RECOVERY AND EVALUATION OF THE SOLID PRODUCTS PRODUCED BY THERMOCATALYTIC DECOMPOSITION OF TIRE RUBBER COMPOUNDS

A Dissertation

by

LAN LIANG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2004

Major Subject: Chemical Engineering

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Approved as to style and content by:

James C. Holste
(Chair of Committee)

Mark T. Holtzapple
(Member)

Charles J. Glover
(Member)

Maria A. Barrufet
(Member)

Kenneth R. Hall
(Head of Department)

May 2004

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ABSTRACT

Recovery and Evaluation of the Solid Products Produced by Thermocatalytic
Decomposition of Tire Rubber Compounds. (May 2004)

Lan Liang, B.S., Dalian University of Technology, Dalian, P. R. China
Chair of Advisory Committee: Dr. J.C. Holste

A thermal catalytic decomposition process has been developed to recycle used tire rubber. This process enables the recovery of useful products, such as hydrocarbons and carbon blacks. During the catalytic decomposition process, the tire rubber is decomposed into smaller hydrocarbons, which are collected in the process. The solid reaction residue, which normally consists of carbon black, catalysts, other inorganic rubber compound components, and organic carbonaceous deposits, was subjected to a series of treatments with the intention to recover the valuable carbon black and catalyst. The process economics depend strongly on the commercial value of the recovered carbon black and the ability to recover and recycle the catalysts used in the process.

Some of the important properties of the recovered carbon black product have been characterized and compared with that of commercial-grade carbon blacks. The composition of the recovered carbon black was analyzed by TGA and EDX, the structure and morphology were studied through transmission electron microscopy (TEM), and the specific surface area was measured by BET nitrogen adsorption. The recovered products possess qualities at least comparable to (or even better than) that of the commercial-grade carbon black N660. Methods for increasing the market value of this recovered carbon black product are discussed.

Anhydrous aluminum chloride ($AlCl_3$) was used as the primary catalyst in the process. A catalyst recovery method based on the $AlCl_3$ sublimation and recondensation was studied and found to be non-feasible. It is believed that the catalyst forms an organometallic complex with the decomposed hydrocarbons, such that it becomes chemically bonded to the residue material and hence not removable by evaporation. A scheme for the further study of the catalyst recovery is suggested.

DEDICATION

To my parents and my husband

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

1.1 Purpose of Investigation

Environmental problems created by discarded tires and waste rubbers have become significant in recent years. In the United States, an estimated 281 million scrap tires are generated each year.[1] In addition, about 2 billion waste tires already have accumulated in stockpiles or uncontrolled tire dumps across the country. Millions more are scattered in ravines, deserts, woods, and empty lots.[2] Even though scrap tires occupy less than 2% in weight of the total solid waste stream, they represent one of the largest problem areas for polymer reuse and recycling in the United States.

For many years, one of the major disposal options for tires was the scrap pile. A very significant health problem associated with scrap tire piles is mosquito infestation.[3] Mosquitoes are reported to reproduce 4,000 times faster in tire piles than in their natural environment, and they are known to carry various types of encephalitis and yellow fever.[4] Mosquito infestation of tire piles appears to be a global problem. Large tire stockpiles are also potential fire hazards. The low bulk density, or loose packing structure of tires, ensures ample access to air. Once large piles of whole tires begin to burn, the fire is virtually inextinguishable. In the open, burning tires emit a lot of undesirable chemicals, including some carcinogens. In addition, substantial quantities of

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petroleum oil are produced and enter neighboring water sources or percolate through the soil, thereby contaminating the groundwater.

Due to the potential fire and disease hazards, over 48 states in the Unite States have adopted regulations to manage collection, storage, and disposal of scrap tires. Over 35 states have banned whole tires landfills, and a few states even have banned landfilling of chopped tires.[1] Increasing legislation that restricts the disposal of used tires demands economically and environmentally sound recycling methods. Now, the issue of how to effectively and efficiently treat and reuse scrap tires becomes a major issue confronting the United States and other countries worldwide. The establishment of recycling technologies for recovering useful resources from the general and industrial wastes for reutilization is the most desirable solution.[5]

Some characteristics of tire rubber, such as stability and durability, which are very attractive and desirable during their use, present a major challenge during the disposal process. The fact that tires are thermoset polymers means that they are not easily melted or separated into their chemical components. Tire rubbers are also virtually immune to biological degradation. The demand for high-quality rubber tires makes the disposal problem more formidable. Some have described this current dilemma as "the synthetic rubber problem all over again."[6] The rubber industry faces a major challenge to find a closed-loop method to recycle this thermoset product.

On the other hand, scrap tires are composed of many valuable constituents, including both natural and synthetic rubber, carbon black, extender oil, steel, fabrics and additives. Therefore, the possibility exists to recover valuable products from waste tires.

A number of research and commercial efforts have been directed toward developing new uses for old tires.[1-7] However, they either have some undesirable side effects or are not economically attractive. A more desirable solution, both environmentally acceptable and economically viable, would be to convert waste tires to reusable hydrocarbon fractions and carbon blacks. In this way, the original valuable resources from which polymerized products were created are recovered.

Most attempts to convert tire rubber into chemicals have involved pyrolysis, a thermal decomposition process in the absence of oxygen. Pyrolysis commonly is conducted at temperatures above 500 ^{o}C, for most hydrocarbons become unstable above this temperature.[8] Pyrolysis processes typically yield 25 to 60% condensable liquids such as benzene, toluene, *etc*., 30 to 50% char (a hydrogen-lean carbonaceous product), and the balance non-condensable fuel gases such as hydrogen, carbon monoxide, carbon dioxide, and light hydrocarbons. The harsh conditions of pyrolysis tend to produce hydrocarbons and other products of limited market value. Some methods for improving the quality of the char have been developed,[9] but at the expense of considerable additional processing.

Recently, a novel patented process has been developed to recycle waste polymers as an alternative way to recycle scrap tires, which can be less costly and have minimal adverse impact on the environment.[10] This technology employs a thermal catalytic decomposition process to convert polymeric waste to valuable hydrocarbons and carbon blacks for reuse. It is noted that molten salts, especially aluminum chloride ($AlCl_3$), of which the base metal has an electron structure that satisfies the acceptor/donor exchange requirement with the polymer undergoing decomposition, can act as catalysts for decomposing tire rubbers.[10] The fact that molten salt catalysis can be used to decompose tire rubbers has been known for several decades.[11-12] However, to date no literature reports a successful commercial catalytic conversion process for the disposal of scrap tires.

Compared to other methods of using scrap tires as an energy source, the recovery of valuable chemicals appears to be more cost-effective. Besides, it provides an opportunity to decrease the environmental burden caused by manufacturing fresh chemical feedstocks from crude oil or natural gas. The thermal catalytic decomposition process produces hydrocarbon products that generally fall in the range of C_4 to C_8, with essentially no light gases, and very few heavier hydrocarbons (or heavy oil) products present. These products potentially have great value in the fuel and chemical feedstock markets.

Another significant product, carbon black, could possibly find its market in the rubber industry. There are approximately thirty grades of carbon black that are commonly used in various industries. The largest market (about 90%) for carbon black is in the tire industry where the carbon black enhances tear strength and improves modulus and wear characteristics of tires.[13] However, it is not clear that the recovered carbon black will retain the superior properties required for reuse in this application. Additional applications of carbon black are found in plastics, filters, printing inks, paints, and toners. The market value of carbon black varies widely, depending on its quality, but generally falls in the range of 30 to 45 cents per pound.[2,14] Carbon black extracted from pyrolysis char is of very low purity and therefore cannot be used in tire manufacturing.[15] In contrast, the significantly milder reaction conditions in some catalytic decomposition processes should produce less useless char and consequently more higher quality carbon blacks. Therefore, the carbon black product recovered from the catalytic decomposition process will have a greater market value than that from pyrolysis processes. The economic value of the carbon black product has the potential to equal or surpass that of the fluid products.

1.2 Objectives of this Research

The general objective of this research is to develop a thermocatalytic decomposition process for the conversion of tire rubber compounds to reusable chemical feedstocks that is both environmentally acceptable and economically viable. Specifically, the objectives for this study are

1) to develop an operation for processing the solid products from the reaction residue that separates and recovers carbon black;

2) to determine the reaction conditions under which the yield and quality of carbon black products are optimum;

3) to evaluate the properties of the recovered carbon black products, to provide a basis for determining its commercial value and possible applications;

4) to investigate a proper method for recovering and recycling the reaction catalyst.

This investigation is a continuation of earlier work performed in our laboratory on the recovery of valuable products from scrap tires by thermocatalytic conversion. The study will provide further laboratory data and understanding required to develop a commercially viable continuous process that can treat a feed stream consisting of used tires, plastics, and other polymeric wastes. Based on information gathered here, a pilot scale reclamation facility will be designed in cooperation with the industrial collaborators.

CHAPTER II

LITERATURE REVIEW

2.1 Scrap Tire Disposal & Recycling Technologies

Tire rubbers are very stable and long-lasting polymers. Progress through decades in making them more resistant to degradation has extended their useful life, but that progress has made the disposal process more difficult. The effective and efficient disposal and recycling of the huge number of scrap tires generated annually becomes a major issue confronting the United States and other countries worldwide.

The best way to reuse used tires is to remove the outside, or tread, of the tire and add a new tread, a process referred to as retreading.[3] Retreading offers a resource-efficient strategy for used tire recovery that saves both material and energy.[7] Retread tires most commonly are used for commercial vehicles such as trucks, school buses, airplanes, and other emergency vehicles. Unfortunately, this market only represents a very small section of the tire market, and it is slow to expand.[16]

Scrap tires cannot be reused in a large scale in new tires because of the vulcanized nature of the rubber. Ground rubber from scrap tires is not chemically the same as natural rubber or synthetic rubber. The vulcanization process during rubber compounding transforms the elastomer into a non-fusible and insoluble substance.[17] The rubber cannot be devulcanized during the grinding process. As an analogy made with baked bread by Serumgard and Eastman[16]: “Yeast and flour cannot be removed from the final product and reused again. Old bread cannot be recycled into new bread.” Using reclaimed ground tire material as filler in new tires will cause lower tensile strength, heat buildup, and oxidative aging. Therefore, ground tire rubber cannot just simply be reused in new tires. In a sense, Charles Goodyear's discovery[18] of vulcanization in 1839 was not only the real start of the rubber industry, but also of the rubber recycling industry as well.[17] Methods to recycle vulcanized rubber products through devulcanization, while technically possible in the laboratory, are impractical for large-scale use.

Some research and commercial efforts have been directed toward the development of new uses for old tires.[1-7] The main strategies of the technology for scrap tire disposal and recycling can be divided into three categories:[19]

1) Combustion as fuel;

2) Grinding into small particles and using in civil engineering constructions and other applications;

3) Decomposing to chemical constituents.

A brief explanation of each recycling technology is given below.

2.1.1 Tire Derived Fuel

Tire Derived Fuel (TDF) as a means of disposal and reuse of scrap tires on an industrial scale has increased significantly over the past decade. It now is the largest market for waste tires in the United States. TDF represented approximately 41% of overall waste tire recycling in 2001.[1] Some major combustion facilities for TDF are cement kilns, power plants, pulp and paper boilers, tire manufacturing plants, and small package steam generators.[20]

Burning scrap tires as fuel is a way to reduce energy costs. The heat values of whole tires average about 35,000 kJ/kg (15,000 Btu/lbm), whereas that for most coal is in the range of 28,000 kJ/kg (12,000 Btu/lbm).[21] Waste tires may be burned whole, or shredded into pieces approximately 1 to 2 inches in size. However, not all tire components contribute to energy generation because tires contain about 30% of metal wire and fabric. The removal of the wire involves an expensive process, such as fine shredding and the use of powerful magnets. Whole tire combustion requires less processing expense. However, most of the plants currently burning tires for fuel do not have the capability to burn whole tires.

The potentially harmful effects of burning scrap tires are not fully known. There are two factors challenging the future markets for TDF. One is the economic feasibility compared with other fuel alternatives, the other is the technological consideration related to emission control from the combustion facilities. From 1992 to 1996, the number of TDF facilities decreased.[1] The reasons are assumed to be increasing environmental pressure and decreasing economic advantage. Although the emission level of pollutants from TDF facilities is comparable with coal, it is potentially higher than from other conventional facilities such as natural gas. Studies have shown that the emissions of metals (zinc, cadmium, lead, nickel, and chromium) are 10 to 100 times higher than from natural gas. Table 2.1 presents the laboratory simulation results of TDF emissions of metals.[22] The test was conducted in a 73 kw (250,000 Btu/h) rotary kiln incinerator simulator in the EPA's Environmental Research Center in Research Triangle Park, NC.[22]

Table 2.1 Estimated TDF Emissions of Metals (Base Fuel - Natural Gas)[22]

metals	0% TDF (natural gas only)		17% TDF (steady state)		100% TDF (estimated)	
	ng/J	lb/MMBtu	ng/J	lb/MMBtu	ng/J	lb/MMBtu
antimony	7.72E-05	1.80E-07	9.05E-04	2.10E-06	5.32E-03	1.24E-05
arsenic	4.80E-04	1.12E-06	1.59E-02	3.70E-05	9.35E-02	2.17E-04
beryllium	ND	ND	2.14E-05	4.98E-08	1.26E-04	2.93E-07
cadmium	1.76E-04	4.09E-07	4.54E-04	1.06E-06	2.67E-03	6.21E-06
chromium	2.78E-04	6.46E-07	1.66E-03	3.86E-06	9.76E-03	2.27E-05
lead	3.45E-03	8.02E-06	2.83E-02	6.58E-05	1.66E-01	3.86E-04
manganese	1.21E-03	2.81E-06	2.48E-03	5.77E-06	1.46E-02	3.40E-05
nickel	3.00E-04	6.98E-07	1.50E-03	3.29E-06	8.82E-03	2.05E-05
selenium	3.56E-04	8.28E-07	1.93E-03	4.49E-06	1.14E-02	2.65E-05
zinc	1.23E-01	2.86E-04	15.21	3.54E-02	89.47	2.08E-01

ng/J – nanograms per joule.
lb/MMBtu – pound per million British thermal units.
ND – not detected.

Even though burning whole or shredded tires for fuel might seem attractive, given that the cost of natural gas and other fuel oils continue to increase, one major drawback still existing is that valuable basic chemical building blocks are consumed, instead of being recovered.[10]

2.1.2 Whole and Processed Rubber Applications

Due to some unique properties and characteristics of rubbers, such as toughness, durability, and resilience to impact, tires are used for their second life in new areas where these merits are beneficial. Whole tires can be used as artificial reefs, breakwaters, playground equipment, and highway crash barriers.[2] Other reuse alternatives require that tires be split or punched into small particles (1 to 12 inch) or ground even finely. Shredded tires are being used as a lightweight road construction material or playground gravel substitutes in civil engineering applications. Split or punched tires are used to produce many useful products, including floor mats, belts, gaskets, shoe soles, dock bumpers, seals, and other miscellaneous products. As another major application, rubber modified asphalt concrete, (RUMAC) is gaining some attention recently. The addition of crumb rubber in asphalt can improve the asphalt binder's rheological properties at low and high temperatures and provide a life up to three times longer than conventional asphalt.[1] In the United States, asphalt rubber is being used in significant amounts in Texas and Nebraska.

Tire shreds contain significant amounts of steel wire. In comparison, ground rubber, also referred to as crumb rubber, is a wire-free fine rubber particle made by size reduction from scrap tires. Various size reduction techniques, such as mechanical grinding and cryogenic reduction, can be used to achieve a wide range of particle sizes down to 600 µm or less.[1] Ground rubber also can be produced from tire buffings, which are by-products from the tire retreading process. Using tire rubber for various products typically requires that the steel wire be removed. Currently, steel removal is a costly process.

From a resource conservation point of view, many applications of the crumb rubber, such as using as bedding for farm animals, mulch for garden applications, are not attractive because they represent a waste of valuable chemical resources. In addition, although it is technically feasible to manufacture many new rubber products from recycled crumb rubber, several of these new products and processes have poor economic viability and have very small and limited markets.[23] Certain objections also must be overcome when using crumb rubber in road construction. The increased cost, which can be 100% more than regular asphalt, is one of the biggest obstacles for the wide acceptance of rubber modified asphalt concrete. Additionally, the crumb product usually is sufficiently fine that it poses a serious fire hazard both during the grinding process and during the lifetime of the application. Therefore, tire derived products cannot replace completely conventional construction materials, and civil engineering projects do not consume sufficient quantities of crumb rubber so as to significantly reduce scrap tire stockpiles.

2.1.3 Decomposing Scrap Tires to Valuable Chemical Feedstocks

The objective of polymer recycling should be two-fold: (1) reduce the volume of rubbish and the burden on the environment; (2) conserve resources. Scrap tires, as a type of polymer wastes, are composed of many valuable constituents, including both natural and synthetic rubber, carbon black, extender oil, steel, fabric, and additives.

Table 2.2 lists the typical composition by weight for a passenger tire and a truck tire.[24] Noting the drawbacks associated with the first two categories of scrap tire disposal and recycling methods, many attempts have been made recently toward finding alternative technologies that are less costly and more resource conservative. Tertiary recycling, a terminology adopted from the American Plastics Council, is rapidly emerging as an economical method for reclaiming valuable materials from a variety of polymer-based waste.[23] This recycling method can be applied but not limited to scrap tires, plastics, and a number of different polymerized products or complex mixtures.

Table 2.2 Typical Tire Composition by Weight[24]

	passenger tire	truck tire
natural rubber	14%	27%
synthetic rubber	27%	14%
carbon black	28%	28%
steel	14-15%	14-15%
fabric, fillers, accelerators, antiozonants, etc.	16-17%	16-17%
average weight	new 11.34 kg, scrap 9.07 kg	new 54.43 kg, scrap 45.36 kg

Tertiary recycling breaks down the polymer chains and converts polymers to low-molecular-weight materials. Both enthalpy and entropy increase during this process. Thus, from a thermodynamic point of view, it is not desirable. However, the advantages can compensate.[16] Firstly, mixed polymers or polymers with additives such as fillers and fibers that cannot be separated readily may be degraded to low-molecular-weight substances. These substances can be separated by conventional means, typically distillation or filtration. Secondly, such low-molecular-weight substances then may be used for new chemical synthesis, such as polymerization, to make new polymers. The molecular nature of the resulting polymer can be controlled better than by simply mixing the original waste polymers. And thirdly, non-renewable petroleum resources are conserved.

Most attempts to convert tire rubber into chemical feedstocks have involved pyrolysis, a thermal degradation process in the absence of oxygen. Pyrolysis is commonly conducted at temperatures above 500 ^{o}C, as most hydrocarbons become unstable above this temperature.[8] Pyrolysis processes typically yield three principal products: gas, oil, and char; each comprises about one third by weight. The fuel gas is mostly low-molecular-weight hydrocarbons (C_1 to C_4). The oil fraction has properties similar to that of conventional heavy fuel oil. The char is a hydrogen-lean carbonaceous particulate composed of carbon black, ash, and other inorganic materials, such as zinc oxide, carbonates, and silicates.[25]

To date, no pyrolysis processes have been commercialized successfully. The problems blocking them have been both technical and economic. The harsh pyrolysis conditions tend to produce hydrocarbons and carbon/char products of limited market value. Some methods for improving the quality of the char have been developed,[9] but at the expense of considerable additional operating cost and the capital cost of the plant. At high temperatures, vulcanized rubber decomposes quickly to low-molecular-weight olefins. Thus, from high-temperature pyrolysis, valuable high-molecular-weight olefins are typically produced in small quantities. Theoretically, high-molecular-weight compounds can be generated by low-temperature pyrolysis; however, lower temperatures require longer process times, which increases the process cost. Therefore, direct thermal pyrolysis does not appear to be a viable method for converting scrap tires to chemicals.

New technologies are being developed to decompose tire rubber, such as microwave pyrolysis,[26-27] ultrasonic devulcanization,[27-28] supercritical fluid depolymerization,[29-30] and the use of special catalysts.[11-12] One advantage of using catalysts is that the processing temperature can be lowered significantly. Another advantage is that no new equipment is required. Thus, compared with other new technology, catalytic conversion of scrap tires may hold a greater promise for further investigation.

Molten salts, such as aluminum chloride ($AlCl_3$), whose base metal has an electron structure satisfying the acceptor/donor exchange requirement with the polymer undergoing decomposition, can act as catalysts in decomposing tire rubbers.[10] Molten salt systems that have been widely studied are basically metallic chloride or metallic chloride eutectics. Most molten salts have excellent heat transfer properties[32] that make them a desirable reaction media if rapid reaction is unavoidable. A cuprous chloride/potassium chloride eutectic has been reported to promote the hydrocracking of propane to smaller molecules.[33] Extensive investigations on the use of zinc chloride-containing melts for hydrocracking of coal products have also been reported.[34-36]

The fact that molten salt catalysis can be used to decompose tire rubber has been known for several decades.[11-12] Reports[37] showed that the yields of oil and gas obtained when molten salts were used as catalysts compare favorably with those from kiln pyrolytic recovery process (at reactor temperature above 700 °C). All early work showed that the choices of catalyst components and composition as well as the reactor operating conditions have significant effects upon the nature of the products. So far, no literature reports a successful catalytic conversion process for disposing of scrap tires on a commercial basis. Studies of this technology, including the nature of the chemical reactions between the catalyst and the rubber compounds and the economical viability are far from complete.

2.2 Background Study of Tire Rubber Compound

A modern tire is essentially a cord/rubber composite. Tires are manufactured from several separate components, such as tread, innerliner, beads, belts, *etc.*, and different components have different rubber compositions. Tire rubber is not pure, but rather is in the form of highly filled compounds, which are mixtures of elastomers and various additives. These additives (compounding ingredients) can be classified as vulcanizing agents, vulcanization activators and retarders/accelerators, fillers (reinforcing, semireinforcing, or diluent), antidegradants, softeners and plasticizers, pigments and organic dyes, and special additives.[38-39] Table 2.3 gives a typical rubber compound formulation and the function of the ingredients.[38]

Rubber compounds are critical engineering materials that offer many special properties required by the tire industry,[38] such as flexibility, low hysteresis, good friction on most surfaces, high abrasion resistance, and good impermeability to contained air. These properties ensure that tires perform a variety of functions under severe conditions. Meeting these properties demands sophisticated rubber compounding technologies and precise compounding ingredients, which on the other hand makes scrap tire disposal more formidable.

Table 2.3 A Typical Rubber Compound Formulation[38]

ingredient	ingredient function	amount (phr)*
natural rubber	rubber	100.0
Whiting	diluent white filler	100.0
HAF N330	carbon black reinforcing filler	50.0
naphthenic oil	softener/process aid	20.0
zinc oxide	vulcanizing activator	5.0
stearic acid	vulcanizing activator	1.0
santoflex 13	antioxidant/antiozonant	1.0
heliozone	protective wax for ozone resistance	2.0
MBTS	accelerator (primary)	1.0
DPG	accelerator (secondary)	0.5
Sulfur	vulcanizing agent	2.5

* Based on 100 parts of rubber hydrocarbon.

Rubbers compounding technology and materials directly affect the thermal catalytic decomposition process of the tire rubber compounds and the recovered products characterization. Some compounding ingredients may be retained in the solid residue or even be present as impurities in recovered carbon blacks. To better explain the mechanism of the thermal catalytic decomposition of tire rubber compounds and to reasonably evaluate the solid products recovered from the reaction residue, it is necessary to understand the general composition of tire rubber compounds and the basic properties of commonly used compounding ingredients. A general overview of elastomers and two most important compounding processes, vulcanization and reinforcement, is provided below. Specific attention is then given in the next section to carbon black, the major reinforcing filler, and one of our main products.

2.2.1 Properties of Elastomers

The term “elastomer”, generally meaning rubber, is described by ASTM[40] as “a material that is capable of recovering from large deformation quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent”. Rubber’s high extensibility combined with an ability to recover from extension has been found to depend upon its molecular structure. Natural rubber, derived from the tree *Hevea brasiliensis*, is the prototype of the various modern synthetic rubbers. All rubbers have similar physical properties, and they share a certain molecular pattern in terms of basic chemical structure.

Natural, styrene-butadiene, polybutadiene, butyl, and ethylene propylene are called general-purpose rubbers[41] because of their wide usage in a variety of products. The International Rubber Study Group[42] estimated that 18.15 million tons of rubber was produced in 2002. Of this amount, 7.27 million tons or 40% was natural rubber, the remaining 10.88 million tons or 60% was synthetic rubber. The most commonly used rubber in tires is the co-polymer styrene-butadiene rubber (SBR) or a blend of natural rubber and SBR.[25] Butyl rubber also is used widely, especially in tire innerliners. Some selected properties of the three most used rubbers in tires: natural rubber (NR), styrene-butadiene rubber (SBR), and butyl rubber (IIR) are lsted in Table 2.4.[41] The chemical structures are showed in Figure 2.1.[41] All three of these rubbers are polymers with long, flexible molecules that can be crosslinked to form a three-dimensional molecular network.

2.2.2 Vulcanization of Rubber

Pure rubber polymer chains are nearly perfectly uniform and symmetrical, thus, the molecular attraction between them will reduce flexibility and even lead to crystal formation.[44] For dimensional stability over long periods of time, it is necessary that the molecular chains be linked together by occasional crosslinks to form a three-dimensional network. Charles Goodyear's[45] discovery of sulfur vulcanization in 1831 improved the properties of rubber and made it a preferred structure for practical applications. Vulcanization today is one of the key processes used in rubber related productions.

During vulcanization, three-dimensional structures are formed between the vulcanization agent and the polymer chains by closslinking reactions. This reaction causes the soft material to become strong and less elastic. After vulcanization, the rubber becomes insoluble in solvents and is more resistant to degradation normally caused by heat, light, and aging. On the other hand, the difficulty with recycling of rubber also results from the crosslinked structure. Rubber vulcanization is a nearly irreversible process, which causes the polymer to become essentially one large molecule.

