the specific

### Table 1 Specific surface area of pyrolytic and commercial carbon blacks

<table>
<thead>
<tr>
<th>Sample</th>
<th>CBp (450 °C)</th>
<th>CBp (500 °C)</th>
<th>CBp (600 °C)</th>
<th>CBp (700 °C)</th>
<th>CBp (800 °C)</th>
<th>N220</th>
<th>N330</th>
<th>N550</th>
<th>N660</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Surface area [m²/g]</td>
<td>34.4</td>
<td>58.15</td>
<td>71.5</td>
<td>68.14</td>
<td>67.67</td>
<td>111</td>
<td>79</td>
<td>40</td>
<td>38</td>
</tr>
</tbody>
</table>
surface area is dependent on the pyrolytic reactor type; for high specific surface area, good heat and mass transfer conditions have to be maintained. For a pyrolytic carbon black obtained in a batch reactor, the specific surface area of only $18 \text{m}^2/\text{g}$ was measured.

**Conclusion**

The laboratory unit developed enables studying the influence of a number of parameters on the amount and quality of pyrolysis products. A screw type reactor with an electric stepping motor provides very good heat and mass transfer conditions and continuous removal of pyrolysis products, which results in their better quality. The temperature range from 550 to 700 was estimated to be optimal for solid waste and biomass pyrolysis. In the developed pyrolysis unit, the residence time of 5 minutes was sufficient for the pyrolysis of waste tires completion at 550 °C. The sizes of used solid particles can vary from 0.1 mm to 10 mm. As the optimal value of $d_p/d_{rt}$, the value of 0.25 was estimated.

The system works at the pressure slightly above the atmospheric. The minimum flow rate of inert gas was found as the optimum one.

The developed laboratory pyrolysis unit enables the realization of a number of different applications related to the characterization and treatment of pyrolysis products. Influence of process conditions on the pyrolysis product yields and influence of pyrolysis temperature on the specific surface area of pyrolytic carbon black were determined.

**Acknowledgement**

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**References**