USING PYROLYZED CARBON BLACK (CBp)
FROM WASTE TIRES
IN ASPHALT PAVEMENTS

by

J. H. Fader*
B. P. Faulkner*
R. J. Unterweger*

Svedala Industries Inc.
Pyro Division
Process Research and Test Center
9180 Fifth Avenue
Oak Creek, WI 53154
Phone: 414-761-1190
Fax: 414-764-3443

Presented at a meeting of the
Rubber Division, American Chemical Society
Cleveland, Ohio
October 21-24, 1997
Using Pyrolyzed Carbon Black (CBp) from Waste Tires in Asphalt Pavements

by
J. H. Fader*  
B. P. Faulkner*  
R. J. Unterweger*

Svedala Industries Inc.  
Pyro Division  
Process Research and Test Center  
9180 Fifth Avenue  
Oak Creek, WI 53154

Presented at a meeting of the  
Rubber Division, American Chemical Society  
Cleveland, Ohio  
October 21 - 24, 1997

Abstract

The numerous previous attempts to commercialize pyrolysis of scrap rubber and other carbonaceous materials have been unsuccessful because of lack of market demand for the crude "raw" pyrolysates; pyro-oil, pyro-gas, and pyro-char.

Ongoing tests at the Svedala Pyro Systems Inc. Process Research & Test Center and the recent comprehensive Joint Highway Research Project (3 volumes) in cooperation with US Dept. of Transportation FHA, the Indiana Dept. of Transportation and Purdue University are discussed.

These test results verify the proprietary processing of the raw pyro-char into an upgraded homogenous pyrolyzed carbon black (CBp) as a viable, value-added asphalt modifier. Commercial carbon black was used as control. Specifically, test results show that CBp contents of 10% to 15% by weight of asphalt produce a number of significant improvements.

Introduction

The potential energy available from scrap automotive tires and automotive shredder residue in the USA can displace 50 million barrels of imported oil per year by only using their thermal heating values. New developments show that by integrating commercial THERMAL and MINERAL processing technologies that much higher value-added products can be produced.

Pyrolysis is the process of breaking organic chemical bonds by heating. Extensive processing attempts to commercially pyrolyse scrap rubber tires shredded as tire derived fuel (TDF) or automotive shredder residue (ASR) have not been able to produce marketable by-products from the resulting raw pyrolysates; pyro-char, pyro-oil, and pyro-gas.

World-wide, approximately 35 million automobiles were sold in 1994.[1] Sooner or later, they will be scrapped and shredded -- most of them in the not too distant future. All major automobile producing countries presently have more than adequate capacity to shred the supply of scrap automobiles.[2]

An average of 10 million cars are shredded each year in the United States. These shredder operations make their profit from the recovery of approximately 11.2 million tons of steel and the other non-ferrous metals; aluminum, copper, zinc, and stainless steel which add up to approximately 0.8 million tons annually.
The remaining waste fraction after the extraction of these marketable metals has been termed automotive shredder residue or ASR - which the trade commonly calls "fluff". This ASR waste fraction is a low density material consisting of textiles, rubber, wood, plastics, glass, water and dirt that instead of being recycled is sent to a landfill.

To date, the technology of vehicle recycling is capable of recovering and reusing about 75% of the weight of scrap vehicles.[2] The ASR waste fraction or remaining 25% is still a Total Life Cycle (TLC) problem.

Since the wheels and tires are generally removed from the vehicle prior to shredding they are not included in these statistics. Approximately 133 pounds of elastomers are used in the typical North American automobile.[2] Assuming an average weight of 20 pounds per tire then 60% to 75% of this is in the tires, especially when the spare tire is included. Recent tests have shown the feasibility of further processing of these raw pyrosates can produce products that are competitive with current materials. This paper will review some of the findings from various laboratory and large pilot production tests of combining the primary thermal pyrolysis into raw materials and then the processing into up-graded "wide-spec" products. The potential markets and economics are discussed first, then followed by a summary of the proprietary manufacturing process development at the Svedala Pyro Systems Process Research & Test Center (PRTC).

The assumption is that there are larger environmental considerations and economical potentials with recycling of scrap tires. After which, this technology could be transferred or adapted to the processing of ASR.