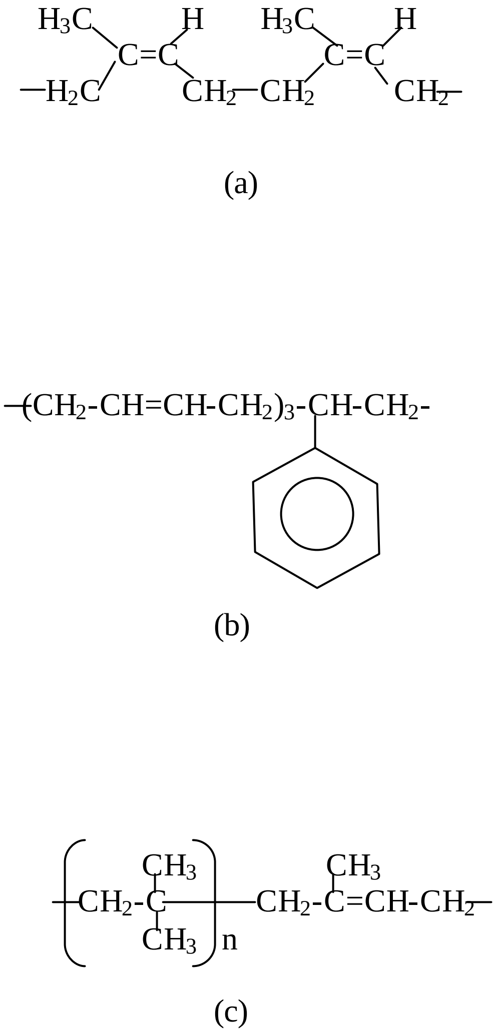
Table 2.4 Selected Properties of the Three Most Common Tire Rubbers[41]

property*	natural (NR)	styrene-butadiene (SBR)	butyl (IIR)
bondability to metals	E	E	G
density, g/cm^3	0.93	0.93	0.92
tensile strength, psi (reinforced, max)	4500	3600	3100
elongation at break, max	550	450	750
Resilience, 73°F	E	G	F
low temperature flexibility	E	G	G
resistance to abrasion	E	E	F
resistance to tearing	E	F	G
resistance to heat aging	F	F	G
resistance to oxidation	G	G	E
resistance to dilute acids	E	G	E
resistance to concentrated acids	F	F	E
resistance to alkalis	G	G	E
resistance to gas/oil/grease	P	P	P
resistance to animal/ vegetable oils	P	P	E

* E, excellent; G, good; F, fair; P, poor.

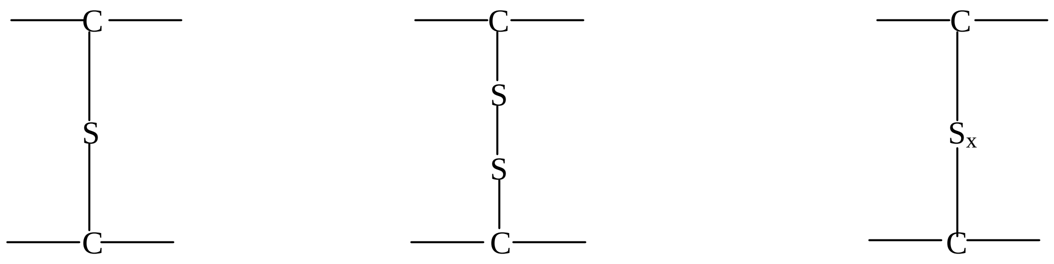
2.2.2.1 Vulcanizing Agents

Generally, all substances that can form crosslinks between the rubber polymer chains may be classified as vulcanizing agents.[39] Successful rubber technology depends



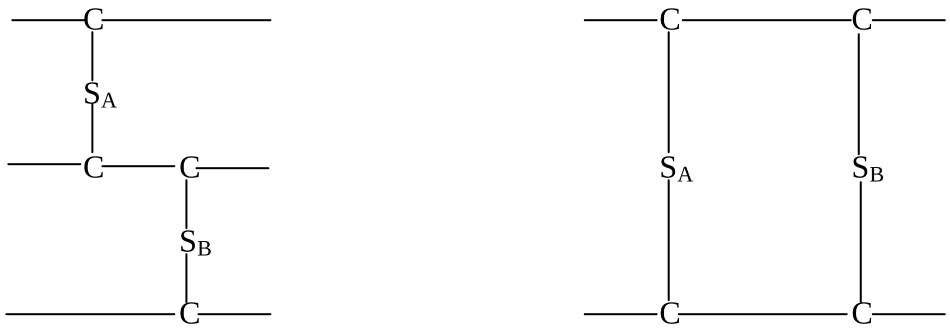
$$\left[-CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}- \right]_n -CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

Figure 2.1 Rubber structures: (a) Natural rubber (repeating unit of *cis*-1,4-polyisoprene), (b) Styrene-butadiene rubber (repeating unit with 75% butadiene & 25% styrene), (c) Butyl rubber (repeating unit with isoprene unit included).[41]



monosulfidic disulfidic polysulfidic

pendant side group intramolecular sulfide



multifunctional vicinal vicinal

Figure 2.2 Structures of sulfur-vulcanized rubber.[48]

largely on the ability to control the vulcanization process. For different types of rubber, different types of vulcanizing agents are required.[46-47] Besides sulfur, some of new vulcanizing agents are peroxides, phenolic resin, and metallic oxides. However, sulfur-rubber systems are still the most widely used method by far. The uniqueness of sulfur as a vulcanizing agent stems from the chemistry of S-S bonds. Through reactions of sulfur with double bonds contained in the polymer, the polymer chains are crosslinked together, yielding mono-, di-, or polysulfidic crosslinks of varying lengths and distributions. Some of the structural features that generally are accepted as occurring in sulfur vulcanized rubbers are shown in Figure 2.2.[48]

There are special cases where non-sulfur vulcanizations are necessary or desirable. Sulfur vulcanization can occur only in unsaturated elastomers,[41] whereas organic peroxides can be used to crosslink a wider variety of both saturated and unsaturated polymers. Peroxides, especially dialkyl peroxides, diacyl peroxides, and dibenzoyl peroxides, are used mainly to vulcanize ethylene-propylene rubber (EPR) and silicone rubber,[39] but are not generally used to vulcanize butyl rubber (IIR) because of a tendency toward chain scission rather than crosslinking when butyl rubber is subjected to the action of peroxides.[41]

Reactive phenolic resins are used as vulcanizing agents mainly for butyl rubber (IIR), which give vulcanizates with increased resistance to elevated temperatures.[39] Natural and nitrile rubber can also be crosslinked with this type of system, but no great advantages accrued.[38] Because of the low crosslinking rate, the phenolic resin vulcanization system requires the presence of catalysts, such as metal halide (most often those of zinc).[39] The phenolic resin vulcanization system is widely used for the bladders in new tires and the curing bags in retread tires.[47]

Metal oxide is another important vulcanization system, which is commonly used to vulcanize chloroprene rubber. The most widely used metal oxides are magnesium oxide, zinc oxide, lead oxide, and red lead.[38] The type of oxide used can influence the water and acid resistance of the vulcanized rubber compound. Other vulcanizing agents may include soaps and strong organic bases used for acrylate rubber, and bisphenols and alkylphenol sulphides for olefin rubbers.[39]

2.2.2.2 Vulcanizing Activators

A vulcanizing activator acts like a catalyst; relatively small additions can considerably increase the degree of vulcanization.[38] Zinc oxide is probably the most important inorganic activator, whereas magnesium oxide and lead oxide are also useful. Activation by zinc oxide depends upon the particle size used. Normally, it requires 3-5 phr (per hundred rubber hydrocarbon), but very fine particle sizes can require as little as 1 phr of zinc oxide for adequate activation.[38] Fatty acids, such as stearic, palmitic, and lauric acids, are the most important organic activators.

2.2.2.3 Vulcanizing Accelerators

Modern methods for rubber vulcanization using sulfur often use a small amount of an accelerator. There are a wide variety of accelerators available today, most of them are nitrogen- or sulfur-containing organic compounds classified as sulfenamides, thiazoles, guanidines, dithiocarbamates, thiurams, *etc.*.[41] Because of their ability to provide good scorch delay and excellent stress-strain properties, thiazoles and their derivatives - sulfenamides, such as 2-mercaptobenzothiazole (MBT) and benzothiazyl disulfide (MBTS), are the most popular accelerators by far.[46,49]

In summary, for over a century, accelerated sulfur formulations remained the most common vulcanization systems for the natural rubber and general purpose synthetic rubbers used widely in commercial and industrial applications.

2.2.3 Reinforcement of Rubber

The rubber obtained by vulcanizing elastomer has some improved characteristics compared with the virgin elastomer, which however do not suffice for its technical utilization. The dimensional stabilities of rubber compounds are improved further and the costs are reduced by incorporating fillers.

Since the introduction of synthetic rubbers, particularly of SBR during World War II, the most commonly used reinforcing agent is carbon black. Before carbon black attained its predominant position, other inorganic fillers, such as clay, whiting, zinc oxide and various types of silica, were used, and some are still in use today in the rubber industry. It is not unusual that as many as four or five different carbon blacks, sometimes blended with finely divided silica, are used in building a single tire.[41]

Reinforcing means the enhancement of tensile strength, modulus, abrasion, and tear resistance of rubber. The reinforcement of rubber depends mainly upon the interactions between filler and the base polymer. Both particle size and loading rate of the filler can affect the interaction with the rubber, and also the structure of the filler plays a role in the polymer movement under deformation.[50] Payne believed that the interaction between filler and elastomer was caused by a phenomenon called bound rubber.[51] If reinforcing carbon black or any other filler is incorporated in an elastomer, part of the rubber becomes insoluble in what are ordinarily good rubber solvents and forms an insoluble gel with filler. This phenomenon has been studied extensively and is recognized as a typical feature of the filler surface activity. A lot of investigations have been done on the mechanism and the factors that affect the formation of the bound rubber and also its influences on properties of the rubber compound.[13,51-55] Another phenomenon of filler-polymer interaction is the formation of a more or less immobilized rubber shell surrounding the filler. This is partly because of the restriction of the molecular motion of the rubber in the vicinity of the filler surface. It may also be related to the increased entanglement due to the filler-polymer attachments.[13]

2.3 Background Study of Carbon Black

Carbon black has been the major reinforcing filler in the rubber industry for over 100 years and it will probably continue for years to come. Because carbon black plays such an important role in rubber compounding, and it is one of the main products from our thermal catalytic decomposition process, it deserves special attention here.

2.3.1 Production of Carbon Black

Carbon black is essentially an amorphous carbon of quasi-graphitic structure, which historically has been produced from natural gas or oil feedstocks using the channel, thermal, and furnace processes.[41] The old channel process no longer is utilized in the United States due to its inefficiency and poor environmental effects. The thermal process mainly is used to manufacture a coarse particle size black used predominately in non-tire applications. In this process, natural gas decomposes thermally to hydrogen and carbon in a preheated brickwork furnace at temperatures as high as 1300 ^{o}C. The resulting products are generally N899 and N900 series carbons. As the price of natural gas increased, thermal black prices followed, and competitive materials took over much of the market. By far the most popular blacks are those made by the oil furnace process, with grades ranging from N100 through N700 series. They were found to be better suited to synthetic rubber. This process utilizes petroleum feedstocks rather than natural gas, and yields much more carbon black from the feed material. Acetylene black is another unique black made by the continuous thermal pyrolysis of acetylene at temperatures above 1500 ^{o}C in the absence of air. This black is used in rubber because its structure affords high electrical and thermal conductivity. Besides, it is relatively clean with less than 0.05% ash due to its feedstock.

All the carbon black manufacturing processes described above can be classified into two categories, incomplete combustion and thermal decomposition of hydrocarbons, depending upon the presence or absence of oxygen.[56] Incomplete combustion gives lampblack, channel black, and furnace black, whereas thermal decomposition gives thermal black and acetylene black. In the plant, the black is first produced as a fluffy powder and further processed into pellets for easier handling. About 50 types of carbon blacks are produced today, the properties of which overlap considerably.[39]

The mechanism of carbon black formation is not well defined. It is likely that no single mechanism can explain carbon black formation from different raw materials and by different processes. Generally speaking, in the production of carbon black, the following basic processes occur: 1) decomposition of the hydrocarbon and its dehydrogenation products; 2) formation of graphitic layers; 3) formation of particles with complex structure; and 4) formation of primary aggregates of these particles.[13,36] The manufacturing process has more influence on product quality than the raw material from which it is made.

The production of carbon black is also possible using a pyrolysis process with scrap tires as the feedstock.[16] When tires are pyrolyzed, a mixture of all the blacks are produced, along with zinc oxide, titanium dioxide, silica and other reinforcing agents. The result is a black-colored char with a carbon content around 88-90% and an ash of 8-12%. These blacks are very coarse and contain much extraneous material, and as a result, have limited market potential without additional processing.[15]

2.3.2 Classification of Carbon Blacks

There are approximately 30 grades of carbon black that commonly are used in rubber products. They are classified by ASTM[57] into classes N100, N200, N300, N500, N600, N700, and N900. In this classification system, they use an initial letter S or N

Table 2.5 Major Carbon Black Classes and Their Typical Applications in Rubber[16]

designation	general rubber properties	typical uses
N110, N121, N166	high abrasion resistance	special tire treads, airplane, off-the-road racing
N220, N234, N299	high abrasion resistance, good processing	passenger, off-the-road, special service tire treads
N326	low modulus, good tear strength, good fatigue, good flex cracking resistance	tire belt, wire carcass, idewall, bushings, weather strips, hoses
N330, N339, N347, N375	high abrasion resistance, easy processing	standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass, retread
N550	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, sidewall, innertubes, hose, extruded goods, V-belts
N650	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, belt, sidewall, seals, friction, sheeting
N660	general purpose, low die swell, smooth extrusion	carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, flooring, MRG
N762	high elongation and resilience, low compression set	mechanical goods,footwear, innertubes, innerliners, mats

followed by three digits. N indicates that the black in rubber has the normal vulcanization rate; S means that vulcanization is slow.[41] The next digit indicates the typical average particle size, the lower the number, the more reinforcing the carbon black. N300 series are the most used carbon blacks, they represent 40% of the entire US carbon black production, N600 and N200 series are the second and third most often used ones.[58] The N100, N200 and N300 series blacks generally are used in treads for abrasion resistance whereas the N300 and N500 series are used in carcasses of radial tires. The N600 and N700 series also are used in carcasses and sidewalls of less critical performance bias and slow speed tires.[16] Some old nomenclatures for carbon black are still in use at present. For example, thermal blacks are identified as MT and FT, representing medium and fine thermal blacks, and furnace blacks are designated as HAF, ISAF, and SAF, meaning high-, intermediate-, and super-abrasion furnace blacks respectively. Table 2.5 shows some common carbon black classes and their typical applications in rubber.

2.3.3 Properties of Carbon Black

The properties of carbon black will significantly affect both rubber processing and product properties. Manufacturers always provide virgin carbon blacks with a detailed specification sheet when selling them. The properties reported typically are ash content, heat loss, 325 mesh sieve residue, pellet crush strength, iodine absorption, DBP absorption and physical properties compared to an IRB reference black in the ASTM D 3192 or D 3191 recipe.[59]

2.3.3.1 Chemical Composition

Most carbon blacks used in the rubber industry are 90 to 99% elemental carbon. Other components found in carbon black could be oxygen, hydrogen, chlorine, nitrogen, sulfur, ash, and moisture.[41] Oxygen and hydrogen are the major constituents other than carbon. Sulfur contents of 0.6% are common in furnace blacks whereas thermal blacks are nearly sulfur free. Some carbon blacks may have as much as 1.5% sulfur. However, studies indicate that, as trapped in the crystal lattice of the black, the contribution of such sulfur to the vulcanizing process is negligible.[41] Some oxygenated functional groups, such as carboxyls, lactones, phenols, and quinines also have been identified on the carbon black surface. Oil furnace blacks with little volatile content usually have a pH of 7.1 to 9.0. Ash content, mostly inorganic substances, normally is low for carbon black used in rubber industry.

The chemical properties of carbon black are not of direct interest to the compounder although undoubtedly reinforcement is influenced by the chemical reactions between the black and the rubber. Carbon black is relatively inert but can be oxidized by concentrated nitric acid.

2.3.3.2 Microstructure and Morphology Properties

The primary characteristics of carbon black that influence the properties of rubber compounds are the particle size, aggregate size, morphology, and microstructure. Because of the fineness of this material and the variety of conditions under which it is produced, precise descriptions of all these properties are difficult to make.[41]

Descriptions of carbon black's microstructures have been developed largely using the electron microscope. Studies indicate that the primary particles of carbon black have spherical (or approximately spherical) shapes, with diameters of 10 to 100 nm. Individual separate particles are rarely found in blacks other than thermal blacks. Carbon black particles generally are connected mutually to form larger structures, such as chains or networks, called aggregates (50 to 500 nm). This characteristic usually is called the structure of the carbon black. The greater the number of particles per aggregate, the higher the structure. Carbon black aggregates may form even larger agglomerates (5 µm or larger), which are held together by van der Waals forces. The structure between carbon black particles and aggregate has a relatively strong strength that resists mechanical destruction, whereas the strength of the connection between aggregates is poor and easily destroyed mechanically during processes like pelletization and mixing into the rubber.[39]

The average number of particles fused into aggregates correlates with the amount of absorbed oils, such as dibutyl phthalate.[60] Dibutyl phthalate absorption number (DBPA)[61] commonly is used by the industry as an index of carbon black structure. The higher the amount of dibutyl phthalate absorbed, the greater the structure. Tinting strength, an indirect method for assessing the overall level of carbon black particle size, is another useful screening method because of its simplicity.[13] This method is based on the reflectance of mixtures of carbon black with a white pigment (zinc oxide) in the oil. The light absorption coefficient is measured and compared with that of a reference black system to determine the relative tinting strength.[62] The value of the tinting strength relates primarily to carbon black particle size, but also depends on the structure and aggregate size distribution.[41] Generally speaking, carbon black tinting strength increases with decreasing particle size but reduces with increasing carbon black structure.[63-65] This method is not suited for very small particle size grades and cannot provide any direct information on the particle size distribution.[13]

Surface area is another very important property in carbon black grade classification. It is also one of the parameters that determine the degree of interaction of the rubber with the carbon black. Thermal blacks are nearly non-porous, so the surface area is inversely proportional to the particle diameter. However, most other blacks have pores, of which the areas are included in surface area measurements but cannot be reached by rubber molecules. Many procedures are available for determining surface area that usually involves the adsorption of specified molecules on the carbon black surface. Three of the most widely used adsorption methods are BET nitrogen adsorption,[66] iodine adsorption,[67] and cetyltrimethyl ammonium bromide (CTAB) adsorption.[68] The BET (Brunauer-Emmett-Teller)[69] nitrogen adsorption method is based on the low temperature Langmuir adsorption theory, which states that the surface area for the solid can be determined from the volume or weight of the molecules that are adsorbed as a monolayer on the solid surface. The BET method has great utility because it is simple to use and generally yields the most accurate surface area determinations compared to other adsorption methods.[13] The adsorption of iodine by carbon black also is commonly used, especially for quality control during manufacturing of furnace blacks. High iodine adsorption indicates a large surface area and also correlates with high reinforcing ability. However, this method is not suitable for blacks with high volatile content or high amounts of extractable matter. For such blacks, adsorption of cetyltrimethyl ammonium bromide (CTAB) from an aqueous solution of the black is preferred.[41] Surface areas of rubber grade carbon blacks can vary from 9 to 143 m^2/g.[70]

2.3.4 Effects on Rubber Reinforcement

The dramatic increase in properties like modulus, hardness, tear strength, and abrasion resistance that appear when carbon black is added to rubber have caused many researchers to try and find the reason for this reinforcement. A review of the mechanism of reinforcement is given by Medalia *et. al.*.[71] Other literatures includes the works of Payne,[52] Lake and Thomas,[72] Bueche,[73] and Dannenberg,[74] *etc.*.

The incorporation of carbon black into the rubber creates interfaces between rigid solid phases and soft solid phases.[13] Due to the interaction between rubber and filler, the polymer molecules are adsorbed onto the filler surface either chemically or physically. Thus the rheological behavior of the rubber is altered, resulting not only in highly non-Newtonian flow, but also in comparatively high viscosity. With the addition of carbon black, the shorter rubber molecules share the stress with longer ones, and the rubber does not break as easily. Carbon black also enhances energy dissipation and improves the fracture properties of rubber materials by adding many points of friction within the molecular system. These effects have a considerable influence on the service performance and service life of rubber products. Also, carbon black surfaces are known to be very heterogeneous because of the presence of different radical groups, which are capable of surface grafting with a polymer matrix.

The main parameters of carbon black that govern its reinforcing ability in rubber are particle size and the general morphology properties. The particle size and its distribution directly determine the surface area of the carbon black.[13] As surface area increases, the viscosity of the uncured stock and the smoothness of extrusions increase, along with the increase of tensile strength, abrasion resistance, and flex resistance. Carbon black structure, such as the degree of irregularity of the carbon black units or the development of branches due to the aggregation of primary particles and the asymmetry of the aggregates, is another parameter. High structure blacks give increased hardness, abrasion resistance, and electrical conductivity, but decrease cut growth and flex resistance.[41] The improved wear is due not only to high surface area, but to the following considerations:[71] high surface activity, narrower distribution of particle size, absence of very large particles that are believed to act as weak spots in abrasion or tensile failure, and more open aggregates. Table 2.6 lists some properties of carbon black compounded SBR and shows a rapid decline in reinforcement as the surface area of the carbon black decreases.[13,41]

2.3.5 Carbon Black Markets

The global demand for carbon black most likely will exceed eight million metric tons in 2004, of which more than one fourth will be used in the North American market.[75] Depending on particle size, structure, purity and methods of manufacture, the prices for different grades of carbon black generally range from 30 to 45 ¢/lb.[2,14] The carbon black markets are split almost equally between hard (N100, N200, N300 series) and soft (N500, N600, and N700 series) grades.[16] About 70% of all carbon blacks is consumed as a reinforcement in tires for automobiles and other vehicles, whereas about 20% goes into other rubber products such as hose, belting, mechanical and molded goods, and footwear. The remaining 10% is used in the non-rubber industry. By far the most important non-rubber applications of carbon black are as a pigment in printing inks and in the plastic industry. The next most important application, especially for the fine particle size, higher-priced blacks, is in the production of black paints and coatings. This is followed by the paper industry, consuming about 4% of the production used in the non-rubber industry. Carbon black is an important pigment for use with xerographic toners. It was reported that over 2000 tons of carbon blacks were consumed in the copier industry during 1990 in the United States.[76] Although this was a relatively small share compared to carbon black used in the tire industry, it was a significant portion of the market for special blacks.

Table 2.6 Effect of Particle Size of Carbon Black on Main Properties of SBR[13,41]

ASTM No.	industry type	average particle size (nm)	surface area (m^2/g)	300% modulus (MPa)	tensile strength (MPa)
N220	ISAF	21	116	17.5	29.8
N330	HAF	30	83	16.7	29.1
N550	FEF	56	41	15.8	23.9
N660	GPF	67	35	13.5	23.5
N990	MT	285	9	4.1	11.3

2.3.6 Health and Safety

Carbon black is one of the safest materials used in rubber production. Unlike other fine particle materials, carbon black does not explode spontaneously. It is difficult to ignite and cannot support combustion. Although it was found that some carbon blacks might contain less than 0.1% of adsorbed polynuclear aromatic hydrocarbons (PAHs), carbon black has not been listed as a carcinogen by the National Toxicology Program (NTP) or by the Occupational Safety and Health Administration (OSHA). Industry investigations of workers in the carbon black producing industries also showed no significant adverse health effect due to occupational exposure to carbon blacks.

2.4 Aluminum Chloride

This section gives a general review of aluminum chloride ($AlCl_3$), an aggressive Lewis acid catalyst used in this project to decompose tire rubber compounds. Good knowledge of this catalyst is necessary as it is desirable to be recovered from the final reaction residue and recycled for reuse. Thus, the chemical and physical properties of pure $AlCl_3$, the properties of mixtures of $AlCl_3$ with other metal halides, and the probable catalytic mechanism for the rubber decomposition reaction are discussed below.

2.4.1 Physical and Chemical Properties of $AlCl_3$

Commercially, aluminum chloride is available as anhydrous $AlCl_3$, hexahydrate, $AlCl_3.6H_2O$, or as an aqueous solution. The properties and uses of the anhydrous and hydrated forms of aluminum chloride are very different.[77] The anhydrous material is a strong Lewis acid that is used widely as an organic synthesis catalyst, while the hydrate is principally used as a flocculating aid. Anhydrous aluminum chloride is a hygroscopic, white powder at room temperature, which reacts with moisture in the air, so that it must be handled in a glove box. The reaction of anhydrous aluminum chloride with water is very violent, evolving heat, hydrogen chloride gas, steam, and aluminum oxide particulates. Some physical properties of anhydrous aluminum chloride are shown in Table 2.7. At atmospheric pressure, $AlCl_3$ sublimes at 180.2 ^{o}C as the dimer, Al_2Cl_6, which dissociates to the monomer beginning at approximately 300 ^{o}C.[77] $AlCl_3$ has a melting point of 173 ^{o}C,[78] a boiling point of 177.8 ^{o}C, and the triple point occurs at 192.6 ^{o}C and 233 kPa.[79] As a molten salt, $AlCl_3$ has an unusually high vapor pressure at moderate temperatures, and the vapor pressure increases nearly exponentially with temperature. Based on this property the overall concept of the process includes separation of the catalyst from the solid residue through sublimation and recondensation. The purpose is to recover the catalyst for reuse and at the same time improve the quality of the solid carbon black product.