SCRAP TIRES

Scrap tires that are not recycled through retreading offer energy conservation opportunities[3] through their use as:

1. Solid fuel: displaced energy = 35 kJ/g or 15,000 Btu/lb
2. Chemical feedstock (oils and fillers) = 25-53.5 kJ/g or 11,000-23,000 Btu/lb
3. Virgin rubber substitute (crumb rubber) = 79-93 kJ/g or 34,000-40,000 Btu/lb
4. Asphalt additive for paving applications = 210 kJ/g or 90,000 Btu/lb

Each day, an estimated 2 million tires are produced worldwide. And, each year, approximately 240 million tires are discarded in the United States - one for every person. The Scrap Tire Management Council in their 1992 "Scrap Tire Use/Disposal Study" suggested scrap tires could be used as fuel in a variety of potential applications because the energy content is essentially that of coal. They also projected asphalt/paving applications, civil engineering applications, and product recovery via pyrolysis. In 1992 it was estimated that approximately 57 million tires were used as fuel and only 5 million in asphalt/paving applications.[5]

A current projection of the European situation indicates that 23% of tires are retreaded, another 30% are recycled by various means, and the remaining 47% are disposed into landfills. It should be noted that Europe includes fuel use as recycling. In Japan 47% of scrapped tires are retreaded or reclaimed and 39% is used as fuel.

A 1984 report for the U. S. Department of Energy[5] concluded that of the available processes for recovery of energy from scrap tires, combustion and pyrolysis appear to be the two processes that can be employed on a large enough scale to have an important impact on the problem.

Today's tire is made to last under extremely severe physical, thermal and chemical conditions. It is chemically complex, precision engineered and designed to be indestructible. A tire only becomes a scrap tire because the tread is worn off or it has been physically damaged or has not been sorted for retreading. The material out of which a tire is made; the fabric, fiber glass, wire and rubber elastomer remain essentially as good as when they were introduced to make the new tire.

Although the physical properties of the tire discourage "recycling" in the pure sense, an analysis of the composition of an average radial passenger tire reveals its energy value.[4]
1. Natural rubber - a renewable that comes from the rubber tree. Material is withdrawn without destroying the tree.
2. Synthetic rubber - produced from crude oil, a high energy fuel much cleaner than coal.
3. Carbon black - also produced from crude oil, and a product with a high energy value.
4. Petrochemicals, extender oils and organic fabric - produced from crude oil, they contribute to the energy value.
5. Steel in the tire - at high temperatures, oxidizes to produce 3,500 Btu/lb.
6. Only 3% of the tire does not contribute to its energy value.

This indicates that tires as a fuel source have a viable market potential, however, only when the economics justify the increased expense for meeting the local environmental and emission requirements.
RECOVERY BY PYROLYSIS

Over 20 years ago research programs by the Argonne National Laboratory[3] and the Firestone Tire and Rubber Company[6] have shown that scrap tires could provide a recoverable source of hydrocarbons (oil and gas) for fuel or chemical feedstocks and a blended carbon rich reinforcing filler to substitute for some carbon blacks. The conversion from scrap tires to these products is accomplished by a process called pyrolysis. Textbooks describe pyrolysis as, "the chemical decomposition of a substance by heat," with the heat applied to the exterior of a sealed vacuum chamber in which the materials are located.[7]

The idea is to degrade them into useful by-products that can be reused, while preserving their energy content. (Burning would release the energy content, but leave the ash that would have to be landfilled.)

Various methods can be used to accomplish pyrolysis. These can involve a number of reactor types, such as; fluidized bed, indirect rotary kiln, traveling grate, molten baths, etc. which can be either oxidative or reductive or vacuum; and batch or continuous in design. A 1984 study for the U. S Department of Energy identified 31 tire pyrolysis plants throughout the world that were in some stage of concept or operation.[8] Since this report many more attempts continue to occur each year trying to produce commercial by-products. So far all have not been successful - indicating that pyrolysis alone can only produce raw materials. Therefore, to obtain marketable products additional technology is required.[9]

The Dedds study showed that the product yields will vary significantly with the different pyrolysis temperatures.[5] See Table 1.

![Table 1. Pyrolysis Temperature and Product](image)

Recently a pilot plant study was conducted at the Universite Laval, Quebec, Canada using a vacuum pyrolysis reactor. An economic model for a 20,000 Mg/yr. (tonnes) plant or approximately 2,000,000 tires per year estimated capital investment of $7 million Canadian dollars. The return on invested capital at the third year was projected at 31%. However, these projections assumed a revenue for disposal (tipping fee) of $1.00 per tire and an expected market value for the oil of $16-18/Mg (approx. $0.60/gallon or $25.00/bbl). Both may be too high for today's markets[10].

ECONOMIC FACTORS - There are three main revenue flows that must be integrated to achieve economic feasibility. The potential market prices can vary based on the site specific demographics; also the assumptions must be realistic, for example;

1. Tipping fees - this is the revenue that can be collected for scrap tire disposal at the recycling site. Where tires can be landfilled this fee must be competitive to divert the scrap tire hauler from the landfill to the pyrolysis site. Many regulations now do not allow whole scrap tires to be dumped in landfills, thereby increasing this disposal cost - if enforced.

Most proforma scenarios assume at least $1.00/passenger tire tipping fee at 20 pounds per passenger tire. These may be the best case assumptions for an initial revenue of $0.05/lb or $100/ton, prior to any other processing or investments. Because scrap passenger tires have worn off some of the rubber and that smaller and lighter tires are certainly becoming more popular, this could be realistically reduced by at least 25% to $75/ton ($0.75/tire). At higher disposal fees there seems to be more opportunity for other recycling technologies; such as crumb rubber and incineration. Even worse it is a temptation for even more illegal stockpiling. In the United States there are estimates ranging from 1 to 3 billion tires already stockpiled nationwide.
This conservative 25% tipping fee reduction will cause the revenue of a 20,000 ton/year plant, such as the Laval study to be reduced by $500,000. A serious impact on the economics.

Also to be considered is a guaranteed constant flow of scrap tire feedstock. Presently there seems to be a practical threshold of 5,000 to 6,000 tires/day that can be effectively collected, received, sorted and managed. Larger ambitions tend to make the recyclers' need for scrap tires a commodity. The supply/demand equation can also reduce the tipping fee - risking further adverse economics. Such as, the large tires-to-energy plants, requiring over 15,000 scrap tires/day, for example; the one in Modesto, California, constructed by the Oxford Energy Company, forced into bankruptcy due to lower than forecast revenue contracts.

2. Pyro-oil - The oil is highly aromatic with a slight burnt odor. It has a gross heating value of about 43 MJ/kg, (18,500 Btu/lb), a specific gravity of 0.95 (17.8 deg API), a flash point of less than 24 deg C (75 deg F), a pour point of minus (-) 6 deg C, initial boiling point 112 deg C with a 50% cut at 376 deg C (simulated distillation).

The residual metal content is < (less than) 0.1% for Va, 0.1% for Ni and 0.6% for Na.

A typical elemental analysis for the oil was 87.3% C, 10.5% H, 0.8% S, 1.2% O and 0.2% N. It yielded on distillation 8% heavy naphtha, 16% kerosene, 24% light gas oil, 35% catalytic feed and 17% bunker (vol%).

The PONA analysis of the fraction boiling below 204 deg C which constituted 26.8% of the crude oils gave 24.9% paraffins, 43.3% olefins, 6.6% naphthenes and 25.4% aromatics.

This oil can be used as a heating oil and would be grossly classified as a No. 4 ASTM bunker oil.[10] There can be a rather high percentage of carbon sludge that enters the off-gas vapor steam due to turbulence in the pyrolysis reactor. This degrades the oil and can plug burner nozzles. It also reduces the amount of carbon black in the pyro-char portion. This transfer of carbon from the solid char residue to the oil and gas fractions can explain the difference in material balances between batch and continuous feed pyrolysis.

There is the potential to use this oil for petrochemical feedstock but there would be additional expense that may not be justified.[15] Presently the more practical market is for blending with other fuel oils. However, this means that the price cannot be more than existing oil markets but at a penalty because of uncertain consistent quality and supply.

Therefore, assuming anything above $0.40/gallon ($17/bbl) or approximately $0.05/lb ($0.023/Kg) is not realistic - instead it might have to be discounted as much as 50%. A recent 5000 gallon tanker-load was sold to a steel mill at $0.15/gallon ($0.02/lb or $0.01/Kg). Assuming 1 gallon (8 pounds) of pyro-oil/20 pound tire, the income would only be between these limits; $0.15 - $0.40/gallon or scrap tire.

3. Pyro-char - Ever since the early scrap tire pyrolysis experiments it was critical that once this material could be economically produced and marketed - then pyrolysis would be a feasible recycling method.[8] This pyro-char residue has the most value-added potential but also has been the most difficult to scale-up from the promising laboratory research results into a commercial manufacturing process.[9][11] Table 2. shows the range of pyro-char properties after the magnetically removing the wire and steel.