Aluminum chloride has a central aluminum atom with only 6 electrons, so it is very electron-deficient. Any electron-deficient atom can act as a Lewis acid (typically Group IIIA elements). By accepting an electron pair, aluminum chloride can act as an acid, according to the Lewis definition. Crystal structure analysis indicates that aluminum chloride exists as the Al_2Cl_6 dimer. The crystal structure can be represented as:

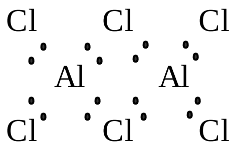


Table 2.7 Physical properties of Anhydrous Aluminum Chloride[80]

property	value
molecular weight	133.34
density at 25 °C, kg/m^3	2460
sublimation temperature, °C	180.2
triple point temperature, °C	192.5 ± 0.2
triple point pressure, kPa	233
heat of formation, 25 °C, kJ/mol	-705.63 ± 0.84
heat of sublimation of dimer, 25 °C, kJ/mol	115.52 ± 2.3
heat of solution, 20 °C, kJ/mol	-329.1
heat of fusion, kJ/mol	35.35 ± 0.84
entropy, 25 °C, J/(K.mol)	109.29 ± 0.42
heat capacity, 25 °C, J/(K.mol)	91.128

. Anhydrous aluminum chloride dissolves readily in polar organic solvents.[80] As a strong Lewis acid, it forms addition compounds with numerous electron donors, such as hydrogen chloride, hydrogen sulfide, sulfur dioxide, sulfur tetrachloride, phosphorus trichloride, ethers, esters, amines, and alcohols. The ability to catalyze alkylation reactions will be lost by complexing aluminum chloride with solvents. However, small amounts of materials can act as “procatalysts” and promote the formation of catalytically active aluminum chloride complexes.[80] It also can react vigorously with other metal chloride to form $AlCl_4^-$. The acidity of aluminum chloride-alkali metal melts varies systematically with the composition, influencing its catalytic behavior.[79]

In aqueous solution, aluminum chloride is hydrolyzed partially to hydrochloric acid (HCl) and aluminum oxychloride (AlClO). For this reason, anhydrous aluminum chloride cannot be obtained by concentrating the solution and calcining the hydrate.[81]

$$AlCl_3 + H_2O \rightarrow 2HCl + AlClO \qquad (2.1)$$

The importance of anhydrous aluminum chloride is due to its catalytic effect in organic reactions including decomposition, polymerization, alkylation, and isomerization.[79] Most of these reactions are classified by chemists as the Friedel-Crafts reactions. The practical applications in a wide variety of manufacturing processes include: cracking high-boiling hydrocarbons to produce gasoline, polymerization of light-molecular-weight hydrocarbons into synthetic resins, lubricants and motor fuels, synthesis of agricultural chemicals, pharmaceuticals, detergents, and dyes.[82]

Due to its importance in the petroleum industry as cracking, refining, and polymerizing agent, the commercial manufacture of aluminum chloride through chlorination of aluminous materials has been investigated thoroughly.[79] In the first step, molten aluminum reacts with chlorine vapor at temperatures between 600 to 750 ^oC. The produced $AlCl_3$ sublimes out of the molten aluminum pool and solidifies on the condenser walls. In some commercial manufacture processes, gamma-alumina is used as the feedstock, and sodium chloride (NaCl) is added to maintain a liquid phase within the reactor and promote the conversion of the solid alumina to aluminum chloride vapor.[83] Sometimes resublimation of aluminum chloride is required to reduce contamination of the reaction products.[80]

Aluminum chloride's catalytic activity depends largely on its purity and particle size.[80] Moisture contamination is also an important concern and must be prevented. Anhydrous aluminum chloride reacts with water or moisture, generating heat, steam, and hydrochloric acid vapors, thus the product containers should be stored inside a cool, dry, well ventilated area and bulk handling systems must be waterproofed. As already indicated above, the product should be transferred only in a nitrogen or dry air system. In storage, some reaction with moisture may occur and over time can lead to a pressure build-up from HCl in the container, so containers should be carefully vented before being opened.[84] Also because of the presence of HCl, iron containers should be avoided because it will result in severe corrosion.

2.4.2 Molten Mixtures of $AlCl_3$ with other Metal Halides

Molten salts have been studied since the early 1900s to gasify coal in the process called molten salt oxidation (MSO).[77,85] Many general characteristics, such as the ability to function like a solvent, good heat transfer characteristics, electricity conductivity, and chemical catalytic properties, make molten salts particularly suitable media for organic reactions. The melt is generally immiscible with hydrocarbon products, which will therefore easily be removed after reaction.

Many studies[78] have been performed on the liquid molecular structure and chemical equilibrium in $AlCl_3/MCl_x$ systems. There is considerable evidence for the existence of a series of anion complexes, $AlCl_4^-$, $Al_2Cl_7^-$, and $Al_3Cl_{10}^-$. The existence of large polyatomic or polymeric ionic species is consistent with the observation that the vapor pressure of $AlCl_3$ is reduced dramatically upon the addition of other salts.

Limited studies on utilizing different double metal halides with aluminum chloride as catalysts in the decomposition of tire rubber also have been conducted.[10-12] An additional metal chloride was frequently used as an "activator" to activate and support aluminum chloride's catalytic activity. A liquid molten bed normally is formed and the melting point of the system is reduced, which results in great process flexibility. Optimum conversion is achieved in fused salts through good contact between the solid reactant and the liquid catalyst. Additionally, the partial pressure of $AlCl_3$ above the liquid also is reduced, which reduces the likelihood of overpressure in the reaction vessel.

Kendall and co-workers[86] studied the solubility of aluminum chloride in several inorganic salt mixtures, including LiCl, NaCl, KCl, NH_4Cl, $CuCl_2$, AgCl, $MgCl_2$, $SbCl_3$, *etc.*. Their method consisted of adding the metallic chloride to aluminum chloride and noting the temperature at which the solid phase disappeared. From the temperature-composition curve, the composition of the double salts formed was determined. Factors influencing compound formation and solubility of fused salts include diversity factor, valence, unsaturation factor, and the atomic number factor.[79] Metals that are much more electropositive or much more electronegative than aluminum provide the most complex and stable compounds with aluminum chloride. Salts of monovalent metals, such as Li, Na, K, form more stable complex compounds than salts of polyvalent metals. Complex compounds of quadrivalent metal salts with aluminum chloride likely are not formed. If a metal can exist in more than one valence form, the complexes produced from its lower valence salt are more stable than those complexes formed from its higher valence salt. If the two metals have the same valences, but one is unsaturated, the complexes of the unsaturated metal salt are easier to form and also with greater stability. Addition compound formation within a given periodic group increases with increasing atomic weight. A typical example of the interaction of $AlCl_3$ with some other metal halides is:[78]

$$2\ FeCl_3 + Al_2Cl_6 \rightleftharpoons 2\ FeAlCl_6 \qquad (2.2)$$

2.4.3 Catalytic Mechanism in Rubber Decomposition Process

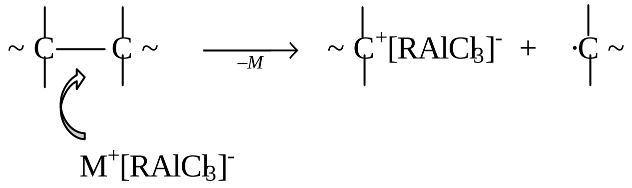
The catalytic effect of aluminum chloride in organic reactions was first announced by Friedel and Crafts as a condensing agent for the syntheses of aromatic hydrocarbons.[82] In the continuation of their work, the reactions in which aluminum chloride could be used as catalyst have been extended to various fields. Some of them are: reaction of organic halides and unsaturated compounds with aromatic and aliphatic hydrocarbons; reaction of anhydrides of organic acids with aromatic hydrocarbons; polymerization of unsaturated hydrocarbons; and cracking of aliphatic and aromatic hydrocarbons.[82] $AlCl_3$ can initiate a chemical cleavage of the monomers from their polymer bond, a reverse process of polymerization. This process involves contact of the polymer and the catalyst under conditions favorable to desired products. The disruptive effect of $AlCl_3$ also has been utilized in petroleum cracking processes.

It was assumed that the formation of intermediate compounds accounts for the origination of the mechanism of reactions catalyzed by aluminum chloride. The fact that aluminum chloride forms complexes with organic compounds is readily explained by the fact that aluminum chloride, having an incomplete octet, is electron deficient, and thus joins with any compound which has an unshared pair of electrons.[79]

$$RX + AlCl_3 \Leftrightarrow RX\bullet AlCl_3 \Leftrightarrow R^+(XAlCl_3)^- \quad (2.3)$$

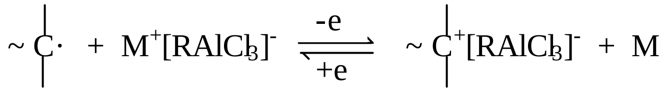
Sangalov and Minsker *et. al.*[87] studied the thermal degradation of polyisobutylene (PIB) in the presence of aluminum chloride complexes. They found that the overall yield of reaction products with the use of acidic catalysts increased from 65 to 90 wt % compared with the thermal process. They also found that under thermal catalytic conditions, in the presence of $AlCl_3$ and a support alkali metal halide, the formation of complex like $M[AlCl_4]$ (M is a group I metal) was likely. With the existence of this complex, the yield of isobutylene content was increased, the quantity of heavy products was preserved, and an appreciable reduction in the temperature of decomposition was also observed. Another aluminum chloride complex catalyst $M[C_2H_5AlCl_3]$ with an increase in acidity was also utilized in their study.

With respect to the polymer degradation, they pointed out a cationic depolymerization mechanism in the presence of aluminum chloride complexes as catalysts. Due to the action of a weakly acidic aluminum chloride complex catalyst, the saturated C-C bond in the main polymer chain can be cleaved randomly at lower temperature:



$$\sim C - C \sim \xrightarrow[-M]{} \sim C^{+}[RAlCl_3]^{-} + \cdot C \sim \qquad M^{+}[RAlCl_3]^{-} \tag{2.4}$$

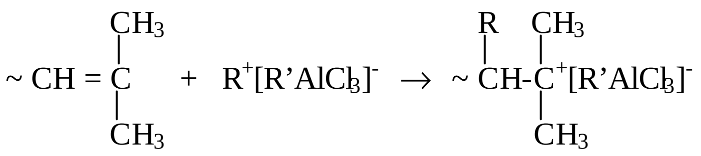
With the macroradicals, further macroion formation occurs by reaction (2.5), the single electron oxidation of free radicals. Thus the thermal degradation of PIB proceeds selectively as a statistical but random free radical degradation of the macromolecules.



$$\sim C\cdot + M^{+}[RAlCl_3]^{-} \underset{+e}{\overset{-e}{\rightleftharpoons}} \sim C^{+}[RAlCl_3]^{-} + M \tag{2.5}$$

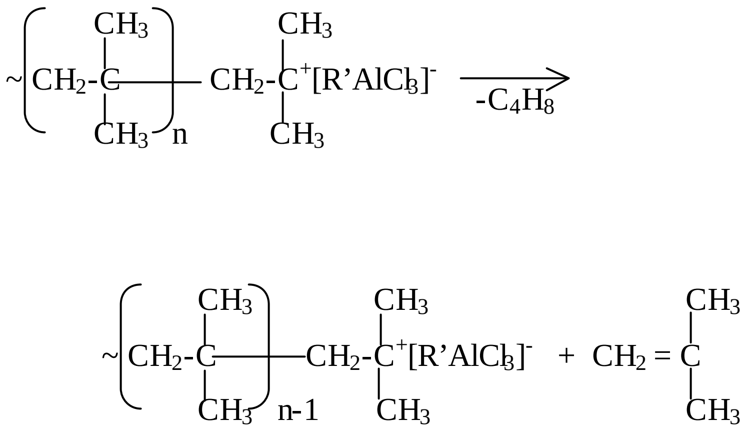
Based on their postulation, the elimination of monomer by a reverse of the cationic isobutylene polymerization reaction is the most thermodynamically probable step in the PIB decomposition process. The use of the specific complex catalyst, $M[RAlCl_3]$, causes the formation of the cationic decomposition center. The occurrence of cationic reactions in the degradation process "effectively reduces the contribution of secondary reactions of the radical centers, which results in an increase in monomer yield and in extended polymer decomposition".[87] In their opinion, the introduction of another metallic halide has no effect on the extent of thermal decomposition, however, the behavior of it in the catalytic decomposition is very likely linked with "the displacement of the equilibrium of reaction (2.4) towards formation of inactive products and a decrease in the role of the decomposition reaction at ionic centers".[87]

Depending on the catalyst nature and process conditions, the main chain cleavage could also be initiated on the terminal C=C bonds. And it also occurs at temperatures much lower than that of purely thermal degradation. Berlin *et. al.*[88] found that it occurred in the thermal catalytic decomposition of PIB with the presence of more active cation in $AlCl_3$ catalyst complex such as $C_4H_9[C_2H_5AlCl_3]$.



$$\sim CH = \overset{CH_3}{\underset{CH_3}{C}} \quad + \quad R^+[R'AlCl_3]^- \rightarrow \sim \overset{R}{C}H-\overset{CH_3}{\underset{CH_3}{C^+}}[R'AlCl_3]^- \qquad (2.6)$$

After the reaction initiation by this route at high temperature, the most likely means of stabilization would be the elimination of isobutylene, the so-called ß-decomposition.[88]

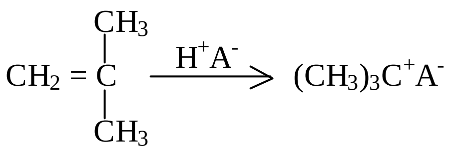


$$\sim\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_n CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}[R'AlCl_3]^- \xrightarrow[-C_4H_8]{} \qquad (2.7)$$

$$\sim\left(CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right)_{n-1} CH_2-\overset{CH_3}{\underset{CH_3}{C^+}}[R'AlCl_3]^- \quad + \quad CH_2 = \overset{CH_3}{\underset{CH_3}{C}}$$

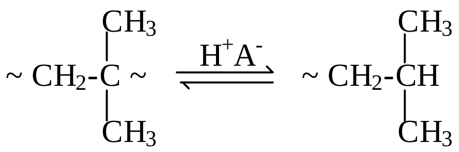
Thermal catalytic break down of butyl rubber (IIR), a copolymer of isobutylene with isoprene (Figure 2.1) in the presence of combinations of $AlCl_3$ with other metal chlorides has been studied by Ivanova, *et. al.*.[12] Their experiments indicated that the breakdown of butyl rubber in the presence of $AlCl_3$ occurred at a much lower temperature and with a considerably higher rate as compared with the purely thermal process. The gaseous products had a higher isobutene content but lower isobutylene content. However, the use of mixed $AlCl_3$ salts with other low acidity metal chlorides led to a substantial fall in the content of isobutene and rise of isobutylene in the gaseous reaction products. This phenomenon was considered to be a characteristic of the depolymerization of PIB blocks in the IIR macromolecules.

The formation of isobutene instead of isobutylene in the presence of an excess of $AlCl_3$ above the stoichiometric amount in the catalyst complexes is most probably due to ionic hydrogenation of the i-C_4H_8 molecules induced by the catalytic action of $HAlCl_4$ and/or HCl.[12,89] The formation of HCl has been demonstrated in conditions of thermal catalytic decomposition of polymers in $AlCl_3$ catalytic systems. The isomerized units of i-C_4H_8 with i-C_5H_8 copolymer could serve as a hydride ions donor. A hypothesis for the isobutane (C_4H_{10}) production scheme can be described as follows.[12]

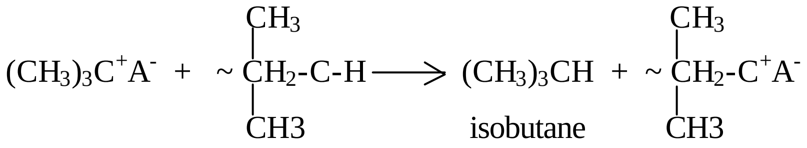


$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \xrightarrow{H^+A^-} (CH_3)_3C^+A^- \qquad (2.8)$$

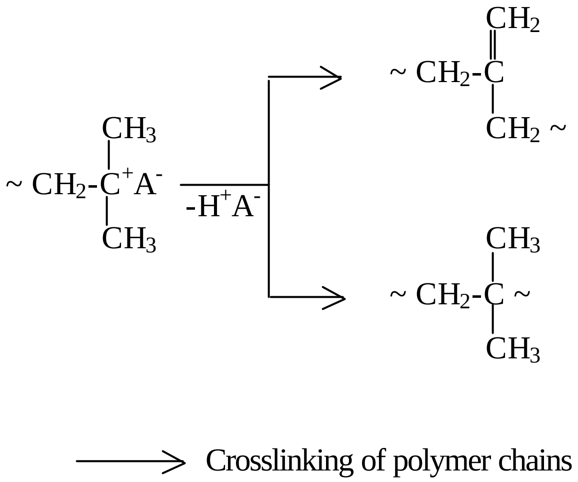
(isobutylene)



$$\sim CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} \sim \; \overset{H^+A^-}{\rightleftharpoons} \; \sim CH_2\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} \qquad (2.9)$$



$$(CH_3)_3C^+A^- + \sim \overset{CH_3}{\underset{CH3}{C}}H_2\text{-}C\text{-}H \longrightarrow \underset{\text{isobutane}}{(CH_3)_3CH} + \sim \overset{CH_3}{\underset{CH3}{C}}H_2\text{-}C^+A^- \qquad (2.10)$$



$$\sim CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}{}^+A^- \xrightarrow[-H^+A^-]{} \begin{cases} \sim CH_2\text{-}\underset{CH_2\,\sim}{\overset{CH_2}{\overset{\|}{C}}} \\ \sim CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\sim \end{cases} \qquad (2.11)$$

$$\longrightarrow \text{Crosslinking of polymer chains}$$

As depicted in the scheme above, the increase in the quantity of isobutene in the gaseous products of butyl rubber decomposition must be accompanied by the rise of the C=C unsaturated bonds in the polymer residue and/or the formation of a crosslinked polymer residue.[12]

All the works[12,87-89] indicated that $AlCl_3$ and its mixture with other metal halides or organic complexes can serve as very effective catalysts in decomposing tire rubbers. However, the component and the composition of the $AlCl_3$ complex profoundly influence the selective thermal catalytic decomposition process, and thus the decomposition products. More investigation is necessarily needed for the complete understanding of this complicated catalytic conversion process.

CHAPTER III

THERMAL CATALYTIC DECOMPOSITION PROCESS

3.1 Introduction

This is a continuation of a research project that began in our laboratory in 1992. The first stage, Phase I, was conducted during the summer of 1992, which evaluated the concept of tire rubber resource recovery by catalytic conversion in a small-scale glass laboratory reactor. Phase I consisted of only three experiments which decomposed tire rubbers in the presence of catalysts in a small 0.3 L glass vessel. The initial study gave little scientific information, but it successfully demonstrated a concept for recycling waste tire rubber. The second stage of this project, Phase II, began nearly a year later in August, 1993. Phase II focused on characterizing raw rubber, the initial design and test of reaction equipment and procedures, and the initial selection of reaction conditions.[90-91] During Phase II, 25 decomposition experiments were completed. Conversion of the tire rubber to hydrocarbon products and a black solid residue product was developed. The laboratory study during this period addressed the effects of reactor operating conditions, such as temperature, pressure, blanket gas composition, *etc.*, on the yield and selectivity of reaction products. The information obtained during this stage provided much experience and insight for this polymer recycling technology. Four U.S. patents[10,92] were published based on the results of the first two research stages during the period 1993-2003.

The Phase II studies provided information on the nature of the fluid hydrocarbon products, but were inconclusive as far as the solid residue characterization due to involuntary contamination during the residue treatment process. For the process to be commercially viable, the process must produce a carbon black product that has considerable market value. Additionally, the reactor used at the time was small (2 L), therefore an increase in size was necessary to confirm parameters before the detailed design of a pilot scale reclamation facility can be conducted. Thus, a new stage of this project, Phase III, began in June 2001 to provide better and more complete information for evaluating the economic potential of this thermal catalytic tire rubber decomposition process. This stage focused on the following three aspects:

1. The effect of process conditions and catalyst selection on the properties of the recovered carbon black products;
2. The effect of process conditions and catalyst selection on the yields and distributions of fluid hydrocarbon products;
3. Methods for recovering the catalyst for reuse.

This dissertation is one of two reports covering the results from the Phase III work. While the emphasis of this dissertation is on the treatment and qualifying the solid product and the catalyst recovery, the second study[93] focuses on the rubber compound decomposition behavior, such as conversion, selectivity, and mechanism. In this chapter, however, for the sake of completeness, we note the most significant aspects of the decomposition study as it applies to this dissertation.

3.2 Raw Materials

3.2.1 Rubber Compound

The rubber compounds used in this study can be divided into two categories. Category 1 includes three model rubber compounds containing typical rubber types used in the tire industry and other known components, including a single grade of carbon black in each case. Category 2 includes three rubber composites chosen to reflect the overall compositions of tires used commercially. All rubber samples were prepared by Cooper Tire & Rubber Company.

The three model rubber compounds were vulcanized styrene-butadiene rubber (SBR), butyl rubber (IIR), and natural rubber (NR). They were ground to create particles approximately 5 mm in size. Each of these rubber compounds contained a single specific type of carbon black in a proportion representative of tires. Model systems were used in an effort to better understand and trace the chemistry during reaction, and to determine whether the vulcanization process used in rubber manufacturing affected the characteristics of the carbon black. The reaction mechanism is reported and discussed elsewhere.[93]

The samples in category 2 are three composites representing specific parts of an automobile tire. The disclosure agreements with the sponsors prohibit the release of the detailed components and compositions of these three samples. The samples are particles approximately 5 mm to10 mm in size.

The primary components of all the rubber feedstock samples are listed below, and the detailed compositions of the three model compounds are shown in Table 3.1.

Table 3.1 Compositions of the Three Model Tire Rubber Compounds[a]

sample designation	402	403	404
major rubber	SBR	butyl	natural
major carbon black	N234	N650	N121
tire part typically used in	tread	innerliner	tread
compositions		Wt. %	
natural rubber (NR)	-	-	57.7
SBR, cold emulsion, 23.5% styrene	54.7	-	-
butyl rubber	-	55.9	-
carbon black N121	-	-	30.0
carbon black N234	35.8	-	-
carbon black N650	-	33.5	-
zinc oxide	1.2	2.8	2.9
stearic acid	0.8	1.1	1.2
dimethylbutyl p-phenylene diamine	1.2	-	1.7
wax	0.6	-	0.9
diary-p-phenylendiamine	0.2	-	0.3
aromatic petroleum oil	4.0	-	3.5
napthenic petroleum oil	-	5.6	-
Elemental sulfur	0.7	0.3	1.2
tert, butyl benzthiazole sulfenamide (TBBS)	0.7	-	0.7
2,2 benzothiazyl disulfide	-	0.8	-
tetramethyl thiuram disulfide (TMTD)	0.1	-	-
total	100.0	100.0	100.0
nonconvertible materials[b]	37.0	36.3	32.9

[a]. Sample compositions were provided by Cooper Tire & Rubber Company.
[b]. Carbon black & zinc oxide were assumed to be nonconvertible materials.

Category 1: three model rubber compounds

Sample 402: Styrene-butadiene rubber (SBR) + carbon black N234

Sample 403: Butyl rubber (IIR) + carbon black N650

Sample 404: Natural rubber (NR) + carbon black N121

Category 2: three tire rubber composites

1. Silica rubber (Silica)

2. White Side Wall rubber (WSW)
3. Black Side Wall rubber (BSW)

3.2.2 Catalyst

Anhydrous aluminum chloride (grade 0025) was used as the primary catalyst. It was supplied by Gulbrandsen Chemicals (La Porte, Texas) in a five-gallon bucket with a PVC liner. Because of the unstable and hygroscopic nature of anhydrous $AlCl_3$ in atmosphere, the storage and transferring were done in a controlled atmosphere glove box, purged with dry nitrogen gas. Handling of this chemical requires rubber gloves and appropriate respiratory protections.

Dual catalyst systems, *i.e.* using a second metal halide as co-catalyst, also were studied during this project.

3.2.3 Gases

All gases except gas chromatograph (GC) calibration gas were supplied by the BOTCO gas company (Bryan, Texas). These gases include argon, used as the reactor blanket gas; helium, used as the gas chromatograph carrier gas; and nitrogen, used as inert medium in the glove box in which catalysts were stored and transferred. The GC calibration gas was supplied by Aeriform Corporation (Houston, Texas), containing methane, ethane, propane, *iso*-butane, *n*-butane and *n*-pentane, which was used to calibrate the gas chromatograph.

Experiments in Phase III use argon or helium as a blanket gas to exclude oxygen from the system while maintaining the necessary system pressure. The blanket gas also sweeps vaporized hydrocarbon products from the reactor to the downstream equipment. The latter is necessary as the catalyst also reacts in the vapor phase. Hence it is desirable to remove the produced hydrocarbons from the reactor as quickly as possible to minimize further chemically cracking to lower value products through continuous contact with the catalyst in the vapor phase.

During the early period of our experiments, we used nitrogen (N_2) as an inert reactor blanket gas. The investigation of $AlCl_3$ catalytic chemistry with time revealed that N_2 is not necessarily sufficiently inert in the presence of $AlCl_3$. The possibility exists that it could participate in the reaction by forming “pyramidal species” complexes like $N_2 \bullet AlCl_3$ at suitable temperatures.[78,94-95] During further reaction, the nitrogen atom could possibly be introduced into the polymer chains. Thus, we replaced nitrogen with argon or helium as the reactor blanket gas from the beginning of Phase III.

3.3 Thermal Catalytic Decomposition Experiment

3.3.1 Experimental System

For the laboratory study, a new apparatus was designed and constructed. This allowed the thermal catalytic decomposition reactions to be performed carefully under controlled conditions. A schematic representation of this apparatus is shown in Figure 3.1. The experimental system may be divided into four sections: 1) the rubber feeding section; 2) the thermal catalytic conversion section; 3) the refluxing and liquid hydrocarbon accumulation section; and 4) the off-gas scrubbing and analysis section. A 10L carbon steel reaction vessel has been used throughout the entire Phase III study. Additional details of the experimental apparatus and procedure are available elsewhere.[93] The experimental variables studied were blanket gas, reactor and condenser temperatures, reactor pressure, reactor residence time, feedstock composition, feeding rate, catalyst composition, and catalyst to feedstock ratio.

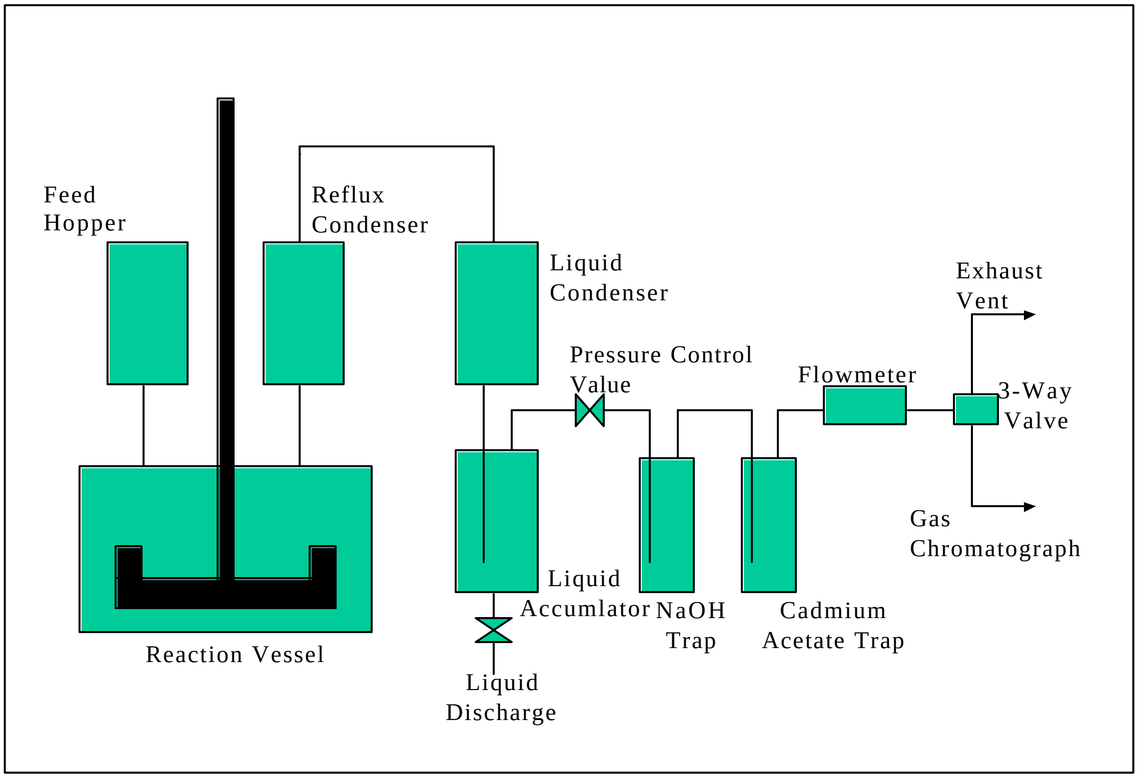


Figure 3.1. Schematic diagram of the experimental arrangement.

3.3.2 Reactor Operating Conditions

Most of the experiments were performed at temperatures between 200 °C and 300 °C and pressures between 274 and 308 kPa (25 to 30 psig). These conditions are sufficient to maintain the catalyst as a fluid inside the reaction vessel. Experience has shown that the thermal catalytic conversion reaction proceeds much more rapidly when the $AlCl_3$ catalyst is a fluid, either in a molten liquid or gaseous state, than when it is solid or granular.[92] When the $AlCl_3$ catalyst exists as a fluid, it is easier to obtain intimate contact between the catalyst and the rubber feedstock surface, thus an increased conversion rate is achieved. Additionally, when $AlCl_3$ catalyst exists primarily as a fluid, heat and mass transfer are more efficient. Reactor temperatures higher than 300 °C, while attainable, generally are not preferred because of possible degradation of the recovered carbon blacks and the high partial pressure of $AlCl_3$ vapor. Higher temperatures also waste energy resources.

Optimized reactor operating conditions provide rapid conversion of rubber feedstock into hydrocarbons. With the optimized conditions, rubber samples having dimensions as large as 5 mm are as efficiently as feedstock with 30 or 40 mesh (about 0.5 mm) particles. Furthermore, the rapid chemical conversion rate results in shorter reactor residence times, reducing the cost of energy required to maintain the reaction system at temperature.

Anhydrous aluminum chloride ($AlCl_3$) was used as the primary catalyst in all experiments during the Phase III study. In some experiments, $AlCl_3$ was used as the sole catalyst component, while in other cases dual catalyst systems containing $AlCl_3$ and a second metallic halide were employed.

Approximately 40 runs were completed between June 2001 and April 2003. The first fifteen runs (III-00A to III-00N and III-0S1) were performed during equipment setup and testing stage. Products from these fifteen runs are not discussed below, but the information obtained was used in the interpretation of other runs. The next fifteen runs (III-1 to III-8, with suffixes A, B, C, *etc*. denoting replications of a particular set of reaction conditions) were performed using three specific model tire rubber compounds with known compositions. Five runs (III-9 to III-11) were performed on rubber samples in category two, and another five runs were performed to study the behavior of the dual salts catalyst system. Table 3.2 summarizes the reaction operating conditions of each experimental run.

3.4 Liquid Hydrocarbon Products

The thermal catalytic decomposition of rubber is an exothermic process that produces volatile hydrocarbons, which leave the reactor as vapors. The yield and composition of the hydrocarbons depend upon the reactor operating conditions, catalyst composition, catalyst/ rubber feedstock ratio, and the specific rubber sample fed.

The hydrocarbon products recovered from this process are generally low molecular weight hydrocarbons having less than fifteen carbon atoms, particularly those having from three to twelve carbon atoms. The specific hydrocarbons evolved can be used as feedstocks for various synthesis reactions, or as octane enhancers for gasoline.

Table 3.2 Reaction Operating Conditions

run no.	rubber feedstock		blanket gas	reactor temperature (°C)	reflux condenser temperature (°C)	pressure (kPa)	catalyst	catalyst/ rubber ratio
	rubber type	carbon black (type/wt.%)						
III-01D	SBR	N234/35.8	argon	225	70	274	$AlCl_3$	1.23
III-02B	NR	N121/30.0	argon	225	70	274	$AlCl_3$	1.26
III-03	IIR	N650/33.5	argon	225	70	274	$AlCl_3$	1.38
III-03A	IIR	N650/33.5	argon	225	70	274	$AlCl_3$	1.36
III-04	SBR	N234/35.8	argon	250	70	274	$AlCl_3$	1.23
III-06	SBR	N234/35.8	argon	225	100	274	$AlCl_3$	1.23
III-07	SBR	N234/35.8	argon	225	70	274	$AlCl_3$	1.23
III-08	SBR	N234/35.8	argon	225	70	274	$AlCl_3$	1.54
III-09	Silica	n/a	helium	225	70	274	$AlCl_3$	1.07
III-09A	Silica	n/a	helium	225	70	274	$AlCl_3$	1.08
III-10	WSW	n/a	helium	225	70	274	$AlCl_3$	1.12
III-11	BSW	n/a	helium	225	70	274	$AlCl_3$	1.13
III-12	SBR	N234/35.8	helium	225	70	274	$AlCl_3$/NaCl (3:2)	1.49
III-13	SBR	N234/35.8	helium	225	120	136	$AlCl_3$/NaCl (3:2)	1.2
III-14	NR	N121/30.0	helium	225	70	136	$AlCl_3$/NaCl (3:2)	16.3

n/a - data not available.

Both uses lead to high market values for the products. This portion of the conversion products is gathered as two fractions: one is referred to as naphtha, which is the content condensed at the system pressure in the 0 °C trap that remains as a liquid at room temperature after the experiment; the other fraction is LPG, which does not condense in the above conditions but leave the accumulator as vapor. (The composition of the LPG product is such that it easily could be liquefied and stored as liquid under normal process conditions.) The total quantity of naphtha and LPG is referred to as the yield of liquid products converted from rubber feedstock. The conversion to liquid hydrocarbons is quantified by defining the liquid yield as

$$\text{liquid yield} = \frac{\text{naphtha mass} + \text{LPG mass}}{\text{rubber feedstock mass}} \tag{3.1}$$

The liquid yield is a useful parameter for evaluating process economics, but it cannot reach 100% because nonconvertible materials are present in the rubber feedstock. A more useful measure of the effectiveness of the conversion process can be obtained by calculating the volatile hydrocarbon products conversion rate based on the convertible fractions of rubber feedstock. The liquid conversion, defined as shown in equation 3.2, provides such a measure.

$$\text{liquid conversion} = \frac{\text{naphtha mass} + \text{LPG mass}}{\text{rubber feedstock mass}\,(1 - \text{fraction nonconvertibles})} \tag{3.2}$$

The total carbon black and zinc oxide in the tire rubber compound (Table 3.1) are assumed to be nonconvertible materials.

Both the SBR and NR rubber samples yield 23 to 27% by weight of liquid products, while the yield from butyl rubber is significantly higher, ranging from 36 to 41%. The ideal conversion of total liquid products range from 35 to 40% for SBR and

NR, and from 57 to 64% for the butyl rubber samples. The liquid products produced from the rubber samples in category two are relatively lower, at 18% by weight of rubber feedstock for the Silica rubber, 22% for WSW rubber and 21% for BSW rubber samples. There probably is a larger fraction of nonconvertible materials in these samples, but the precise compositions are not available to us for proprietary reasons. The total hydrocarbon products yield was unchanged, but the product spectrum exhibited a shift in favor of the naphtha fraction for the dual catalyst systems. This is positive as it has higher commercial value. The hydrocarbon yields are shown in Table 3.3.

Table 3.3 Experimental Hydrocarbon Yields

run no.	rubber feedstock	non-convertibles	total liquid		naphtha		LPG	
			liquid yield	liquid conversion	liquid yield	liquid conversion	liquid yield	liquid conversion
		(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
III-01D	SBR	37.0	23.2	36.9	1.3	2.1	21.9	34.8
III-02B	NR	32.9	22.8	34.0	1.8	2.7	21.1	31.3
III-03	IIR	36.3	36.2	56.9	2.7	4.2	33.5	52.7
III-03A	IIR	36.3	41.0	64.4	2.3	3.6	38.8	60.8
III-04	SBR	37.0	22.1	35.1	1.9	3.0	20.2	32.1
III-06	SBR	37.0	26.1	41.5	1.3	2.1	24.8	39.4
III-07	SBR	37.0	36.9	58.5	0.6	1.0	36.2	57.5
III-08	SBR	37.0	15.5	24.6	0.0	0.0	15.5	24.6
III-09	Silica	n/a	5.9	n/a	2.2	n/a	3.7	n/a
III-09A	Silica	n/a	17.9	n/a	1.8	n/a	16.1	n/a
III-10	WSW	n/a	22.4	n/a	0.8	n/a	21.6	n/a
III-11	BSW	n/a	21.4	n/a	0.8	n/a	20.6	n/a
III-12	SBR	37.0	28.2	44.8	0.0	0.0	28.2	44.8
III-13	SBR	37.0	19.6	31.1	9.7	15.4	9.9	15.7

n/a - data not available.

The detailed description and discussion of the experimental system setup, control, process operation, and hydrocarbon products composition and properties are provided elsewhere.[93]

CHAPTER IV

SOLID RESIDUE TREATMENT AND PHYSICAL EVALUATION

4.1 Characteristics of Solid Residue

The material remaining in the reactor after the experiment is completed (solid residue) typically is composed of carbon black, catalyst, nonvolatile hydrocarbons formed during the decomposition of rubber, and inorganic ash. The solid residue usually contains large amounts of catalyst, even when the catalyst was pure $AlCl_3$. This is a surprising result, because the vapor pressure of pure $AlCl_3$ at reactor conditions is such that it should evaporate from a physical slurry of molten salt and solid organic material. There also is no evidence of unreacted rubber remaining in the solid residue after the completion of the run.

When pure $AlCl_3$ is used as the catalyst, the physical state of the solid residue near ambient temperature also is unusual. When the salts (both pure and mixed) are heated sufficiently to obtain a molten state and then cooled, they solidify to a rock-hard state upon cooling to ambient temperature. When binary salt mixtures were used, the behavior of the reactor residue containing the carbon black and nonvolatile hydrocarbons was similar to that of the salts. However, when only $AlCl_3$ was used, the residue did not solidify upon cooling. Instead, its consistency became “gooey”, much like that of a thick mud.

4.2 Solid Residue Treatment Procedures

After the decomposition run was completed and the reactor cooled sufficiently, the remaining residue in the reaction vessel was removed from the reaction vessel and subjected to a series of treatments intended to recover products with significant economic value. The residue treatment procedures are illustrated in Figure 4.1. Removal of the residue was straightforward for the experiments using pure $AlCl_3$, because the physical state of the residue was sufficiently soft that it could be scooped from the reactor using a large spatula. The rock-hard dual salt residues could be removed by chipping them away with a sharp tool, but only with great difficulty. As a result, the residues from the dual salt experiments were removed by opening the reactor at elevated temperatures (~140 °C) while the salt still was in a molten state.

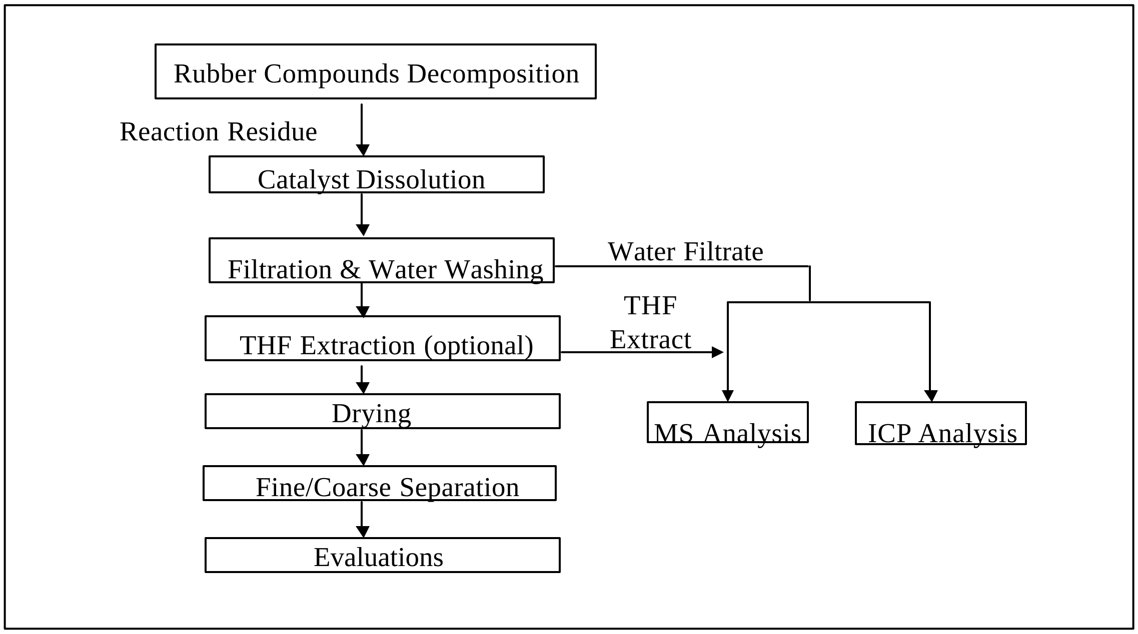


Figure 4.1 Carbon black recovery procedures.

4.2.1 Catalyst Removal

The catalyst most easily is removed from the residue by hydrolysis of the $AlCl_3$ and $MgCl_2$ and dissolution of NaCl and KCl in water. This was done by mixing the residue with a hydrochloric acid (HCl) solution with a pH value of approximately 3, and stirring continuously for about 24 hours. This procedure hydrolyzed or dissolved nearly all catalysts present within the solid residue. Acid is used rather than pure water to inhibit the formation of the insoluble Al_2O_3 species, minimizing the introduction of grit into the residue. The reactions involved in the hydrolysis procedure are described by Cotton & Wilkinson[78] as

$$AlCl_3\text{ (solid)} + 3H_2O\text{ (gas)} \rightarrow 6HCl\text{ (gas)} + Al_2O_3\text{ (solid)} \tag{4.1}$$

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \tag{4.2}$$

$$2AlCl_3 + 10H_2O \rightarrow [Al_2H_{18}O_{10}]^{+4} + 2H^+ + 6Cl^- \tag{4.3}$$

$AlCl_3$ reacts violently with water, evolving heat and a gas consisting of hydrogen chloride and steam. The reaction is sufficiently exothermic that the temperature of the residue slurry easily can rise to 130 °C, which is above the boiling point of water. Also, because reactions 4.1 through 4.3 result in the net production of H^+ and Cl^-, the acidity of the solution increases. The hydrolysis procedure therefore must be carried out with extreme care.

4.2.2 Residual Wash and Filtration

The residue slurry produced by the hydrolysis step was filtered to separate the organic solids from the aqueous liquid. The resulting filter cake (mostly carbon black) was washed with copious amounts of deionized water to remove any water-soluble contaminants. During the washing procedure, the pH value of the wash filtrate was measured and the filtrate samples were collected for a further characterization with Inductive Coupling Plasma (ICP) and Mass Spectrometry (MS).

4.2.3 Tetrahydrofuran Extraction (Optional)

Selected water-washed residues were subjected to a Soxlett extraction using tetrahydrofuran (THF) to determine the fraction of THF soluble nonvolatile hydrocarbon material present in the residue. THF was used both because it is an effective solvent for heavy hydrocarbon molecules and because it commonly is used as a benchmark solvent to distinguish between “soluble” and “insoluble” hydrocarbon species. The THF extracts were analyzed by mass spectrometry (MS) to determine the nature of the nonvolatile hydrocarbon species.

4.2.4 Drying

After water washing and filtration, the wet residue cake normally contained large amounts of water (60 to 80% by weight), so the residue samples were dried in air in a convection oven overnight. Two significant problems were encountered with the solid residue drying procedure: the oxidation (decomposition) of the carbon black and nonvolatile hydrocarbons, and the incomplete removal of water.

During the early runs, we did not expect significant oxidation to occur at solid residue temperatures of 100 to 120 ^{o}C, because this is well below the ignition temperatures of most hydrocarbons. However, on occasion we did observe a brownish ash layer on the dried material after the solid residue was washed with water and dried overnight at 100 ^{o}C. Once, brown "smoke" was observed coming from the drying oven. The consumption of the residue material by oxidation caused difficulty in closing the mass balances. After discovering the possibility of carbon black oxidation during drying at 100 °C to 120 °C, the drying procedures were adapted. Temperatures were lowered to 80 to 90 ^{o}C and processes were monitored carefully. As a result, the drying process was extended to more than 48 h. Sometimes, although the sample appeared dry, it is suspected to still contain high moisture.

Because of the difficulties encountered with oxidation, we also evaluated vacuum drying. A vacuum oven operated at approximately 125 ^{o}C and purged with argon was used to remove the large quantities of water present in the residue cake. The weight loss, most of which is assumed to be water, was as much as 80% of the initial un-dried sample weight. The vacuum drying procedure is safer and easier to control, and it produced in a better final product and better product particle size distributions. Thus, we suggest that the vacuum drying method should be used in any future experiments.

The most likely explanation for the unexpected oxidation of the solid product during drying is the large surface area of the residue product. The large surface area may allow for reaction of the oxygen with the nonvolatile hydrocarbon, perhaps catalyzed by the carbon surface. As the reaction begins to occur, poor heat transfer through the powder allows the surface temperature to rise, thereby accelerating the reaction. Non-uniform oven temperature profiles also might contribute because higher temperatures than expected may exist in some areas, especially adjacent to the bottom and walls of the oven. However, sufficient monitoring of the temperatures in the oven were done to provide strong evidence that spontaneous oxidation can occur at surprisingly low temperatures. The amount of decomposition of solid residue material varied from experiment to experiment. This may be due to differences in composition of the nonvolatile hydrocarbons on the carbon black surface, or to differences in heat transfer characteristics of the powder allowing for more or less spontaneous temperature rise. Spontaneous oxidation can be suppressed by removing the air, which can be done either by purging the oven with inert gas or by operating the oven under vacuum.

4.3 Physical Characterization of the Solid Product

After performing the residue treatment procedures described in the previous sections, the solid black powder can be described as “carbon black” with both organic and inorganic impurities present. The organic impurities are nonvolatile hydrocarbons, mostly highly unsaturated, hydrogen-lean compounds, with sufficiently high boiling points that they remain in the reactor after being formed. These nonvolatile hydrocarbons probably are adsorbed on the surface of the carbon black particles, so they are not easily removed during the treatment steps. They can be removed only by THF extraction or vacuum thermal treatment (see Chapter V). The inorganic impurities are nonconvertible materials present in the rubber compound feedstock. They include metal supports and sulfur used in the rubber manufacture process, metal compounds from the catalyst, and ash. The content of both organic and inorganic impurities are discussed in Chapter V.

4.3.1 Carbon Black Yield

The final black solid residue consists of the recovered carbon blacks that were used originally as a reinforcement filler in rubber compounds (see Table 3.1), inorganic components (*e.g.* zinc oxide) and carbonaceous deposits that may have been formed during the rubber conversion process. Carbonaceous deposits are defined here as heavy molecular weight hydrocarbons (mostly aromatics and cyclic compounds) both chemically and physically bound to the carbon black surface. The presence of these carbonaceous compounds was confirmed by TGA and GC/MS composition analysis (described in detail in Chapter V).

By means of a mass balance it is possible to make a rough estimate of the amount of this carbonaceous deposits. The carbon black yield is defined as

$$\text{carbon black yield} = \frac{\text{mass of treated solid residue}}{\text{mass of rubber feedstock}} \tag{4.4}$$

There are two primary sources of inaccuracy when calculating the carbon black yield. The loss of weight due to oxidation during the drying process will cause the carbon black yield to be too small, while incomplete drying will cause the yield to be too large.

The rubber feedstock contains approximately 30 to 36% carbon black and 1 to 3% inorganic components (ZnO). These two components are assumed to be nonconvertible materials (see Table 3.1) in rubber feedstocks that end up in the solid residue. Therefore, if no carbonaceous deposits are formed and the catalyst is removed completely during the residue treatment, the process should yield approximately 33 to 37% recovered carbon black products (see Table 3.1). Higher carbon black yields suggest the formation of carbonaceous deposits during the decomposition process. The fraction of carbonaceous deposits formed is

$$\text{fraction carbonaceous deposits} = \text{carbon black yield} - \text{nonconvertibles in feed} \qquad (4.5)$$

The carbon black yields and the estimated carbonaceous deposits are summarized in Table 4.1. All cases show the production of carbonaceous materials. Mass balance calculations including the fluid hydrocarbon products also support this result.[93] Although no “unreacted” rubber is present in the residue, there likely are significant quantities of longer chain hydrocarbons in the solid products.

The yield of fluid hydrocarbon products from the rubber decomposition reaction is lower than we expected, while significant amounts of nonvolatile hydrocarbons appear in the solid residue. The most likely explanation is the hydrogen deficient reaction environment with respect to the reaction stoichiometry (also see discussion in Chapter

VI). The hydrogen to carbon ratio is higher in the fluid products than in the original rubber, therefore other products must be formed that have lower hydrogen to carbon ratios (the nonvolatile hydrocarbons). The addition of a hydrogen donor source, such as hydrogen or methane, might increase the hydrocarbon product yield while improving the quality of the carbon black product.

Table 4.1 Carbon Black Yields

	rubber feedstock				
run no.	rubber type	carbon black (wt. %)	non-convertibles (wt. %)	carbon black yield (wt. %)	fraction carbonaceous deposits (wt. %)
III-01D	SBR	N234/35.8	37.0	47.3	10.3
III-02B	NR	N121/30.0	32.9	63.2	30.3
III-03	IIR	N650/33.5	36.3	44.0	7.7
III-03A	IIR	N650/33.5	36.3	51.9	15.6
III-04	SBR	N234/35.8	37.0	60.0	23.0
III-06	SBR	N234/35.8	37.0	77.8	40.8
III-07	SBR	N234/35.8	37.0	77.3	40.3
III-08	SBR	N234/35.8	37.0	n/a	N/a
III-09	Silica	n/a	n/a	70.4	N/a
III-09A	Silica	n/a	n/a	71.3	N/a
III-10	WSW	n/a	n/a	67	N/a
III-11	BSW	n/a	n/a	68.3	N/a
III-12	SBR	N234/35.8	37.0	n/a	N/a
III-13	SBR	N234/35.8	37.0	67.1	30.1

n/a – data not available.

4.3.2 Solid Particle Size Distribution

U.S. standard sieves were used to determine the distribution of particle sizes in the solid product. These sieves with mesh numbers of 18, 25, 35, 50, 120, 230, 325, 400, and 500 have openings of 1000, 710, 500, 300, 125, 63, 45, 38 and 25 μm, respectively. The sieve pans were 25 mm (1 in) in height and 200 mm (8 in) in diameter. The testing procedures followed ASTM D 1511-98.[96]

In most cases, the recovered solid product appears to be a soft fine powder after washing and drying. The samples were crushed gently to break up agglomerations formed during drying until the powder passed through sieves No. 18 and 25, and then transferred to a sieve assembly with sieves of 35 to 500 mesh from top to bottom. The sieve assembly then was shaken for 1 hour on an automatic sieve shaker. The particle size distribution was obtained by calculating the fraction of residue retained on each sieve and the bottom receiver pan.

The particle size distributions of the recovered solid product are listed in Table 4.2. The appearances of the particles and the particle sizes differ from run to run, primarily because of the different rubber feedstock used. The catalyst system used also affects the particle size distribution. Generally speaking, most products were retained on the sieves with sieve Nos. 50, 120 and 230. Products recovered from butyl rubber have coarser particles than those recovered from SBR and natural rubber. Products from silica, WSW and BSW rubber feedstock have finer particles than those from SBR, NR and IIR rubber. The results also indicated that the particle size decreased significantly when dual salts were used as catalysts. Other reaction conditions, such as the reactor temperature and pressure, have little effect on the particle size distribution. Comparisons of solid products particle size distributions from different rubber feedstocks and from different catalyst systems are showed in Figure 4.2 and Figure 4.3 respectively.

The current residue treatment procedure produces 80 to 90% of the products with sizes larger than 230 mesh. Only a few particles pass through the 325 mesh sieve and hardly any pass through the 500 mesh sieve. However, the results suggest that the carbon black material could have finer particle size distributions if a vacuum drying process is employed. A wet sieving process also was used to assess the particle sizes. Selected dried carbon black samples were re-slurried with deionized water sieved in suspension using the same sieve assembly with the help of a soft brush. All particles in the slurry passed through the 500 mesh sieve without difficulty. This leads to the conclusion that the larger particle sizes observed by dry sieving result from particle agglomeration that occurs during drying, therefore the solid product from this process has the potential to meet the requirements of sieve residues for industry applications as determined by ASTM method[97].

4.3.3 Composition Analysis of Wash Solution

The aqueous solution used to wash the solid products (as described in 4.2.2) were analyzed by Inductive Coupling Plasma (ICP) and Mass Spectrometry (MS). ICP detects inorganic materials present in the sample, even at very low concentrations, while MS was used to obtain a qualitative indication of the molecular weight of organic compounds contained in the sample.

Table 4.2 Particle Size Distribution of the Solid Product (wt. %)[a]

run no.	sieve no.[b]						
	50	120	230	325	400	500	>500
III-01D	24.40	25.61	33.66	8.52	4.03	2.97	0.80
III-02B	52.34	33.44	9.91	2.83	0.37	0.07	0.02
III-03A	60.15	28.06	10.86	0.89	0.03	0.00	0.00
III-04	18.65	56.93	19.43	4.63	0.35	0.00	0.00
III-06	19.27	30.73	40.36	5.59	2.09	1.52	0.42
III-07	25.02	35.11	32.89	6.09	0.83	0.04	0.00
III-09	0.00	13.28	60.41	21.33	4.32	0.61	0.04
III-09A	0.00	17.96	52.70	23.77	5.23	0.00	0.00
III-10	0.00	10.30	58.21	17.16	5.25	0.00	0.00
III-11	0.00	21.10	63.29	13.06	2.54	0.02	0.00
III-13[c]	15.30	35.52	24.35	13.95	9.08	1.80	0.00
III-14[c]	0.00	0.00	26.40	42.20	21.60	9.70	0.00

[a] based on the total solid product weight from each run.