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBON</td>
<td>84% - 89%</td>
</tr>
<tr>
<td>VOLATILES</td>
<td>0.5% - 3.0%</td>
</tr>
<tr>
<td>SULFUR</td>
<td>1.0% - 2.0%</td>
</tr>
<tr>
<td>ASH</td>
<td>10% - 16%</td>
</tr>
<tr>
<td>SURFACE AREA</td>
<td>24 - 65 SQ M/g</td>
</tr>
<tr>
<td>pH</td>
<td>7.0 - 8.0</td>
</tr>
</tbody>
</table>

Table 2. Properties of pyro-char

The untreated pyro-chars are very coarse and contain much extraneous material, and as a result, have limited market potential.[9] Much investigation and research has been devoted to recover the carbon black from the char since in its original form it will have the highest market value. However, the highest grades of carbon black are only used in the tread rubber which has mostly worn off the scrap tires. Therefore, the ability to recover anything of higher value than for a blend of the other semi-reinforcing carbon blacks is not realistic. Also this raw carbon black blend will be diluted by the amounts of ash or inert matter that remains from the char mixture.

Of the identifiable properties of carbon black; surface area, particle shape, purity, etc. the most important characteristic is particle size. Generally, the finer the particle size - the better the reinforcing properties.
Development projects by Firestone and Marathon resulted in a vicious patent law suit to obtain the technology rights to a process for pulverizing the char particles to a very small particle size < (less than) 5 microns.[12]

THE ATR SYSTEM

<table>
<thead>
<tr>
<th>Pyro Product</th>
<th>Yield%</th>
<th>Pounds</th>
<th>Btu/ Ib</th>
<th>Total Btu’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>35</td>
<td>7.0</td>
<td>12,500</td>
<td>87,500</td>
</tr>
<tr>
<td>Oil</td>
<td>40</td>
<td>8.0</td>
<td>17,500</td>
<td>140,000</td>
</tr>
<tr>
<td>Gas</td>
<td>15</td>
<td>3.0</td>
<td>19,950</td>
<td>59,850</td>
</tr>
<tr>
<td>Steel</td>
<td>10</td>
<td>2.0</td>
<td>6,325</td>
<td>12,650</td>
</tr>
<tr>
<td>Fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Misc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>20.0</td>
<td>15,000</td>
<td>300,000</td>
</tr>
</tbody>
</table>

Table 3.
Pyrolysis Material Yields And Energy Balance
For 20 Pound ScrapTire

After more than 5 years of research and testing by the Akron Rubber Development Laboratory, an integrated process to pyrolyse and refine the char into carbonaceous semi-reinforcing fillers was patented worldwide by American Tire Reclamation Inc. (ATR).[13] Actual test runs by various pyrolysis equipment suppliers resulted in the target performance specifications for a modular ATR continuous process plant as shown in Table 3 with the emphasis on extraction of the pyro-char.

It was discovered that with pyrolysed carbon black, fine particle size alone does not assure good reinforcing properties. Ongoing research at Universite Laval, Canada and the University of Liege, Belgium, confirm this ATR breakthrough.[14] The surface reactivity and “structure” also appeared to be lost or reduced in the pyrolysis process.

The ATR process involves commercially available processing equipment that mechanically post-treats the pyro-char to improve the particle size, shape, surface reactivity and purity in a cost effective, dry and closed loop system.

This new product was called ATR-077 and the secondary filler product ATR-099. The independent test results by the Akron Rubber Development Laboratories[25, 26] comparing this new ATR-077 to commercial N-990 carbon black in a SBR rubber compound are shown in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>ATR-077</th>
<th>N-990</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile, psi</td>
<td>2250</td>
<td>1420</td>
</tr>
<tr>
<td>300% Modulus, psi</td>
<td>1048</td>
<td>660</td>
</tr>
<tr>
<td>Elongation%</td>
<td>440</td>
<td>580</td>
</tr>
<tr>
<td>Hardness</td>
<td>64</td>
<td>55</td>
</tr>
<tr>
<td>Tear, C, ppi</td>
<td>201</td>
<td>151</td>
</tr>
<tr>
<td>Comp Set MthB</td>
<td>19.0</td>
<td>19.3</td>
</tr>
</tbody>
</table>

Table 4. ATR-077 vs N-990 in SBR 1502 Rubber
Reference ASTM D-3192
MARKETS AND ECONOMIC POTENTIALS