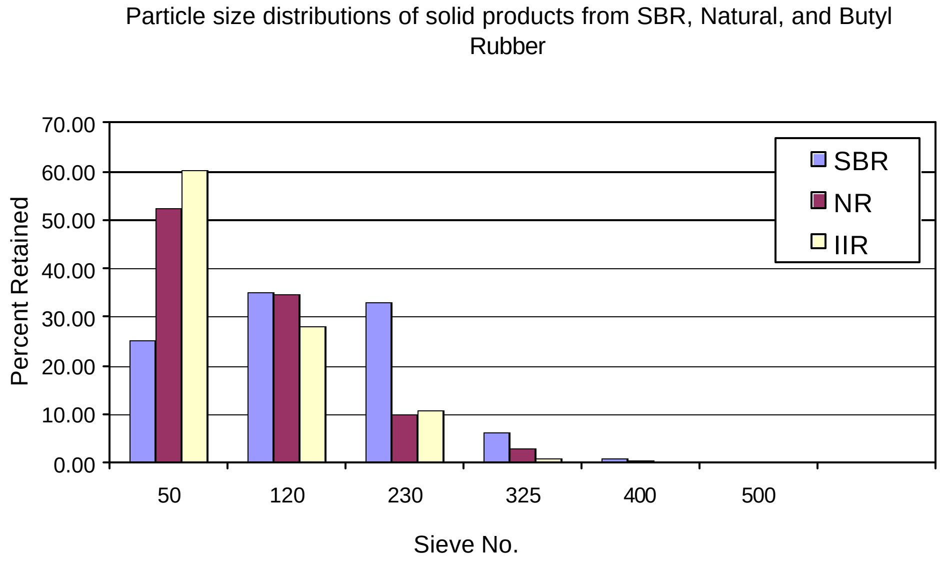
[b] calculated by the residue retained on each sieve.

[c] dual salts system was used as catalyst.

Table 4.3 Quantitative and Qualitative ICP Analysis of Water Washing Filtrates

sample no.*	Al^{3+} concentration (ppm)	qualitative components scan
1	1427	Na/Mg/Al/Si/V/Cr/Mn/Fe/Zn/Cd/Ta
2	717	Na/Mg/Al/Si/S/Ca/Cr/Mn/Fe/Zn/Ta
3	8	Na/Al/Si/S/Fe/Zn/Nb
4	4	Al/Si/S/Fe/Zn/Nb
5	0.2	Si/S/Fe/Nb
deionized water	0	Si/S/Nb

* samples were collected after every 4 L water was used to wash the solid residue.
sample 5 was collected after the final wash.


Particle size distributions of solid products from SBR, Natural, and Butyl Rubber

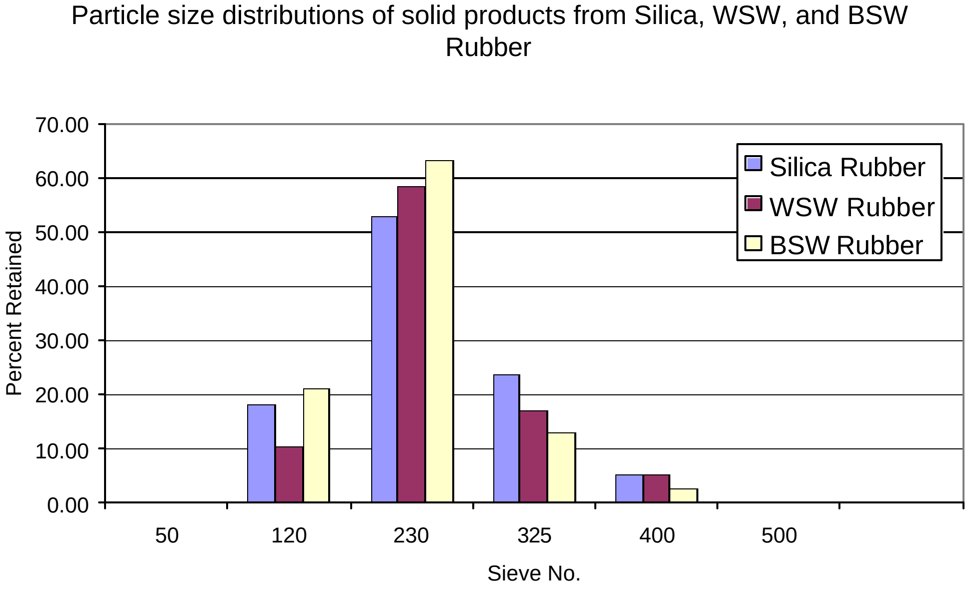
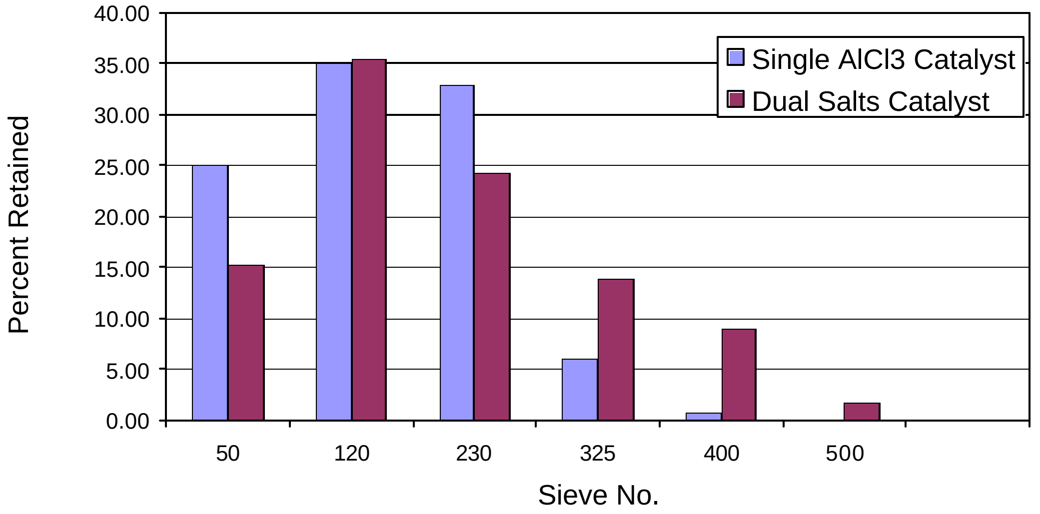
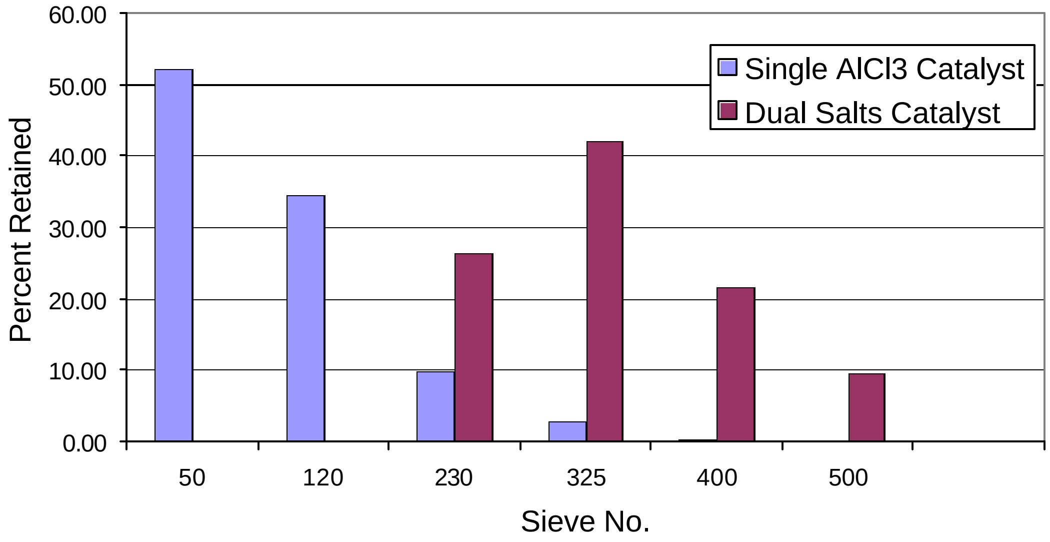

Particle size distributions of solid products from Silica, WSW, and BSW Rubber

Figure 4.2 Particle size distributions of solid products from different rubber feedstock



Particle size distributions of solid products from SBR with different catalyst system



Particle size distributions of solid products from NR with different catalyst system

Figure 4.3 Particle size distributions of solid products using different catalyst systems

The initial wash water has both strong chloride and gasoline odors and appears dark brown in color. The concentration of Al^{3+} was as high as 1500 ppm. After more water was used during the washing process, both the odor and the color of the filtrates became clear, and the concentration of Al^{3+} decreased significantly. The quantitative and qualitative ICP analysis results of the water washing filtrates are listed in Table 4.3.

The elemental analysis by ICP suggests that several metals are present in the initial filtrate. This is consistent with the carbon black bulk elemental composition analysis, which is described in Chapter V. Some of the metal elements most likely come from the carbon steel reaction vessel employed during the decomposition runs, because they are not present in any of the feedstocks, or in the washing water. Significant quantities of Mn, Si, S, Cr, Fe, Mg, and V are present in the type of carbon steel from which the reaction vessel was constructed.[98] The weight loss of the reactor during each run was as much as 20 g. This observation is consistent with the previous studies (Phase II) during 1994/1995. Hence, to reduce the contamination caused by the reactor corrosion, it may be advantageous to use a stainless steel reactor vessel in future research.

The first wash solution sample also was subjected to a qualitative GC/MS analysis. The solution first was filtered using VWR grade 413 general-purpose filter paper to remove any suspended solid material from the aqueous solution. The solid material was dissolved in THF and both the THF and the aqueous solution were analyzed by GC/MS. The GC/MS results are listed in Table 4.4.

Table 4.4 Qualitative GC/MS Analysis of the First Water Filtrate Sample

	moleclar weight groups (strong groups are given in ***bold italics***)
THF solution	***83.5, 90.9, 95, 101.6, 109***, 119.9, 131.1, 145.8, 161.2, ***170.6***
aqueous solution	91.1, 93.1, 119.1, 133.2, ***137.2, 155.1***, 157.1, 191, 193.1, 207.1, 228.3, 246, 251.1, ***267.1***, 268, 269.1, 270.1, 293.2, 323.1, 339, ***355.2***, 356.2, 357.2, 358.2, 359.1

It is clear from Table 4.4 that some heavy compounds are present in the first water wash sample. These compounds are probably hydrocarbons or metalorganic compounds. The THF solution appears to contain lower molecular weight compounds, which probably include some hydrocarbons in the range of C_{10} to C_{12}. Further investigations are needed to characterize the heavy compound in more detail.

CHAPTER V

CARBON BLACK CHARACTERIZATION

5.1 Introduction

The carbon blacks recovered from the tire rubber decomposition process could be different in structure, morphology and chemical composition from that of the carbon blacks used as reinforcing filler in that particular rubber compound. Typical carbon black properties that determine its performance in rubber include the particle size distribution, the aggregate size, the surface activity and the agglomerate tendency.[99] Other important control parameters are the moisture, volatile, and ash contents. The recovered carbon black will be contaminated to some extent by various additives present in the original rubber compound and by the hydrocarbon products produced during the rubber conversion. Unremoved catalyst and extraneous materials originating from the solid residue workup process and experimental equipment also may add some contamination to the product. A serious concern is that the degradation of carbon black, *i.e.* the transformation of high structure carbon black into a form of graphite with no reinforcing ability needed for the majority of applications, could also take place during the rubber decomposition process. Thus the characterization of the recovered carbon black quality is required to assess its market value and contribution to the economic viability of this tire rubber decomposition process.

The recovered carbon black cannot replace commercial carbon black in some applications unless it possesses properties similar (or superior) to that of commercial carbon blacks. The largest market (about 90%) for carbon black is in the tire manufacturing industry where the carbon black enhances tear strength and improves modulus and wear characteristics of tires. Additional applications are found in plastics, filters, printing inks, paints, and toners. The characterization work is intended to assign a qualitative carbon black grade to the recovered product, which will suggest what applications it is suitable for, and hence its approximate economic value.

In this chapter several evaluation procedures that determine the characteristics of the recovered carbon black product are described. An approximate bulk composition is obtained by thermogravimetric analysis (TGA). The elementary composition analysis is performed by the energy dispersive X–ray spectroscopy (EDX). The hydrocarbon oil extracted from the recovered carbon black is analyzed by GC-MS. The structure and morphology of carbon black are studied through transmission electron microscopy (TEM), and the specific surface area is measured by BET nitrogen adsorption. Commercial carbon black grades N220, N330, and N660 are used as reference materials.

5.2 Sample Preparation

The carbon black samples described here were recovered from the thermal catalytic decomposition of tire rubber compounds. The reaction conditions for each run are summarized in Table 3.2. The detailed description of the reaction process, resulting products and decomposition mechanism are reported in Chapter III, Chapter IV, and elsewhere[93]. The commercial carbon black grade N220, N330, and N660, used as reference samples were provided by the Sid Richardson Carbon Co., Akron, Ohio.

These three grades of commercial carbon blacks are used widely in the tire industry as filling materials.

5.3 Composition Analysis

The main differences in composition between the recovered carbon black and the commercial virgin carbon black filler are the volatile content and the ash content. The recovered carbon black contains almost all of the inorganic materials originally present in the rubber feedstock. In addition, the final carbon black product may contain catalyst salt if the washing and filtration process is not efficient. Contamination also can come from the corrosion of the carbon steel reactor, and hence contribute to a higher ash content of the recovered carbon black. The volatile material discussed in this chapter is mostly hydrocarbons that are adsorbed on the carbon black surface and do not vaporize at 100 ^{o}C. This material is considered “volatile” compared to fixed carbon and inorganic ash contained in carbon black, but may be referred to as “nonvolatile hydrocarbons” else in this dissertation when compared to hydrocarbon products that leave the reactor as vapors.

5.3.1 TGA and Ash Content Determination

Thermogravimetric analysis (TGA) is a technique in which the weight loss of a sample is monitored as a function of temperature or time as the sample specimen is subjected to a controlled sequence of elevated temperatures. TGA offers a rapid analysis because of the small sample size and fast heating rates. This method was used to characterize the moisture, volatile, fixed carbon and ash contents of the carbon black samples. ASTM method D 1506 – 99[101] was also performed to confirm the ash content of carbon black samples.

5.3.1.1 Apparatus

The TGA experiments were performed with a Q500 Thermogravimetric Analyzer from TA Instruments Company. The instruments were provided by Dr. Clearfield's research group in Chemistry Department, Texas A&M University. The TGA analyzer has a sensitivity of 0.1 μg.

A muffle furnace, capable of temperature regulation of ± 25 °C at 550 °C, was used for ash content determination of large carbon black samples. The furnace was provided by Dr. Anthony's research group in Chemical Engineering Department, Texas A&M University.

5.3.1.2 Procedures

TGA Analysis

1. The system was initially purged with nitrogen. A 30 to 40 mg carbon black sample was heated at a rate of 10 °C/min. from room temperature to 110 °C; the sample was then kept isothermal until no further weight loss was observed (usually about 30 min). The weight lost during this step was considered as moisture content.

2. The sample then was continuously heated to 600 ^{o}C and kept isothermal again until no further weight loss was observed (at least 60 min). The weight lost in this step was considered to be the volatile content present in the sample.
3. Switching the purging gas from nitrogen to oxygen while the furnace was kept at 600 ^{o}C for 30 min so that all the carbon-based material was burned away. The weight lost during this step was taken to be the amount of fixed carbon present in the sample.
4. The weight of the remaining residue was taken to be the ash content.

ASTM Ash Content Determination

1. Approximately 10 g of carbon black was placed in an uncovered crucible and weighed. The uncovered crucible and its cover were placed into the muffle furnace and heated from room temperature to 550 ^{o}C. The sample was maintained at this temperature for 20 h to ensure no further weight loss took place.
2. The crucible containing ash was covered and removed from the furnace to a desiccator. The sample was allowed to cool to room temperature.
3. The weight of the ash residue was taken to be the ash content of the carbon black sample.

5.3.1.3 Results and Discussion

Table 5.1 summarizes the results of the TGA analysis and the ash content determined using ASTM method D1506-99 for the three commercial grade carbon black samples and nine carbon black samples recovered by thermal catalytic decomposition of tire rubber compounds. The ash content generally is less than 3%. The results from the TGA studies are consistent with those obtained using the ASTM method. These results indicate that catalyst removal by hydrolysis is effective. The low ash content has a positive effect on the specific area of the carbon black, because the existence of mineral salt crystals or oxides will contaminate the active surface of the carbon, and consequently decrease its specific area and porosity.[99]

Significantly higher ash contents are found for carbon black samples from Run III-09 and Run III-09A, at approximately 17%. This sample contained a significant amount of silica replacing carbon black as a reinforcing agent as used in current rubber compounding development. The exact composition was not made available for proprietary reasons. A significant amount of silica is used in off-the-road (OTR) tire treads.[41] Generally, up to 20 or 25 parts of the carbon black loading may be replaced by silica to lower rolling resistance, improve traction, and ensure bonding to the textile and steel cords used in the carcass. When combusted, silica forms a stable silicon oxide and is retained as ash residue. Run III-09A was a duplication of Run III-09 with the same feedstock, same catalyst and the same reaction conditions. The consistent TGA analysis results of the carbon black samples from these two runs demonstrates a good repeatability of the experimental work and the carbon black composition.

The TGA analysis also indicates that the recovered carbon blacks have slightly higher moisture contents and significantly higher volatile contents than the commercial carbon blacks. Higher moisture retention indicates a reactive carbon black surface, while the high volatile content is mainly due to the presence of high molecular weight hydrocarbons produced by the decomposition reaction. These hydrocarbons are adsorbed on the carbon black surface and are not removed during the water washing or drying process.

To enhance the commercial value of these recovered carbon blacks, it may be necessary to develop a treatment to remove all or most of the organic materials formed during the reaction. Three samples, III-03A, III-04, and III-09, were degassed under vacuum at 300 ^{o}C for 3 h. This temperature was chosen because temperatures above 350 ^{o}C are detrimental to the activity and reinforcing properties of carbon black.[19] Table 5.2 indicated that the vacuum treatment removed about half of the organics in all three cases.

The material evaporated under vacuum from sample III-03A, which had the appearance of a hydrocarbon oil, was characterized qualitatively by GC-MS. Typical compounds identified (based on the NIST Chemistry WebBook[102]) are shown in Figure 5.1. Additional studies are required to confirm the identities of these compounds, but it is clear that the carbon black product from the rubber conversion process contains high molecular weight hydrocarbons, mostly aromatics and unsaturated cyclic compounds. The multi-ring aromatic structures deserve special attention as they are carcinogenic in nature. As already indicated, this aspect of the study should be addressed during future research. No carbon bonded sulfur or chlorine compounds were identified by the GC/MS analysis of this hydrocarbon sample.

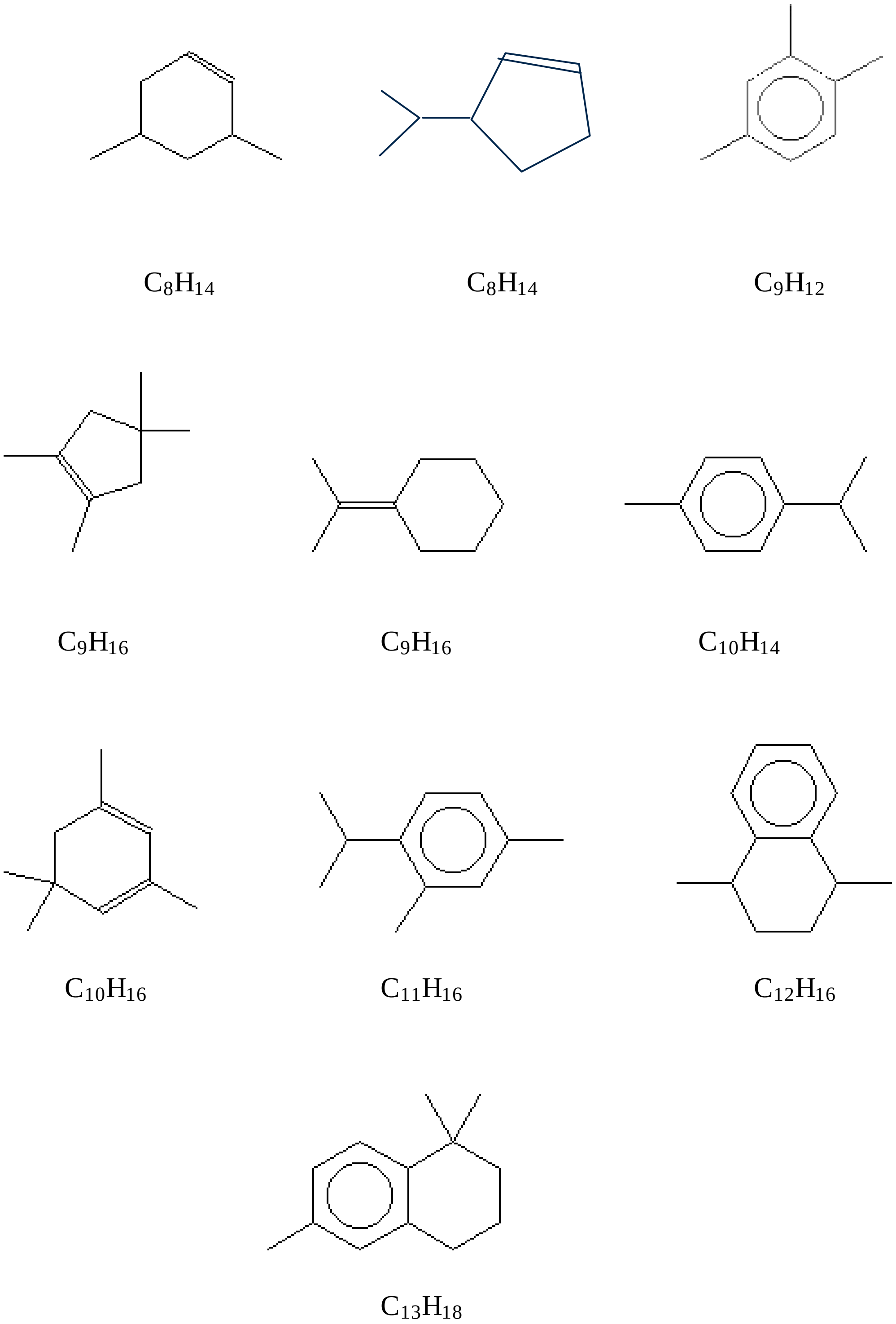
Table 5.1 Composition Analysis of the Carbon Black by TGA and Ash Content Determined Using ASTM Method (wt. %)

carbon black sample		TGA				ASTM method
		fixed carbon	moisture	volatiles	ash	ash
commercial	N220	96.89	0.85	1.35	0.73	0.77
	N330	97.88	0.59	1.081	0.42	0.43
	N660	98.74	0.32	0.74	0.22	0.27
recovered	III-02B	77.33	3.42	17.00	2.10	1.68
	III-03A	69.75	2.69	25.27	2.30	2.26
	III-04	77.33	3.48	16.84	2.35	2.16
	III-06	81.65	5.40	11.32	1.64	1.65
	III-07	77.58	2.59	17.66	2.17	2.17
	III-09	57.18	1.94	23.16	17.71	18.19
	III-09A	56.99	2.03	23.36	17.62	17.93
	III-10	69.93	1.84	24.14	4.09	4.38
	III-11	73.19	1.72	22.71	2.38	2.27

Table 5.2 Volatiles Content of the Recovered Carbon Black Products

carbon black	volatiles(wt.%)	reduction ratio
III-03A	25.27	
III-03A (degassed)*	11.56	54.25
III-04	16.84	
III-04 (degassed)*	8.82	47.62
III-09	23.16	
III-09 (degassed)*	12.14	47.58

* samples degassed under vacuum at 300 ^{o}C for 3 h.



C_8H_{14} C_8H_{14} C_9H_{12}

C_9H_{16} C_9H_{16} $C_{10}H_{14}$

$C_{10}H_{16}$ $C_{11}H_{16}$ $C_{12}H_{16}$

$C_{13}H_{18}$

Figure 5.1 Typical organic compounds in carbon black sample III-03A as identified by GC/MS (based on NIST Chemistry WebBook[102]).

5.3.2 Elemental Analysis by EDX

Energy dispersive X-ray spectroscopy, or EDX (sometimes called EDS or EDXS) was used to determine the bulk elemental composition of the recovered carbon black. EDX is the most reliable method and is used widely in the field of materials science.[103] This quantitative analytical technique is based on the principles of emission of characteristic X–rays and their specific detectors. An EDX instrument normally is attached to an electron microscope and used to detect and analyze X-rays emitted from the sample surface when impinged upon by the primary electron beam. The emission of X–rays is a phenomenon produced by inner-shell electron excitation of an element. Because characteristic X–rays have specific energies corresponding to each element, the element can be identified from the peak energy. The amount of the element in the compound is determined by integrating the intensity of the peak.

5.3.2.1 Apparatus

The microanalyses were taken with an Oxford Instruments eXL EDX system attached to a JOEL JEM-2010 high-resolution transmission electron microscope. This EDX system is capable of light element ($Z > 5$) analysis. A commercial software package, Cynapse for Electron Microscope, from Emispec Systems, Inc. was used for data acquisition, processing and analysis. All the instruments and analytic tools were provided by the Microscopy and Imaging Center at Texas A&M University.

5.3.2.2 Results and Discussion

Table 5.3 summarizes the element composition of the carbon black samples. The EDX spectra for all the samples are presented in Appendix A. Qualitatively, the EDX survey spectra of the commercial carbon blacks show only peaks of carbon, oxygen, sulfur, and silicon, whereas most of the recovered carbon black samples contain carbon, oxygen, sulfur, silicon, chlorine, aluminum, and iron. Some other elements, such as magnesium, zinc, scandium, tantalum, chromium, and osmium also are identified in some of the recovered carbon black samples. Our results indicated no significant difference in elemental composition between the three commercial grades carbon black samples studied.

All recovered carbon black samples, except for III-09, have significant carbon content (over or close to 90%). The elemental spectrum that most closely resembles the three commercial grades carbon black is from sample III-13. This carbon black sample was obtained using dual ionic salts as the catalyst. Sample III-09 showed significantly higher silicon content than the others, which is consistent with the results obtained by TGA analysis and with the special nature of the rubber sample. The aluminum contents from all samples are low, less than 0.5%. This indicates that the residue washing procedure is effective for catalyst removal. The unexpected presence of some of the other metal elements can be traced to the corrosion of the carbon steel reactor utilized in the rubber conversion reaction as well as other equipment setups used during the residue treatments.

Table 5.3 Elemental Composition of Carbon Blacks (Analyzed by EDX)

carbon black	element (wt. %)												
	C	**O**	**S**	**Si**	**Cl**	**Al**	**Fe**	Mg	Zn	Sc	Ta	Cr	Os
III-02B	92.40	3.20	0.61	1.00	0.39		0.46						1.95
III-03A	93.35	1.83	1.16	0.73		0.49							2.44
III-04	90.15	5.56	1.23	1.34	0.44	0.21	1.05		0.01				
III-06	94.49	3.16	1.13	0.08	0.33	0.09	0.72						
III-07	86.67	6.04	1.48	1.84	1.38	0.43	2.03	0.06		0.07			
III-09	79.29	7.34	1.69	7.87	0.47		0.51					2.84	
III-10	87.30	3.49	1.40	2.14	0.30	0.34	0.67				2.41		
III-11	91.66	2.89	1.52	0.63	0.42	0.11	1.26		1.11		1.41	0.20	1.94
III-13	95.88	2.37	0.90		0.30	0.40	0.16						
N220	96.19	1.13	1.38	1.30									
N330	96.40	0.20	1.63	1.78									
N660	96.95	0.81	1.79	0.44									

5.4 Surface Area Measurement

The degree of interaction of the rubber with the carbon black depends largely on the contact area between the carbon black surface and the rubber, which is roughly equal to the product of the specific surface area of the carbon black and its concentration in the rubber compound.[39] Thus, surface area is an important property in carbon black grade classification. The BET (Brunauer-Emmett-Teller) nitrogen adsorption method is the most widely used procedure for determining carbon black surface area, pore size distribution, and pore volume. This method is based on the low temperature Langmuir adsorption theory, which states that the surface area for the solid can be determined from the volume or weight of the molecules that are adsorbed as a monolayer on their surface. Once this volume has been determined, the surface area can be calculated by simply multiplying the number of adsorbed molecules or atoms by the cross-sectional area of the adsorbate.[13]

5.4.1 Apparatus

An ASAP 2000 Micromeritics BET apparatus was used to determine the surface area and average pore diameter of carbon black samples. The measurement is performed at liquid nitrogen temperature (77 K) using nitrogen as the adsorbate. The machine was controlled by a computer using the ASAP 2010 software package. This software also was used to process data after the experiment was completed. The BET system was provided by Dr. Anthony's research group in Chemical Engineering Department, Texas A&M University. The BET measurement and analysis procedure followed ASTM method D 4820 – 99.[66]

5.4.2 Results and Discussion

The BET surface area, t-plot surface area, and BET average pore diameter of recovered carbon black samples and the three commercial grades carbon black samples are listed in Table 5.4. The surface area of the recovered carbon black depends on the carbon black present in the feedstock. Table 5.5 shows the differences between the BET surface areas of the recovered carbon blacks from those of the virgin carbon blacks originally used in the rubber compounds. The surface areas of the high structure carbon blacks, N121 and N234, are reduced significantly during the rubber conversion and residue treatment process, while the low structure carbon black, N650, is relatively unaffected. Generally, based on the BET surface area alone, the recovered carbon black material appears to be in line with the commercial grades between N660 and N330. This suggests a marketable product can be recovered from waste tires.

Table 5.4 Surface Area and Average Pore Diameter of Recovered Carbon Blacks (Measured by BET)

carbon black		BET surface area (m^2/g)	external surface area, t-method (m^2/g)	average pore diameter (nm)
commercial	N220	107	95	8.5
	N330	76	70	42.4
	N660	31	28	27.4
recovered	III-02B	36	19	8.0
	III-03A	34	26	7.3
	III-04	52	51	25.0
	III-09	28	28	21.8

Table 5.5 Surface Area Alterations of Recovered Carbon Black

carbon black sample	BET surface area (m^2/g)*		
	recovered	originally in the feedstock	
III-02B	36	N121	120
III-03A	34	N650	35
III-04	52	N234	109

* The values of the BET surface area of carbon blacks used originally in the rubber compounds feedstock are estimated based on the values of the measured three commercial grades N220, N330, and N660 as well as Reference 13.

The BET method permits a reliable determination of the total specific surface area of carbon black. However, the nitrogen molecules can enter the particle pores. Therefore, the specific surface area represents the total area, including the area within the micropores. It is probable that the surface area, as determined by BET nitrogen adsorption, cannot take part in the reinforcing action completely.[13] The value of the effective external surface area is determined by the "t-plot" method, which can also be obtained by the BET measurement system. The t-plot surface areas of the recovered carbon blacks also are comparable to the commercial carbon black grade N660.

Because of the high hydrocarbon oil content in the recovered carbon black samples, it is difficult to reach the end point in the BET experiments. The high hydrocarbon oil content likely will influence directly the specific surface area of the carbon black as well. The reduction of these organic compounds likely will be necessary to clean the active surface of the carbon and increase its specific surface area and porosity. Although the average pore diameters of carbon blacks were also measured by BET, it gives no systematic information on the porosity for either commercial carbon blacks or recovered carbon blacks.

5.5 Structure Characterization

5.5.1 Terminology

It is necessary to give some definitions before discussing the structure of carbon black. Based on ASTM[104] conventions, carbon black, carbon black particle, carbon black aggregate and carbon black agglomerate are defined as:

Carbon black – material consisting essentially of elemental carbon in the form of near spherical colloidal particles and coalesced particle aggregates of colloidal size.

Carbon black agglomerate – a cluster of physically bound and entangled aggregates.

Carbon black aggregate – a discrete, rigid, colloidal mass of extensively coalesced particles; it is the smallest dispersible unit.

Carbon black particle – a small spherically shaped, paracrystalline, non-discrete component of a carbon black aggregate; it is separable from the aggregate only by fracturing.

The aggregation of the individual particles into larger complexes is usually called "***carbon black structure***". Hence, ***primary structure*** means the connection of the primary particles to the aggregates, which are resistant to mechanical destruction. The ***secondary structure*** represents the connection of carbon black aggregates to the even larger agglomerates, which are held together by van der Waals forces.[39] The ***secondary structure*** has a poor strength and is easily destroyed mechanically by carbon black handling and processing, such as pelletization and mixing into the rubber.

5.5.2 Apparatus

The electron microscope is the most accurate means of characterizing the structure of carbon black. The micrographs were taken with a JOEL JEM-2010 high-resolution transmission electron microscope (TEM), which was provided by the Microscopy and Imaging Center at Texas A&M University.

5.5.3 Results and Discussion

The reinforcement potential of the carbon black when used as reinforcing filler in rubber is governed by its particle size and structural level. In general, the larger the particle size, the lower the surface area and the poorer the reinforcement potential of the material. The loss of reinforcement is indicated by a reduction in modulus, tensile strength, abrasion resistance, and other physical properties.[41]

Typical micrographs of commercial grades carbon black N220, N330, N660 under different magnifications as examples for low-, medium-, and high-structure commercial carbon blacks are shown in Figures B-1, B-2 and B-3 (Appendix B) respectively. The micrographs of recovered carbon black samples are shown in Figures B-4 to B–12. These micrographs indicate that the particles of recovered carbon black are nearly spherically shaped. In general, these particles form aggregates in the form of chains or clusters. When the differences in magnification are noted, the fineness of the recovered carbon black particles is readily apparent.

The aggregation of carbon black particles into aggregates is shown in Figure 5.2 below. An aggregate is the smallest dispersible unit of carbon black. Figures B-4 to B-

12 show that the structure of virgin carbon black is largely preserved in the recovered carbon black. Generally, all recovered carbon black samples have a high degree of aggregation and the particle size is on a scale of 10 nm to 100 nm, which is between low-grade commercial carbon black N660 and medium-grade N330.

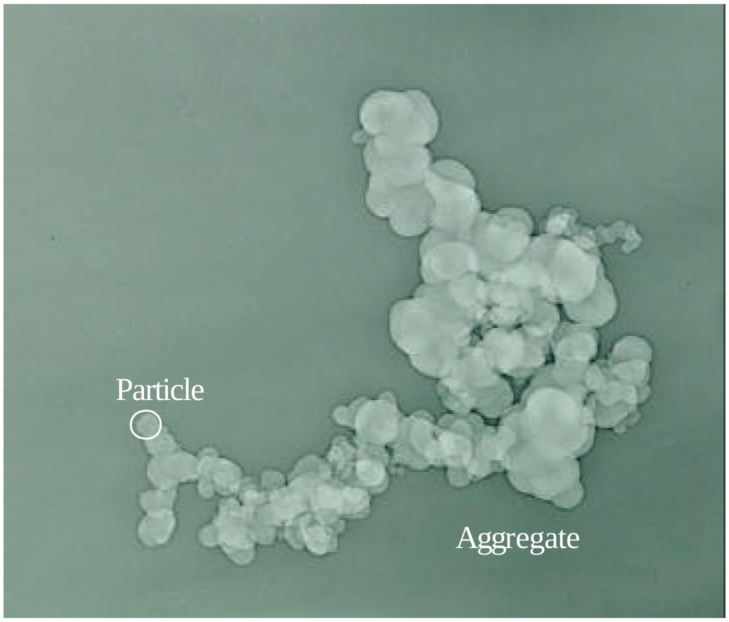
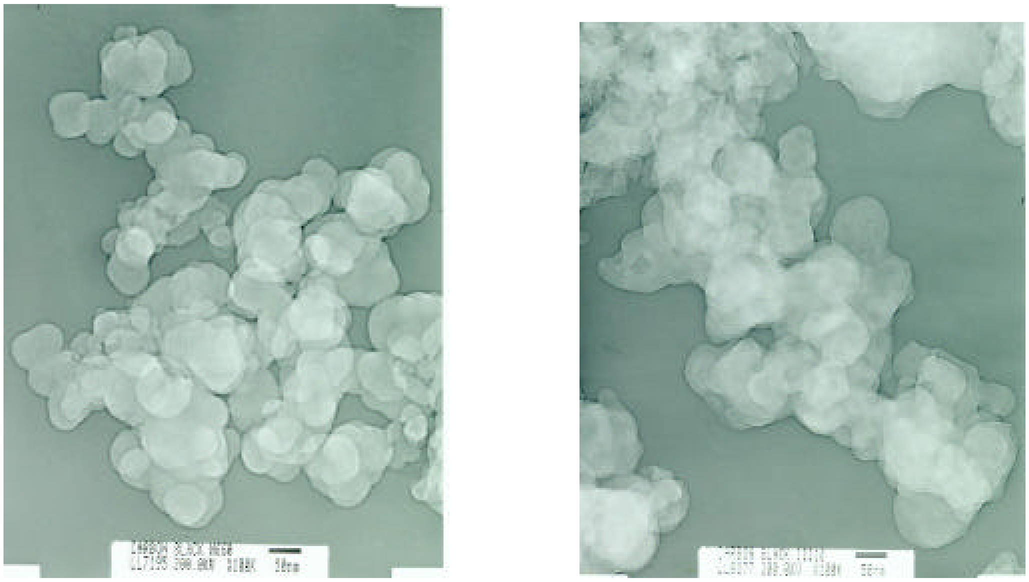


Figure 5.2 Electron micrograph showing the aggregation of virgin commercial grade carbon black N660 particles.

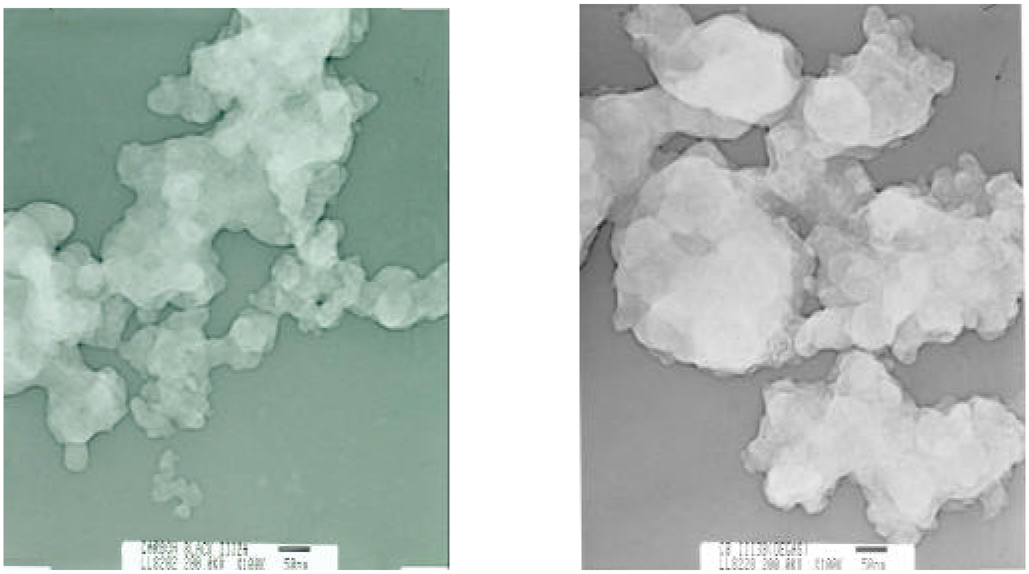
In addition to the structure of the recovered carbon black, other information can be obtained from the micrographs. Compared to commercial grade carbon black N660, some morphology changes can be found in the recovered carbon black samples (see Figure 5.3). Nearly all recovered carbon black samples show a continuous carbonaceous layer between the primary particles in the aggregate, which was not observed from the commercial grade carbon black. This carbonaceous layer could either be some nonvolatile hydrocarbon deposits adsorbed on the carbon black surface or free carbon formed during rubber decomposition reaction. Because the reaction temperature of the rubber conversion was relatively low, it is more likely that the carbonaceous layer is heavy hydrocarbons than free carbon. This notion is supported by the TGA composition analysis and GC/MS spectrum analysis.



N660 III-10

Figure 5.3 Comparison of recovered carbon black from run III-10 with commercial carbon black N660 – magnified 100,000 times.

Some carbon black samples were exposed to a vacuum at 300 °C for 3 h. The TEM micrographs for these samples (Figure 5.4, Figure B13 to B15) indicate that there is no noticeable change in the carbon black structure for the degassed sample, even though a substantial amount of mass was removed. This suggests that thermal vacuum treatment could be a good method to remove excess organic impurities from the carbon black product.



III-02B

III-02B (degassed)

Figure 5.4 Structure of recovered carbon black sample after vacuum degas treatment – magnified 100,000 times.

5.6 Conclusions

The particle size, structure, surface area, and bulk elemental composition were characterized for carbon blacks recovered by thermal catalytic decomposition of tire rubber. The results suggest that the recovered products possess qualities comparable to or better than commercial grade carbon black N660. However, the heavy hydrocarbon content of the recovered carbon black is significantly higher than that of the commercial grades carbon black. These hydrocarbons, which generally are high molecular weight aromatics and unsaturated cyclic compounds, can be removed partially by heating to 300 °C in vacuum.

CHAPTER VI

CATALYST RECOVERY STUDY

6.1 Introduction

Anhydrous aluminum chloride ($AlCl_3$) was used as the primary catalyst in all experiments during the Phase III study. In some runs, $AlCl_3$ was used as the sole catalytic component, while in other runs a dual catalyst system, using $AlCl_3$ with a second metallic halide, was employed. This ionic salt catalyst is an expensive component to the current process. Furthermore, large quantities (the ratio to rubber feedstock is more than 1:1 by weight) of catalyst, primarily aluminum chloride ($AlCl_3$), are used in the process. Thus, an efficient and economic method for the catalyst recovery and recycle can significantly influence the cost effectiveness of this thermal catalytic conversion process. It is necessary not only to reduce the consumption of fresh catalyst, but also to retain the initial activity and to minimize the amount of a secondary waste from the process.

A natural idea for $AlCl_3$ catalyst recycling is to remove $AlCl_3$ from the solid residue by sublimation and recondensation. As a low melting point salt, $AlCl_3$ has a relatively low sublimation temperature of 180.2 ^{o}C, and the triple point occurs at 192.6 ^{o}C and 233 kPa. The basis for this idea is illustrated in Figure 6.1, which shows a representative $AlCl_3$ pressure-temperature phase diagram. Through this procedure, it was assumed that most of the catalyst could be recycled for reuse by evaporation from the catalyst + residue slurry. However, $AlCl_3$ was present on the top plate or other peripheral parts of the reactor only in small quantities after the experimental runs were completed. Further studies confirmed that catalyst recovery through this method does not appear feasible. More work is required to understand fully the behavior of the catalyst during the thermal conversion process. Hence we embarked on series of studies in an effort to recover the catalyst. These studies and their results are described and discussed below.

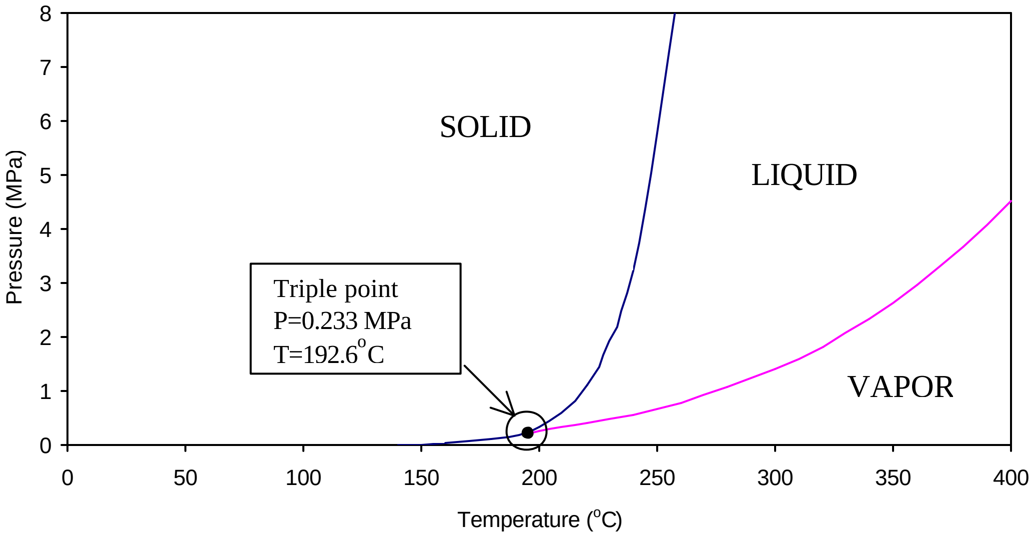


Figure 6.1. Pressure-temperature phase diagram of $AlCl_3$.[105]

6.2 Vacuum Evaporation Test

A vacuum evaporation test was performed to test the viability of recovering $AlCl_3$ catalyst from the carbonaceous residue through sublimation and subsequent condensation. The experimental setup is depicted schematically in Figure 6.2.

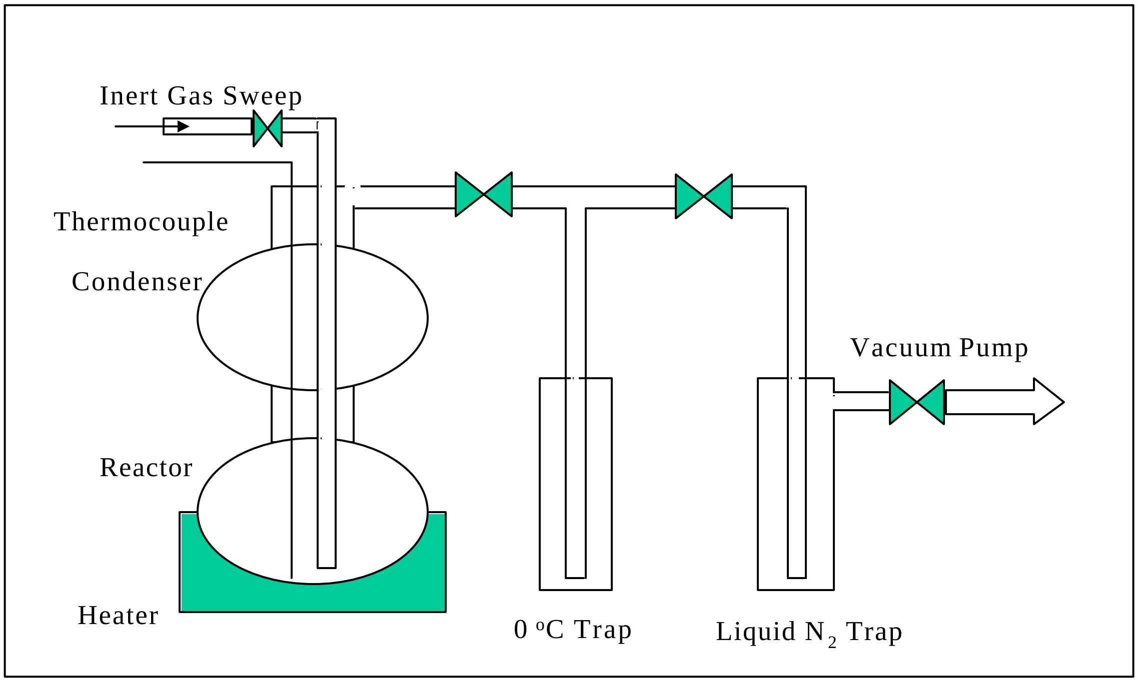


Figure 6.2. Experimental equipment for catalyst recovery through vacuum evaporation.

Approximately 62.3 g of catalyst + residue mixture ($AlCl_3$ single catalyst) produced by Run III-08 was heated slowly in a glass reactor from room temperature to 574 °C (the highest temperature the heater could provide) and maintained for 2 hours. Argon was used as an inert sweeping gas at a flow rate of 30 cm^3/min. A vacuum was imposed slowly upon the catalyst + residue mixture before the heating was started to remove moisture and oxygen. A condenser maintained at room temperature was used to collect the vaporized catalyst as solid $AlCl_3$, and two product traps, one maintained at 0°C and the other at liquid nitrogen temperature (-196 °C), were installed downstream to collect any volatile discharges. During the heating process it was evident that white fumes appeared and condensed in the condenser at a reactor temperature of 215 ^{o}C. As the temperature rose further, the color of the collected materials became darker, from the initial white to yellow, brown, and eventually dark brown. This change in colors was presumed to be due to heavier hydrocarbon products that were released at high temperatures.

After the test was completed and the reactor was cooled to room temperature, the collected material in the condenser was weighed to be 22.0 g. In addition, 6.4 g of white solid material was found in the liquid nitrogen trap. Unfortunately, it escaped gradually when the container was removed from the liquid nitrogen trap and warmed to room temperature. Hence, no analysis of the composition is available, but it most likely was a mixture of HCl and light hydrocarbons, such as propane and isobutane. The escaped material passed through a deionized water trap (initial pH ~ 7.0), resulting in a highly acidic solution. This observation strongly suggests that some $AlCl_3$ was converted to HCl (with a melting point of –74 ^{o}C) during the vacuum evaporation process. The odor also suggested that small quantities of hydrogen sulfide (H_2S) might also be present.

A second vacuum evaporation test was performed with 28.2 g residue material left from the first vacuum evaporation attempt after crushing this residue into fine particles to expose more surface area for evaporation. An additional 3.39 g catalyst was recovered with no additional liquid or gas products collected in the liquid nitrogen trap. However, the gas passing through the downstream system still showed strong acidity, indicating the presence of HCl resulting from decomposition of the catalyst at high temperatures.

The vacuum evaporation tests also indicated that it is very difficult to remove the catalyst from the residue under a vacuum environment, even at temperatures as high as 400 °C. Although the vapor pressure of $AlCl_3$ is several MPa at this temperature, the pressure in the reactor is much lower. When the temperature is raised above 550 °C, about 60 to 70 weight percent of the original amount of catalyst could be removed from the solid residue, but not all as $AlCl_3$ because of the formation of HCl. Surprisingly, not all the catalyst appears to evaporate or decompose to form HCl at the temperatures employed.

The two most likely explanations for the inability to remove all the catalyst are: 1) The solid residue material may encapsulate the catalyst, thus preventing the evaporation of pure $AlCl_3$; and 2) the catalyst is chemically bonded to the residue material and hence not removable by evaporation. The former is unlikely as no proof of physically encapsulated catalyst could be found when dissecting the cooled residue material, and crushing the residue powder into finer particles caused no noticeable change in catalyst evaporation. There are however strong indications that the catalyst is chemically bonded into the residue. There are several reports[11-12,78-79,82] which suggest that a stable metal organic complex may be formed as a result of the hydrogen deficient rubber decomposition environment. This is discussed in more detail below. We also found that after washing and drying, the solid material remaining after catalyst separation by evaporation was not the fine powders normally produced, but a hard and brittle material that produced very coarse particles when crushed.

6.3 Discussion

Results from the vacuum evaporation tests indicate that the catalyst cannot be recovered effectively from the residue by simple sublimation and condensation. This conclusion also is supported by observations during the experimental runs. During some of the runs, we attempted to drive off the catalyst from the solid residue in the reactor vessel after the chemical conversion was believed to have been completed. The heating system to the reactor top was shut off while leaving the bottom heating unit operational during the completion stage of the run. Because of the high vapor pressure of $AlCl_3$, this procedure was expected to provide the necessary driving force to drive $AlCl_3$ to evaporate from the residue and accumulate at the colder segments (on the top) of the reaction vessel. Only trace amounts of catalyst were recovered this way. In contrast, when a reaction was terminated early with only a little rubber fed into the reactor, very large quantities of $AlCl_3$ accumulated on the reactor top plate.

The optimized ratio of catalyst to feedstock and the rubber catalytic conversion mechanism have been studied during these experiments. The results suggest that weight ratios of catalyst to rubber compounds from 1:1 to as high as 2:1 are preferred. The high ratio promises high conversion rates. Ratios less than 1:1 resulted in slower reaction rates and lower conversion rates. The rubber catalytic conversion mechanism is actually very simple. The catalytic activity of $AlCl_3$ is believed to be due to its electron deficiency. As a stronger Lewis acid, $AlCl_3$ can accept electrons from organic molecules, forming an intermediate organic metallic complex during the reaction. This intermediate complex can be further hydrogenated to give hydrocarbon products and release the catalyst for further use. The mechanism of this catalytic decomposition reaction most likely is as follows:

1) Catalyst initiation:

$$AlCl_3 + MCl\ (\text{cocatalyst}) \rightleftharpoons [AlCl_4]^- + M^+ \tag{6.1}$$

2) Polymer chain break down:

$$CH_3CH_2CH_2\text{-}R + [AlCl_4]^- \underset{}{\overset{\text{decomposition}}{\rightleftharpoons}} \underset{\text{(intermediate complex)}}{[RAlCl_3]^-} + CH_3CH_2CH_2\text{-}Cl \tag{6.2}$$

3) Catalyst regeneration:

$$[RAlCl_3]^- + H^+ \rightarrow R\text{-}H + AlCl_3 \tag{6.3}$$

The thermal catalytic decomposition reaction forms an intermediate organic metallic complex ($([RAlCl_3]^-)$)[11-12,78-79,82] from which the catalyst can be recovered only through reaction 6.3. However, as the rubber is decomposed, the environment becomes more hydrogen deficient as the hydrocarbon fluids evaporate, so that reaction 6.3 cannot be sustained indefinitely. Hence the catalyst is retained as a stable organic metallic complex. The formation of this stable organic metallic complex during the rubber decomposition process in the hydrogen deficient environment makes it nearly impossible to recover the catalyst in its original active form by simple resublimation. One must therefore free the catalyst during the rubber decomposition reaction by supplying additional hydrogen to sustain reaction 6.3.