**ATR-077, A New Black Reinforcing Filler.**

The uniqueness of this product is that previous attempts to produce carbon black from grinding tire pyrolysis char or grinding other black residues have, at best, produced fillers that have very low reinforcing characteristics - more often only that of ground coal.[9][24]

The black filler produced with the Svedala PRTC process performs equal to, or slightly more reinforcing than SRF (N-770 type) and approaching GPF (N-660 type) carbon blacks. Table 4. This has been accomplished without using energy intensive (expense) grinding systems or wet chemical acid baths (expensive and hazardous) that prior technologies required.[25]

The North American 1995 market consumed about 3 billion pounds (1.59 million tonnes) of the worldwide carbon black consumption of over 12 billion pounds (6.2 million tonnes) per year that is split almost equally between the hard series: N100, N200, N300 and soft; N500, N600, and N700 grades. In North America, of the 1.59 million tonnes used, almost 70% is consumed in tires and tire related products. The remaining 30% is used in non-tire applications such as molded MRG, extruded MRG, foam and sponge, wire and cable, flooring, matting, solid wheels, and roofing membrane.

It is this non-tire segment, using 900 million pounds of carbon black per year and which is virtually all soft black and thermal black, that pyrolysis blacks will first find a home.[9] It is also possible that certain tire applications such as innerliner, carcass and sidewall would be able to utilize these refined pyrolysis carbons in blends with other virgin carbon blacks. The refined pyro-char according to ATR-077 specifications can be profitably manufactured and sold at 15% to 20% below current carbon black prices or at approximately $0.20 - $0.25 per pound.

A modular plant designed to recycle 50 tons of scrap tires (TDF) per day or 15,000 tons per year would produce 5,000 tons of ATR-077 or only 1% of the potential targeted carbon black market. At $0.20 to $0.25 per pound, ATR should be able to sell at least 100 million pounds (50,000 tons) per year.[24] To fill this market study estimated by the Akron Consulting Company would require 10 recycling plants to meet this existing potential in North America (26% of world carbon black consumption). For the other markets in West/East Europe (35%) and in E/SE Asia (28%) could be extrapolated into market potential for at least 20 more plants in these areas.

**CBp, An Asphalt Modifier.**

**BACKGROUND**

The inclusion of additives in pavement materials as reinforcing agents has been practiced for a long time. Some of these, such as limestone dust, hydrated lime and portland cement produce more or less an improvement in pavement properties when added into the asphalt cement.[34]

However, a new market to use an engineered pyrolyzed carbon black (CBp) as an asphalt modifier shows even more value added potential. Especially, when it is produced with consistent specified quality and performance at lower market pricing than commercial carbon blacks.

Using carbon black(CB) to reinforce asphalt cement was first reported in the early 1960's [Alcoi 1962, Martin 1962]. The idea was based on the concept that carbon black is known to impart dramatic effects as a reinforcement of rubber polymers and thus might show some beneficial effects as an additive to asphalt binders.[32] In the mid 1970's, Cabot Corporation introduced a special carbon black called Microfil in which laboratory and field tests showed improved rheological and aging characteristics of the asphalt binders. In spite of its effectiveness as a modifier, however, the use of CB has been limited due to its relatively high material cost.[35]

A recent 3 year test, 1993-96, by the Indiana Department of Transportation (INDOT) and Purdue University concluded that pyrolysed carbon black contents of 10% to 15% by weight of asphalt produce a number of significant improvements. The rutting potential, the temperature susceptibility and the stripping potential can be reduced by the inclusion of pyrolysed carbon black(CBp) in the asphalt mixture. Added material costs of about 6% may well be justified by expected improvements in performance.[27]
CBp LABORATORY TESTS

The laboratory tests and evaluations for the Joint Highway Research Project were conducted at INDOT and Koch Materials. The gyratory tests were conducted by the US Army Corps of Engineers 8A/68/4C model.[35] The 3 Part Research Study[27,34,35] is much too comprehensive to include here. Some selected examples to indicate the findings that lead to the summarized conclusions are given. Other laboratory testing conducted at INDOT were; specific gravity test, kinematic viscosity test, penetration test, softening point test, ductility test and aging test.[35]

HAMBURG WHEEL TRACKING TEST: This was introduced to the United States in 1990 and purchased by Koch Materials for their asphalt test laboratory in Terre Haute, Indiana. This device can be used for permanent deformation (rutting) and stripping potentials of asphalt specimens. Generally, a load is applied to a steel wheel that is cycled in water on the asphalt being tested. Figure 1 shows the test results of samples used for the Indiana SR 46 road test section. These tests with 5%, 10% and 15% additions of CBp indicate rutting performance improvements in the modified asphalts (MAC) proportionally increasing to over 400%.