$AlCl_3$ is used traditionally as a Friedel-Craft catalyst in alkylation and isomerization reactions. As these reactions progress, the catalyst also degrades to a less active state and forms a separate sludge phase. Methods directed to the recovery of $AlCl_3$ from this sludge have been proposed.[81,106] A recent U.S. Patent[106] claims a 100% recovery of $AlCl_3$ catalyst by hydrogenation of the sludge at low temperature (150 ^oC) and high pressure (10.44 MPa) with metallic aluminum as a promotion agent.

The investigation of this hydrogenation reaction and hence the catalyst recovery is not possible with our current experimental equipment. We have thus not verified whether the catalyst can be recovered completely from the organometallic complex through hydrogenation. This issue must be resolved during additional studies. The small amounts of catalyst collected by evaporation and condensation react readily upon contact with tire rubber compounds in a small-scale glass reactor, indicating that the activity is not degraded by evaporation.

Finally, no phase separation between the residue and the catalyst was observed when using pure $AlCl_3$ as the catalyst. However, employing an appropriate second salt resulted in a homogenous molten liquid phase, which formed at relatively low temperatures. The dual salt system also appears to form a liquid + solid slurry that would allow the catalyst to be separated from the reaction residue using on-line ultrafiltration.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Thermal catalytic decomposition of used tire rubber has several advantages over other tire recycling methods in that it is both environmentally benign and economically viable. The rubber portion of used tires can be converted by thermocatalytic decomposition into valuable hydrocarbon products and the carbon black filler is recovered. The economics of this process depends strongly upon the commercial value of the recovered carbon black and the ability to recover and reuse the catalysts employed in the process.

The carbon black recovered from this decomposition process is potentially suitable for a number of applications. The structure and surface morphology of the recovered carbon black resemble that of commercial carbon black with only slightly changes. In general, the recovered products possess qualities comparable to or even better than commercial grade carbon black N660. However, a significant amount of hydrocarbon oil is present on the recovered carbon black surface and it may deactivate part of the active sites on the carbon black surface. These oil compounds, which generally are heavy aromatics and unsaturated cyclic hydrocarbons, can be removed partially by vacuum thermal treatment. Reducing this oil content should increase the surface area of the carbon black particles as well as improve the market value and the range of applications of the recovered carbon black products. An effective posttreatment procedure also will also increase the yield of valuable hydrocarbon products, and hence the overall economics of the process.

The molten salt catalyst effectively catalyzes the tire rubber decomposition reaction in both the vapor and liquid phases. However, $AlCl_3$ forms a stable organometallic complex with the hydrocarbon material produced during the decomposition process in a hydrogen deficient environment. The result is that it is nearly impossible to recover the catalyst in its original active form. Therefore, it is necessary to add hydrogen donor molecules during the reaction, most probably through a feed gas, to keep the catalytic activity of the catalyst at the required level.

Dual salt systems appear to have significant advantages over pure aluminum chloride as catalyst. Further studies are needed to determine the nature of the interrelationship between the primary catalyst and the co-catalyst, and the optimum co-catalyst. The interaction of the dual salt system with the reaction residue also should be investigated. It should be possible to separate the dual salt catalyst system from the reaction residue using on-line ultrafiltration. The feasibility of this molten salt catalyst recovery method should be studied further both theoretically and experimentally.

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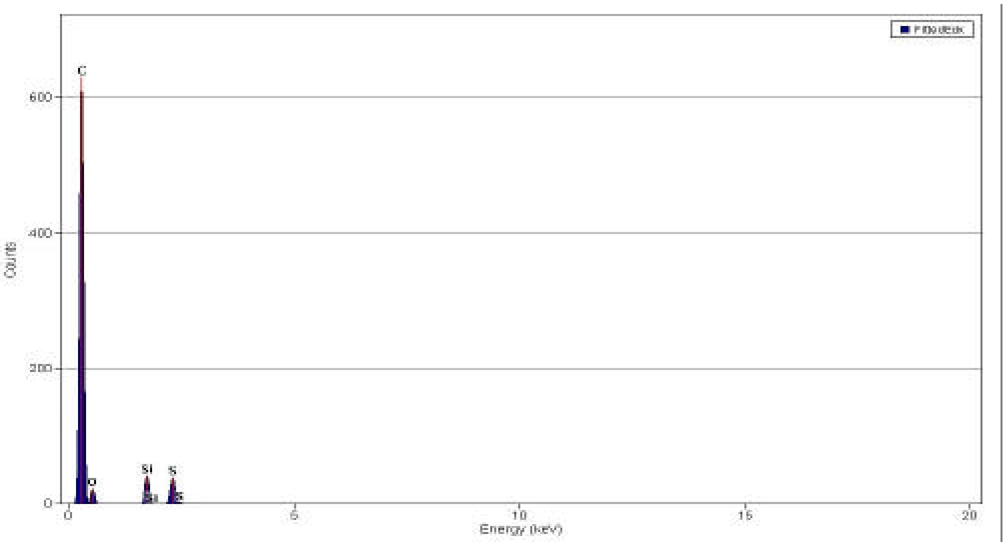
APPENDIX A

ELEMENTAL COMPOSITION OF CARBON BLACKS --- ANALYZED BY EDX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S
Si
S
Counts
0
200
400
600
Energy (keV)
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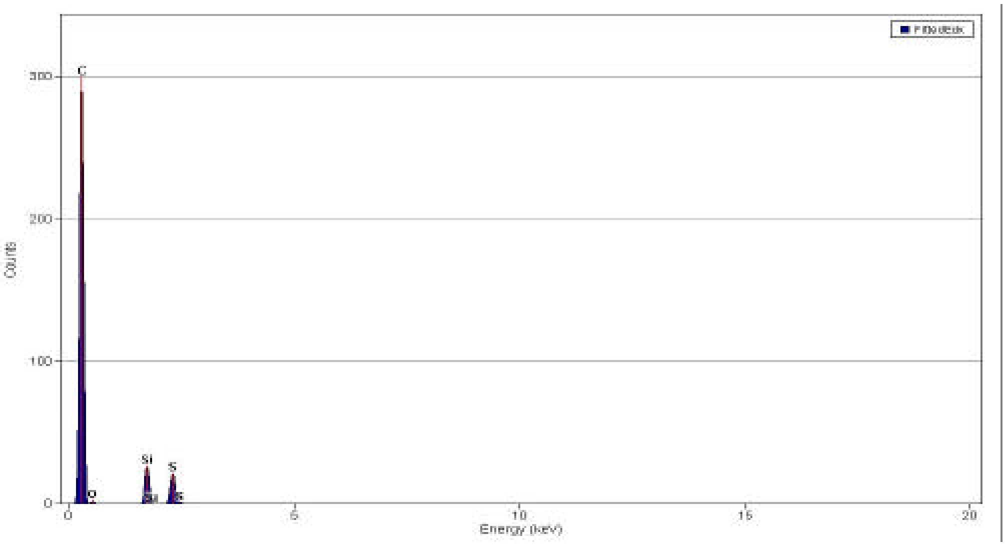
5
10
15
20

N220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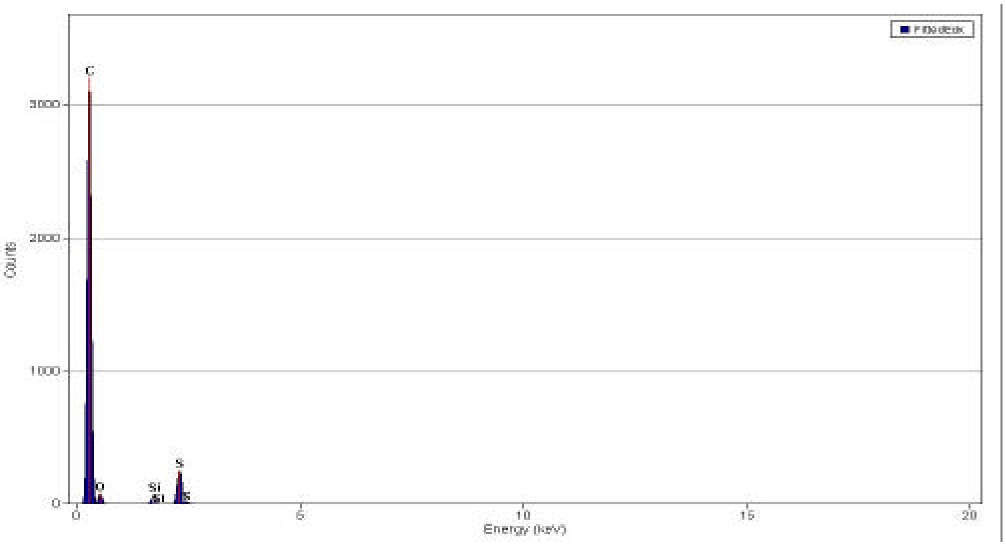
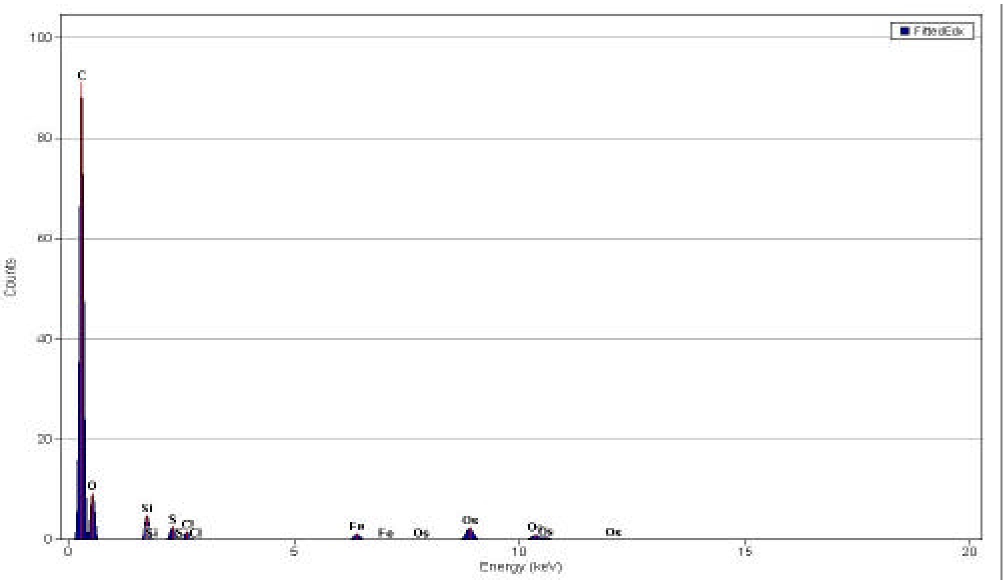
O
Si
S
Si
S
Counts
0
100
200
300
Energy (keV)
0
5
10
15
20

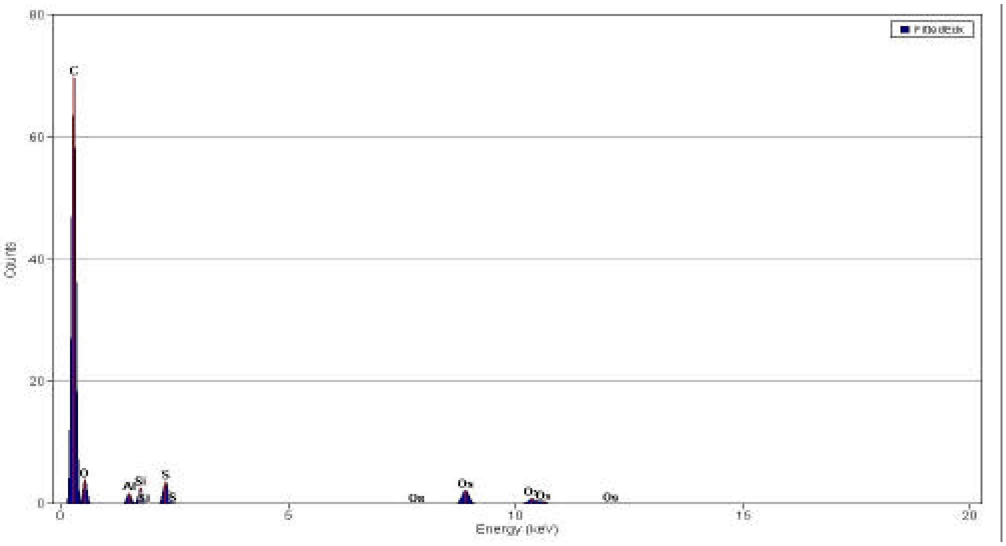
N330


FittedEdx
C
O
Si
Si
S
S
Counts
3000
2000
1000
0
0
5
10
15
20
Energy (keV)

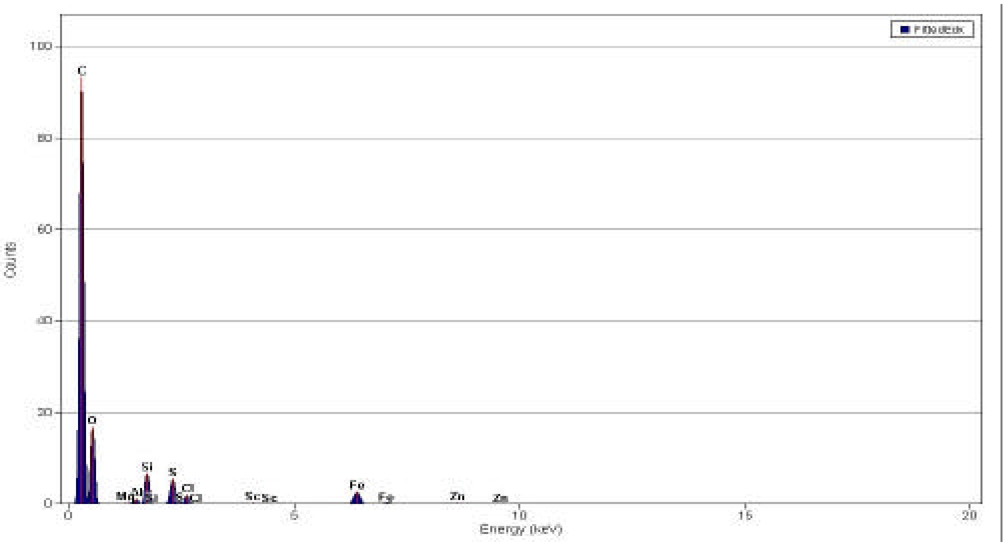
N660


FittedEdx
C
O
Si
Si
S
S
Cl
Cl
Fe
Fe
Os
Os
Os
Os
Os
Counts
100
80
60
40
20
0
0
5
10
15
20
Energy (keV)

III-02B



III-03A



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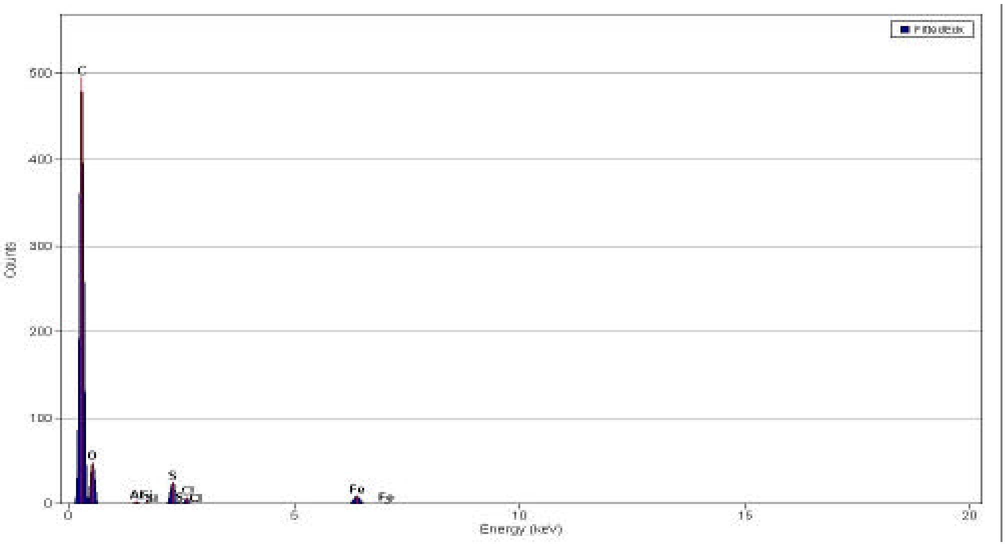
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Al
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S
Cl
Fe
Fe
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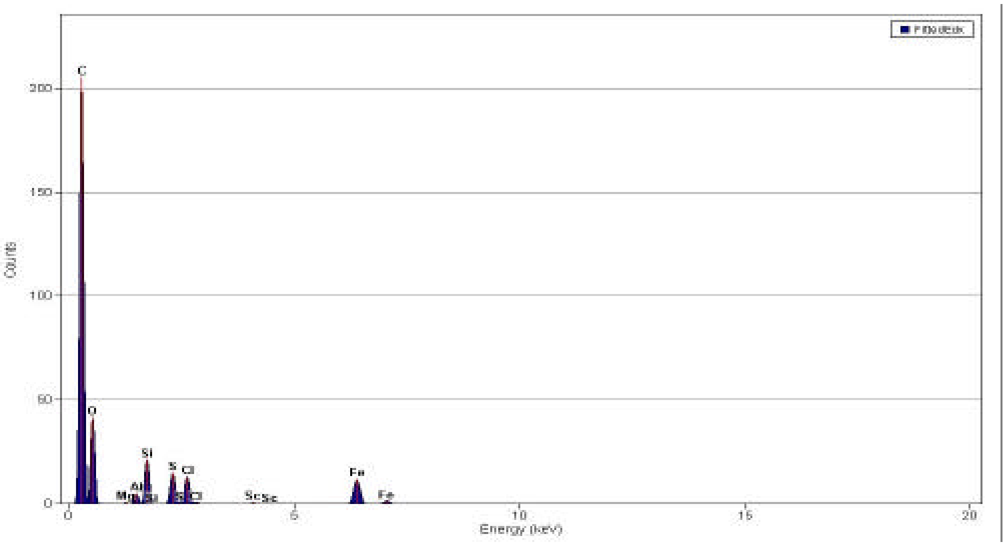
300
200
100
0
Counts
0
5
10
15
20
Energy (keV)

III-06


C
O
Si
Mg
Al
S
Cl
Sc
Sc
Fe
Fe
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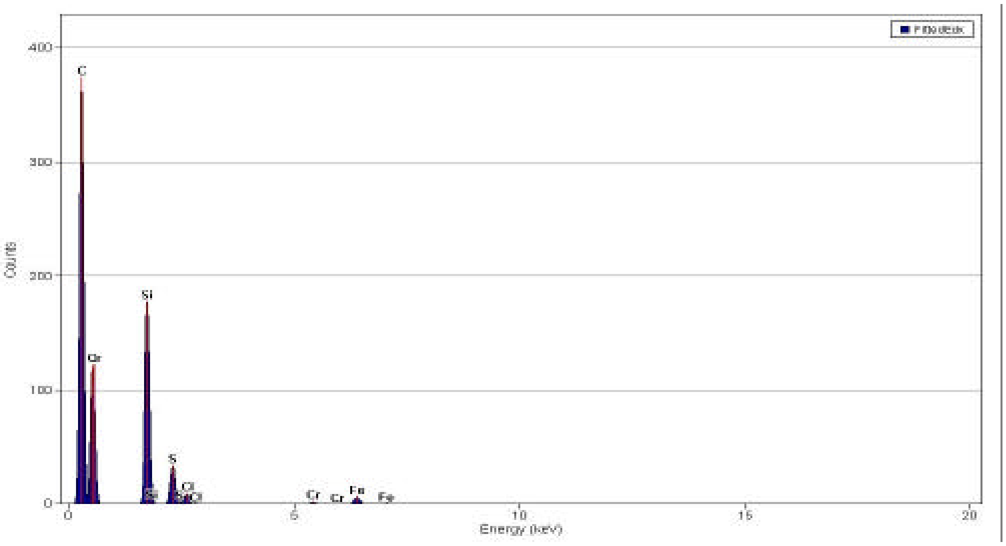
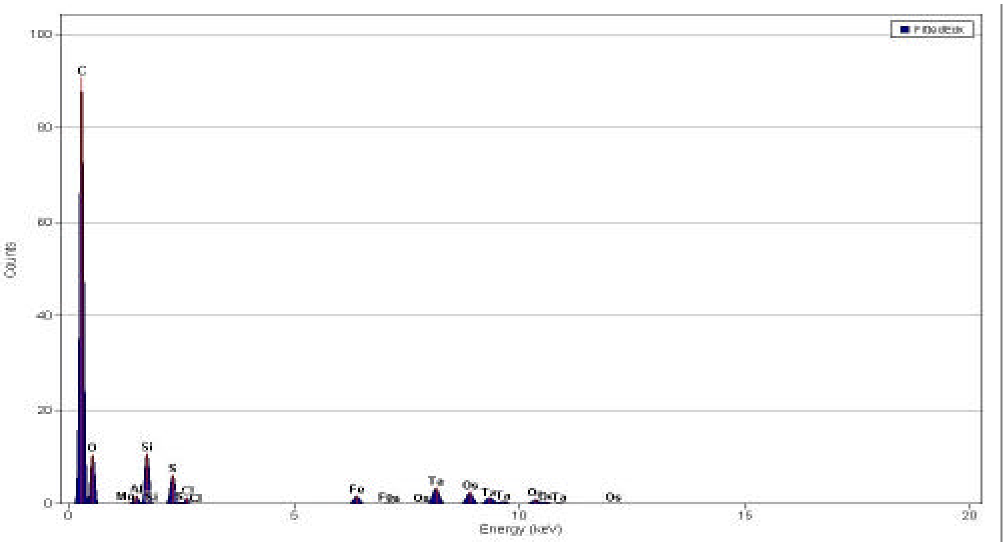
150
100
50
0
Counts
0
5
10
15
20
Energy (keV)

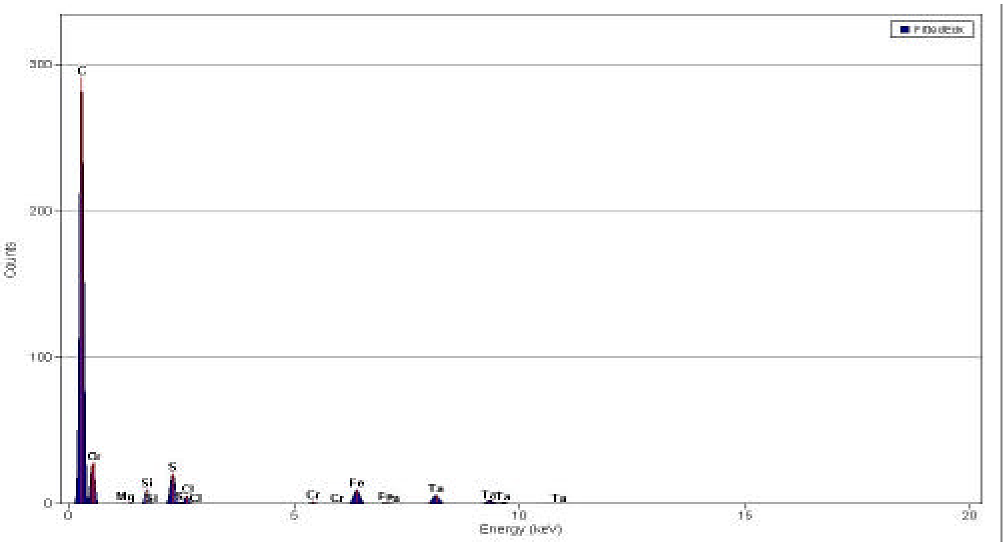
III-07


Fitted edx
400
300
200
100
0
Counts
C
Cr
Si
S
Si
Cl
Cl
Cr
Cr
Fe
Fe
0
5
10
15
20
Energy (keV)

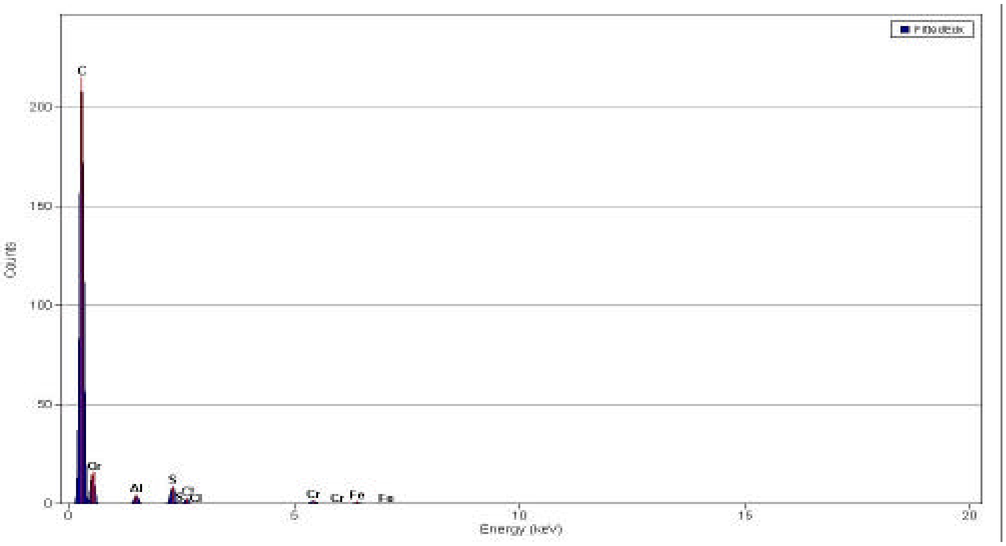
III-09


Fitted edx
100
80
60
40
20
0
Counts
C
O
Si
S
Mg
Al
Si
Cl
Cl
Fe
Fe
Os
Ta
Os
Ta
Ta
Os
Ta
Os
0
5
10
15
20
Energy (keV)