PAVEMENT TEST: The laboratory study of the properties of asphalt cements modified by CBp also indicated an improved temperature susceptibility of the binders. In order that the performance data be comparable, three sections of the experimental pavements were constructed on Indiana SR 46, using different asphalt binders. The location of these sections is shown in Figure 2. The length of the first section is 3.45 miles, and it was constructed using conventional AC-20 as asphalt binder. The length of the second portion is 3.8 miles, constructed with polymer modified AC-10 (MAC-10). The length of the last section is 3.5 miles, and the binder is CBp modified MAC-10 (MAC-10/CBP).

Considering the specific purpose of this project 4 types of asphalt distress conditions were inspected for the Performance Condition Index (PCI) rating.
1. Alligator cracking; These are interconnecting cracks caused by fatigue failure of the asphalt concrete surface under repeated traffic loading.
2. Longitudinal cracking; These are parallel to the pavement's center-line or laydown direction. Caused by poorly paved lane or shrinkage of the AC surface due to low temperature or hardening of the asphalt.
3. Rutting; This is a permanent deformation in any of the pavement layers or subgrades. Usually caused by traffic loads.
4. Edge cracking; This distress is very common in almost all pavements and can be caused by traffic loading, by frost weakened base or subgrade near the edge of the pavement.

Inspection and Analysis of Results: The inspection was performed on October 16, 1995. The results of these 21 samplings were statistically summarized in Table 5.

<table>
<thead>
<tr>
<th>Variable</th>
<th>PCI Mean</th>
<th>Sample Size</th>
<th>Std.Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-20</td>
<td>98.268</td>
<td>7</td>
<td>1.3801</td>
</tr>
<tr>
<td>MAC-10</td>
<td>98.857</td>
<td>7</td>
<td>1.9518</td>
</tr>
<tr>
<td>MAC-10/CBP</td>
<td>99.571</td>
<td>7</td>
<td>0.7868</td>
</tr>
</tbody>
</table>

From this data analysis it can be seen that the PCI mean value and standard deviation of the pavement section using MAC-10/CBP is better than those of the other two sections, indicating the value-added properties of CBp.
Location of the experimental sections

FIGURE 2
MODULAR MANUFACTURING PLANTS

The ability to extract the maximum amount of carbon black in the pyro-char residue is of vital economic importance to the commercial success of an integrated pyrolysis plant. The production economies-of-scale also require that the pyrolysis process be continuous as opposed to static or batch reactors.

In order to maximize to production of the carbon-rich pyro-char Svedala Industries Pyro System dedicated a research program to increase these yields from the 25% obtained by the continuous pyrolysis for the INDOT tests[34,Pg.22] to the theoretical and lab yields of 38%-40% obtained by the Firestone laboratory tests[6] and Dodd's report[8] for the US Dept. of Energy. This productivity improvement would increase the revenue potentials by 160% over prior State-of-the-Art for continuous scrap tire pyrolysis.

Prior continuous methods were attempting on pyrolyzing as much scrap tire feedstock as possible instead of focusing on the productivity and quality of the end products. With the emphasis on high volume through-put there is violent agitation and turbulence in the pyrolysis bed. This causes the valuable carbon black particles to become captured in the hot pyro-vapor exhaust stream, resulting in a pyro-gas and pyro-oil contaminated with an undesired carbon soot.

Svedala Pyro Research and Test Center

The Svedala Process Research and Test Center (PRTC) located in Oak Creek, Wisconsin, is a fully equipped production test facility which can perform complex pilot runs on materials to complete commercial flowsheet simulations. The PRTC encompasses an area of over 60,000 square feet, which allows the design and testing of integrated processes supported by lab and quality control equipment. PRTC is the primary research and test facility for worldwide Svedala Pyro Division.

1. Batch Tests: Indirect Rotary Kiln: Laboratory scale testing allowed for experimenting with the time-temperature, through-put and material balance pyrolysis variables. This establishes the empirical relationships for scale-up to the continuous indirect rotary kiln experiments. In early 1997, the pyro-char yields were successfully increased from 25% to a range of 35%-40% verifying Table 3 parameters. Figure 3 is a graph showing 62% weight loss stabilizing at 495 degC. This means that 38% was the retained pyro-char. Larger scale testing was continued until similar results were obtained with the next process integration phase as shown in the flow sheet, Figure 4.

2. Continuous Tests: Indirect Rotary Kiln: Figure 5 shows the typical outline of the continuous pyrolysis reactor that is being designed to obtain the Step 1 Batch Test pyro-char product yields. Proprietary methods have been developed and are in final pilot plant tests for:
   - Continuous feed of the shredded tire chips into the pyrolysis reactor through air locks preventing any oxygen from entering the pyrolysis reactor,
   - Shape of internal shell and pyro-vapor extraction designed to keep carbon in the pyro-char residue
   - Separation of the wire and pyro-char at the reactor discharge
   - Use of pyro-gas for process heat

3. Pyro-Char Upgrade Processing: This is also a patented technology as part of the PRTC process integration. Figure 6 shows a general layout of the PRTC equipment system. New breakthroughs in this process are also being realized. Figure 7 shows a particle size analysis of a sample with 99% under 22 microns. Figure 8 is a data sheet showing the improved reinforcing properties of this refined CBp sample, called P-Black 079, in a blind test comparison at the BF Goodrich R&D Laboratories to commercial N762 control samples. Of importance is that the average tensile properties of the P-Black 079 were nearly 30% higher than the N782 control. This should even increase the marketability of this engineered reinforcing black filler over the previous ATR-077 filler potential of 100 million pounds/year on Page 6 of this paper.
INDIRECT BATCH KILN FLOW SHEET
FOR
TIRE PYROLYSIS PROJECT

OFF-GAS TO VENT STACK

COMBUSTION CHAMBER

FURNACE GAS TO VENT STACK

OIL COLLECTION SYSTEM

FIGURE 4.
Figure 6

Tire Pyrolyzing Development Project
97-013
Carbon Black Classifying/Upgrading Step
### Volumetric Analysis

<table>
<thead>
<tr>
<th>EQUIV.</th>
<th>STAND. TYPYLER</th>
<th>MICRONS</th>
<th>CUM. % ON</th>
<th>CUM. % PASSING</th>
<th>VOL. ON</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 MESH</td>
<td>423</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>40 MESH</td>
<td>300</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>60 MESH</td>
<td>212</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>80 MESH</td>
<td>176</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>125</td>
<td>125</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>88</td>
<td>88</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>63</td>
<td>63</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>325 MESH</td>
<td>44</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>31</td>
<td>31</td>
<td>0.00</td>
<td>100.00</td>
<td>0.00</td>
<td>1</td>
</tr>
<tr>
<td>22</td>
<td>22</td>
<td>1.00</td>
<td>99.00</td>
<td>0.70</td>
<td>1.7</td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>9.70</td>
<td>90.30</td>
<td>15.2</td>
<td>15.3</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>23.00</td>
<td>77.00</td>
<td>65.8</td>
<td>66.8</td>
</tr>
<tr>
<td>7.8</td>
<td>7.8</td>
<td>41.80</td>
<td>58.20</td>
<td>25.6</td>
<td>25.9</td>
</tr>
<tr>
<td>5.6</td>
<td>5.6</td>
<td>59.00</td>
<td>41.00</td>
<td>21.7</td>
<td>21.9</td>
</tr>
<tr>
<td>3.9</td>
<td>3.9</td>
<td>82.70</td>
<td>19.30</td>
<td>12.9</td>
<td>13.0</td>
</tr>
<tr>
<td>2.6</td>
<td>2.6</td>
<td>93.60</td>
<td>6.40</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>1.9</td>
<td>1.9</td>
<td>99.40</td>
<td>0.60</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>1.4</td>
<td>1.4</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>FINE</td>
<td>0.0</td>
<td>100.00</td>
<td>0.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

**NOTES:**

- 1.5 GRAM SAMPLE DISPERED WITH ISOPROPYL ALCOHOL AND THREE MINUTES ULTRA-SOIC DISPERSON.

**FIGURE 7.**
P-BLACK 079
A Carbon Black Generated from Tire Pyrolysis

ASTM D3191 SBR TEST RECIPE

<table>
<thead>
<tr>
<th>Date Tested:</th>
<th>12/15/95 N762 Control</th>
<th>12/15/95 P-Black 079</th>
<th>1/5/96 N762 Control</th>
<th>1/5/96 P-Black 079</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured 50 min. @ 293°F</td>
<td>100% MODULUS psi</td>
<td>295</td>
<td>300</td>
<td>288</td>
</tr>
<tr>
<td></td>
<td>200% MODULUS psi</td>
<td>793</td>
<td>546</td>
<td>772</td>
</tr>
<tr>
<td></td>
<td>300% MODULUS psi</td>
<td>1526</td>
<td>1135</td>
<td>1477</td>
</tr>
<tr>
<td></td>
<td>400% MODULUS psi</td>
<td>2293</td>
<td>1745</td>
<td>2241</td>
</tr>
<tr>
<td></td>
<td>500% MODULUS psi</td>
<td>2893</td>
<td>2475</td>
<td>2902</td>
</tr>
<tr>
<td>TENSILE psi</td>
<td>3020</td>
<td>3920</td>
<td>2900</td>
<td>3730</td>
</tr>
<tr>
<td>ELONGATION %</td>
<td>512</td>
<td>547</td>
<td>498</td>
<td>650</td>
</tr>
<tr>
<td>HARDNESS Shore A</td>
<td>64</td>
<td>65</td>
<td>64</td>
<td>65</td>
</tr>
</tbody>
</table>

Rheometer 1°Arc @ 320°F

<table>
<thead>
<tr>
<th></th>
<th>12/15/95</th>
<th>1/5/96</th>
</tr>
</thead>
<tbody>
<tr>
<td>T max</td>
<td>37.9</td>
<td>37.0</td>
</tr>
<tr>
<td>T min</td>
<td>7.4</td>
<td>8.4</td>
</tr>
<tr>
<td>ts 2</td>
<td>6.1</td>
<td>6.2</td>
</tr>
<tr>
<td>t 50</td>
<td>10.5</td>
<td>11.3</td>
</tr>
<tr>
<td>t 90</td>
<td>16.3</td>
<td>17.7</td>
</tr>
<tr>
<td>t 95</td>
<td>19.0</td>
<td>20.6</td>
</tr>
<tr>
<td>Cure Rate Index</td>
<td>8.93</td>
<td>7.64</td>
</tr>
</tbody>
</table>

P-Black 079 exhibits excellent reinforcing properties in the above ASTM D3191 SBR recipe. N762 data is provided for comparison.

JAN96R1

FIGURE 8.

FILLERS for RUBBER and PLASTICS
Large Scale Integrated Modular Plant

Figure 9 is an isometric view of a conceptual modular manufacturing plant. These 30 to 100 ton per day plants could cost from $4,000,000 to $10,000,000. Experience shows that capital/equipment investments of this size and risk will require special considerations. The purpose of the PRTC testing and development research is to be able to supply these turnkey plants with process and performance guarantees.

Also provided will be worldwide support to market the refined CBp in the regional markets of the installed plants. For example, road tests are being coordinated in Europe and USA. In Sweden and Canada rubber customers have products being tested.

Proforma spreadsheet flow charts have been run showing various expected revenue and return on investment scenarios. A typical turnkey plant to process 50 tons (5000 tires) per day equipment investment of $4,000,000 is projected to realize revenues of $6,000 per day from CBp sales ( $0.15/pound) or $3,000,000 per year. The land/building/labor costs and subsidy/tipping fees are local site specific parameters and will vary for each plant.

SUMMARY

Scrap tires and automotive shredder residue (ASR) are a worldwide waste problem. The utilization of pyrolysis to recover valuable hydrocarbon products offers many advantages over other disposal practices. Scrap tires are source separated as opposed to the heterogeneous nature of the ASR waste stream. In addition, the scrap tire problem has more environmental risks but also more potential to recover marketable products. The technology and market knowledge could then be adapted for recycling ASR.

Both scrap tires and ASR can be economically recycled if the pyrolysis of these materials is followed by additional processing techniques of the raw pyrosates. These refined or upgraded pyro-products can compete for use with other existing products in the major carbon black and asphalt modifier markets.

The present North American market demand for an upgraded pyro-char for industrial rubber goods with compounding characteristics such as the ATR-077 equivalent of N-700 commercial carbon black is at least 50,000 tons per year when discounted by 20%.

The amount of hot mixed asphalt (HMA) produced and placed in the United States is estimated at more than 500 million tons annually at a value of approximately $10.5 billion[30]. If only one percent (1%) was used with the pyrolyzed carbon black filler, CBp, the total recycling problem of finding a market for recycling of scrap tires and ASR would be solved.
REFERENCES