III-10


300
200
100
0
Counts
C
Cr
Mg
Si
Si
S
S
Cl
Cl
Cr
Cr
Fe
Fe
Fe
Ta
Ta
Ta
Ta
0
5
10
15
20
Energy (keV)

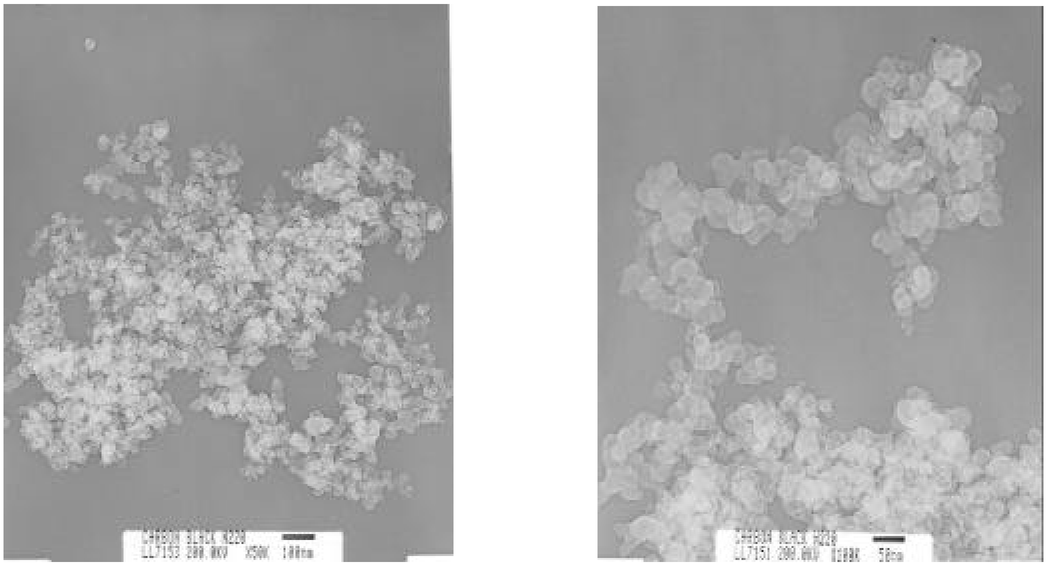
III-11


200
150
100
50
0
Counts
C
Cr
Al
S
S
Cl
Cl
Cr
Cr
Fe
Fe
0
5
10
15
20
Energy (keV)

III-13

APPENDIX B

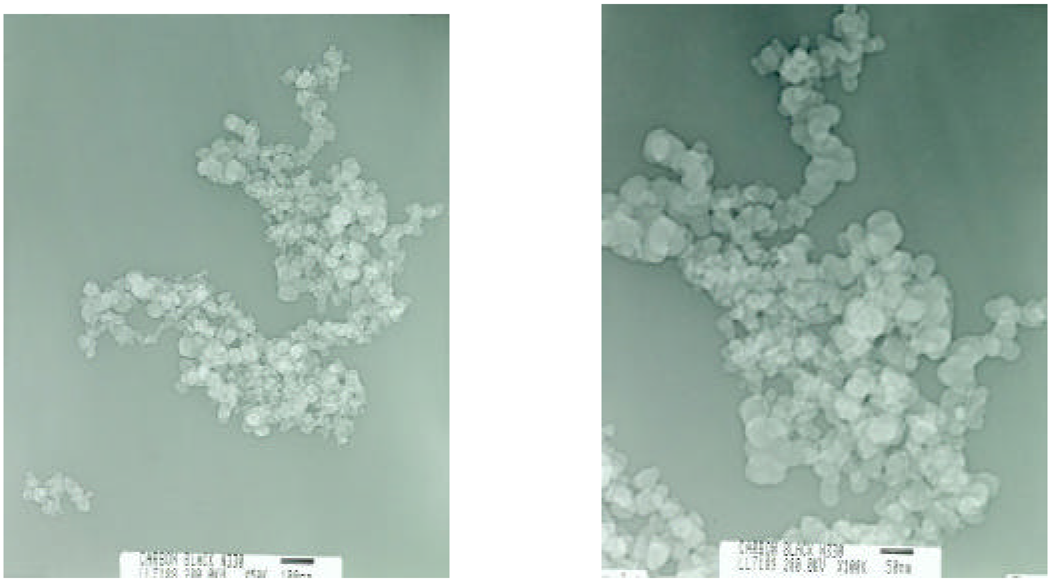
MICROGRAPHS OF CARBON BLACK TAKEN BY TEM



N220 X50K

N220 X100K

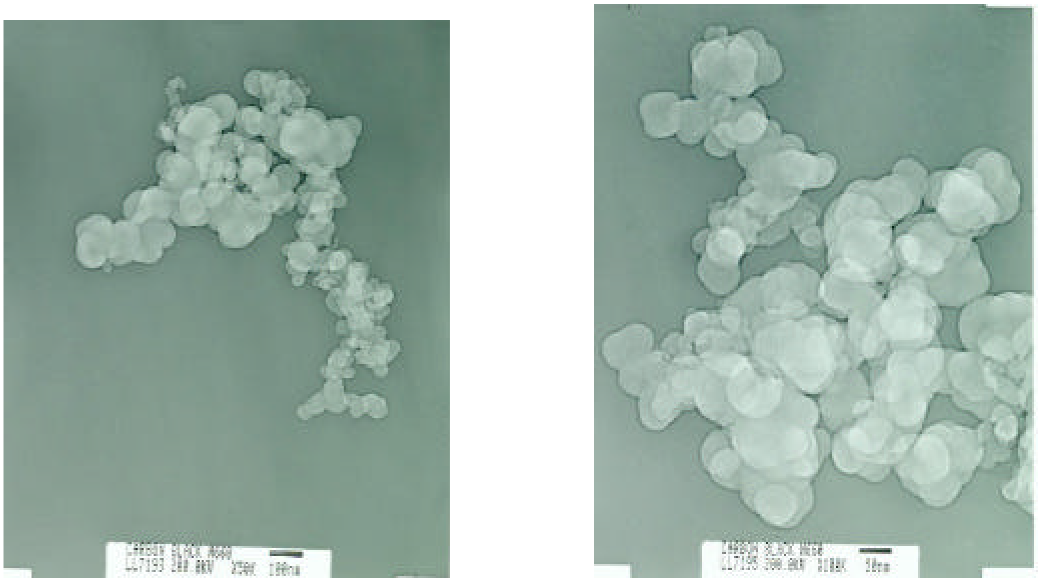
Figure E-1 Commercial carbon black N220 – magnified 50,000 and 100,000 times respectively.



N330 X50K

N330 X100K

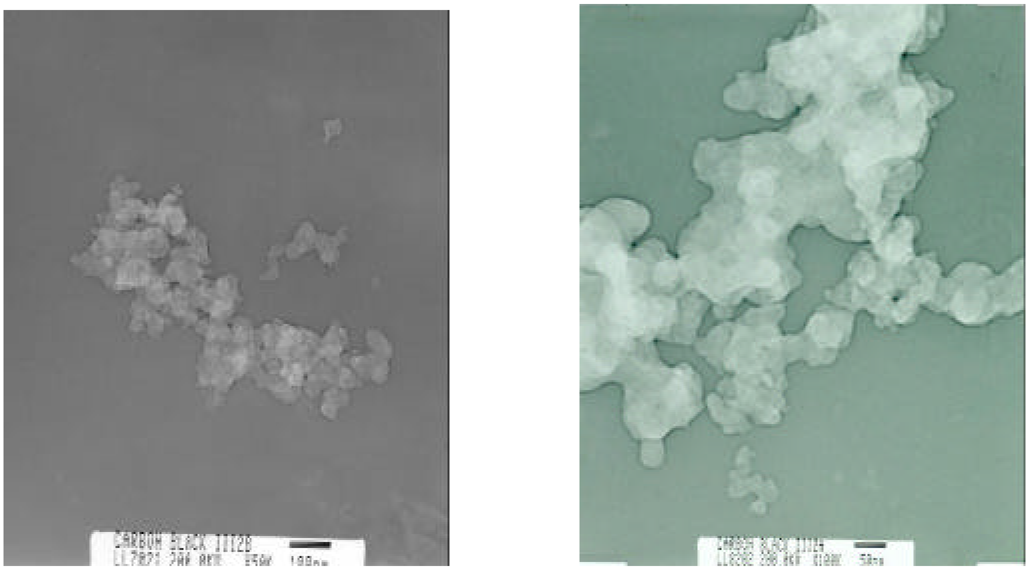
Figure E-2 Commercial carbon black N330 – magnified 50,000 and 100,000 times respectively.



N660 X50K

N660 X100K

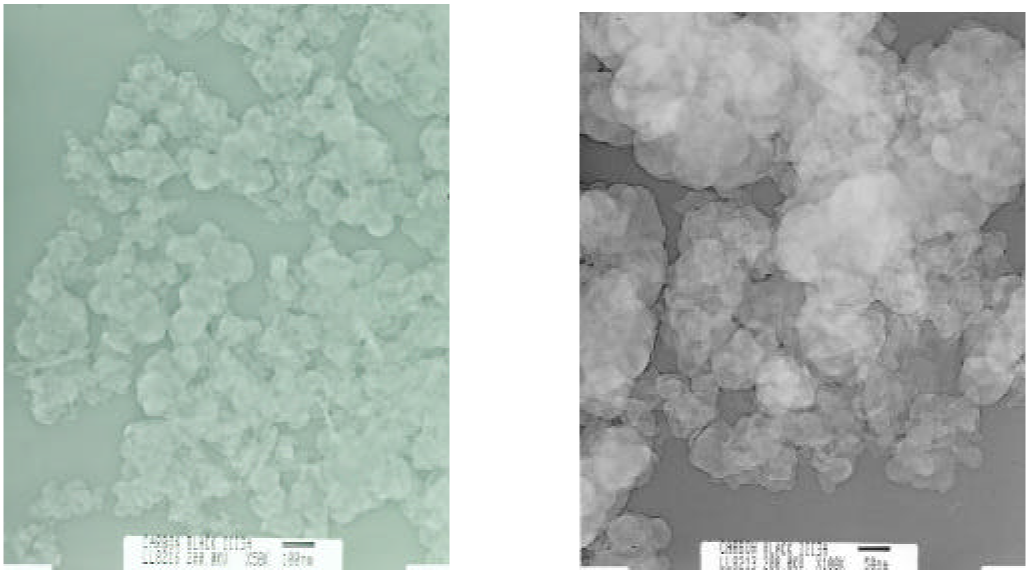
Figure B-3 Commercial carbon black N660 – magnified 50,000 and 100,000 times respectively.



X50K

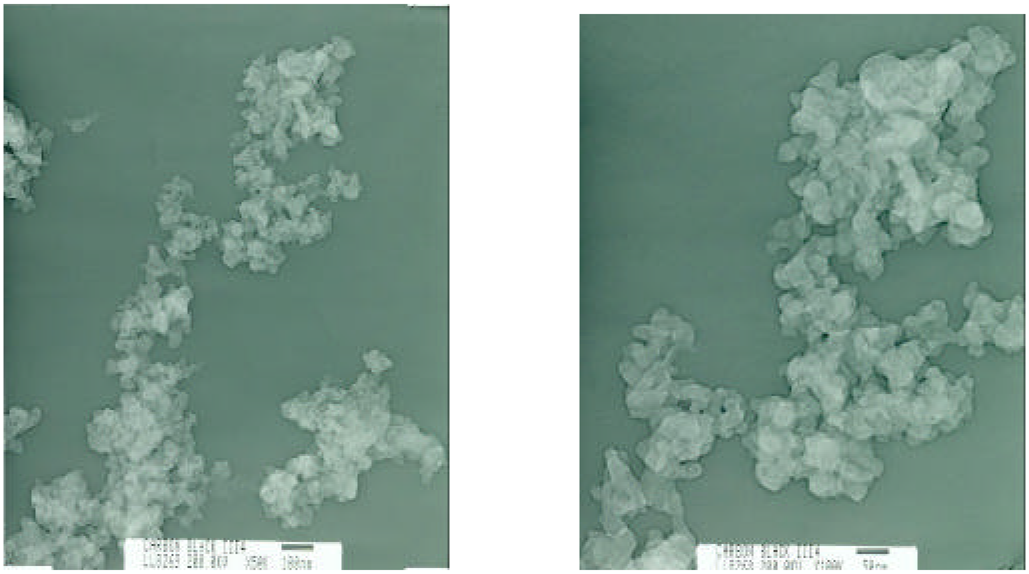
X100K

Figure B-4 Carbon black recovered from Run III-02B – magnified 50,000 and 100,000 times respectively.



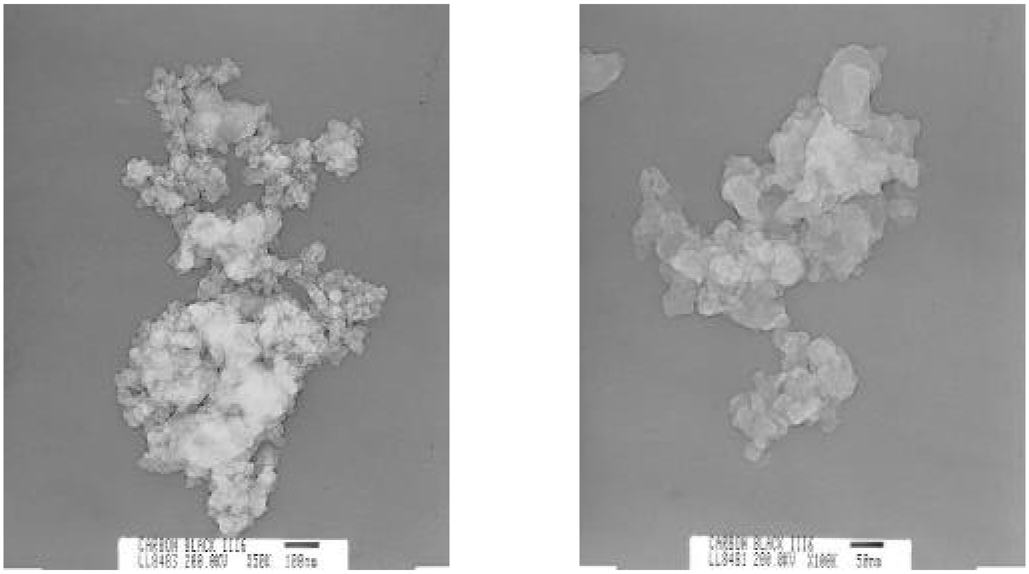
X50K X100K

Figure B-5 Carbon black recovered from Run III-03A – magnified 50,000 and 100,000 times respectively.



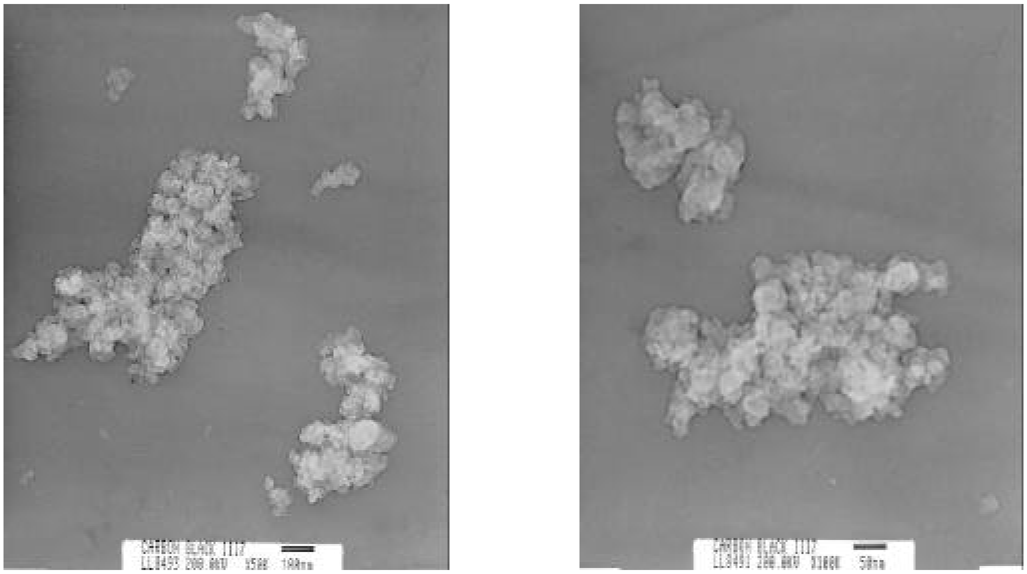
X50K X100K

Figure B-6 Carbon black recovered from Run III-04 – magnified 50,000 and 100,000 times respectively.



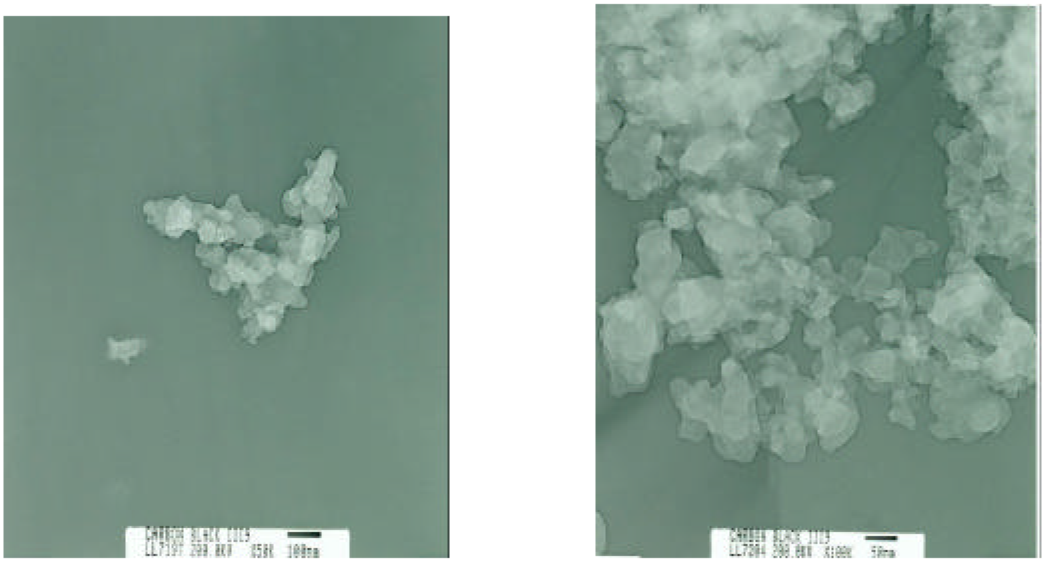
X50K X100K

Figure B-7 Carbon black recovered from Run III-06 – magnified 50,000 and 100,000 times respectively.



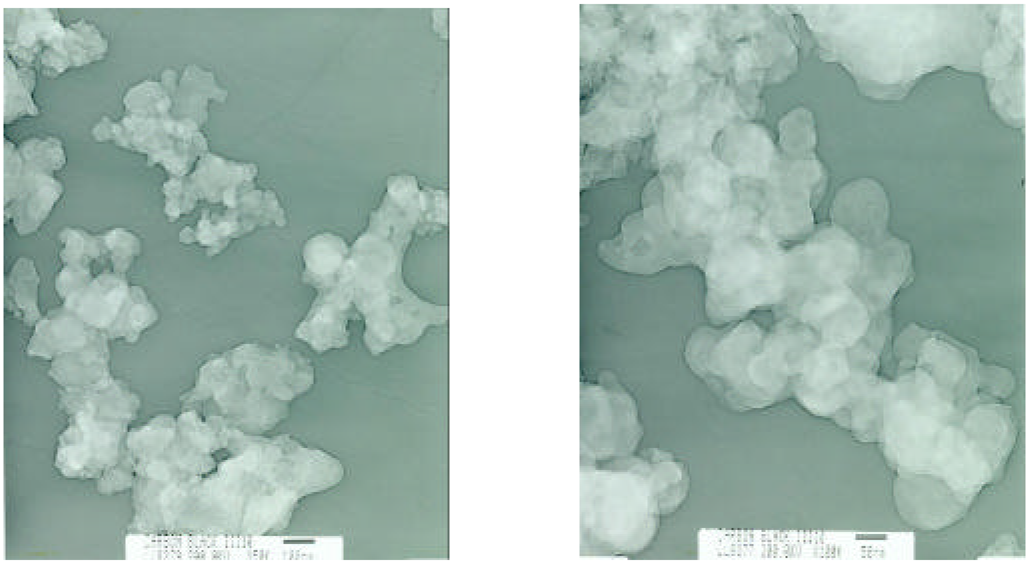
X50K X100K

Figure B-8 Carbon black recovered from Run III-07 – magnified 50,000 and 100,000 times respectively.



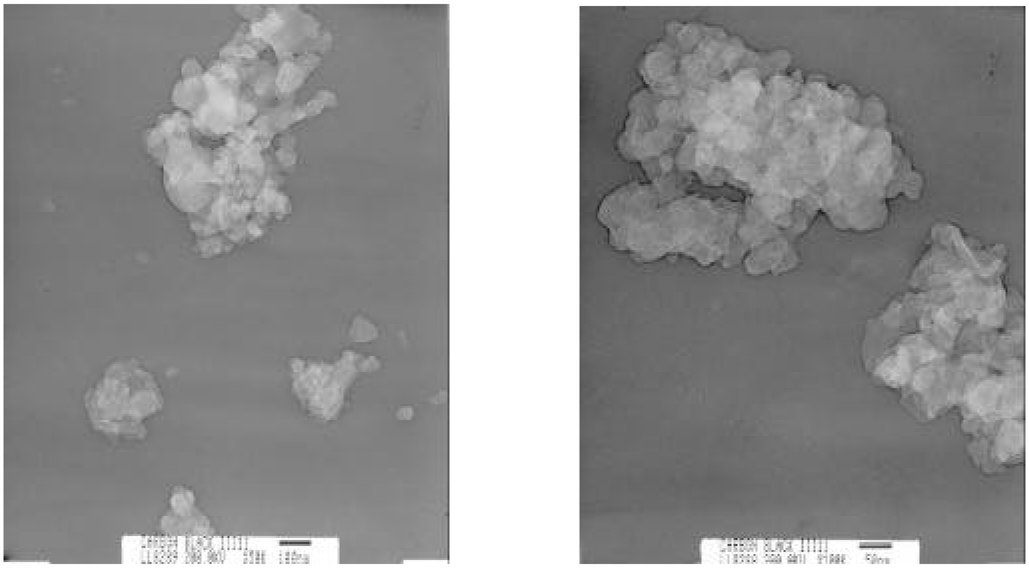
X50K X100K

Figure B-9 Carbon black recovered from Run III-09 – magnified 50,000 and 100,000 times respectively.



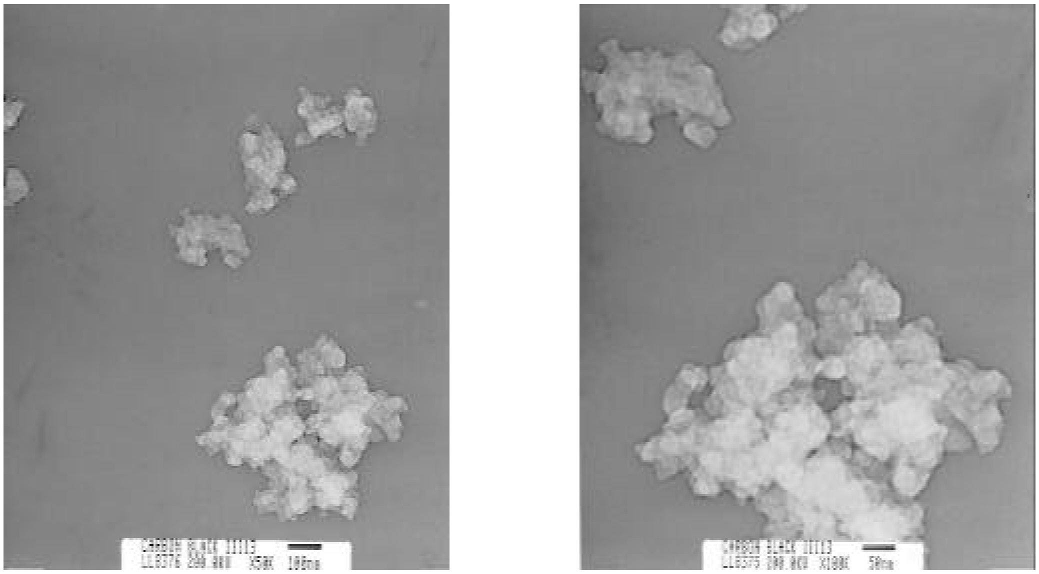
X50K X100K

Figure B-10 Carbon black recovered from Run III-10 – magnified 50,000 and 100,000 times respectively.



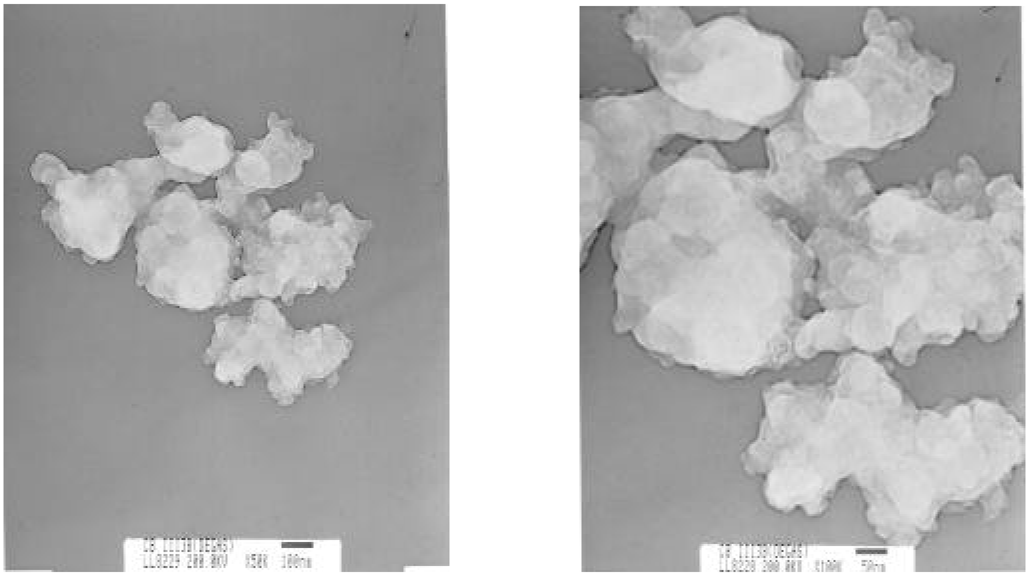
X50K X100K

Figure B-11 Carbon black recovered from Run III-11 – magnified 50,000 and 100,000 times respectively.



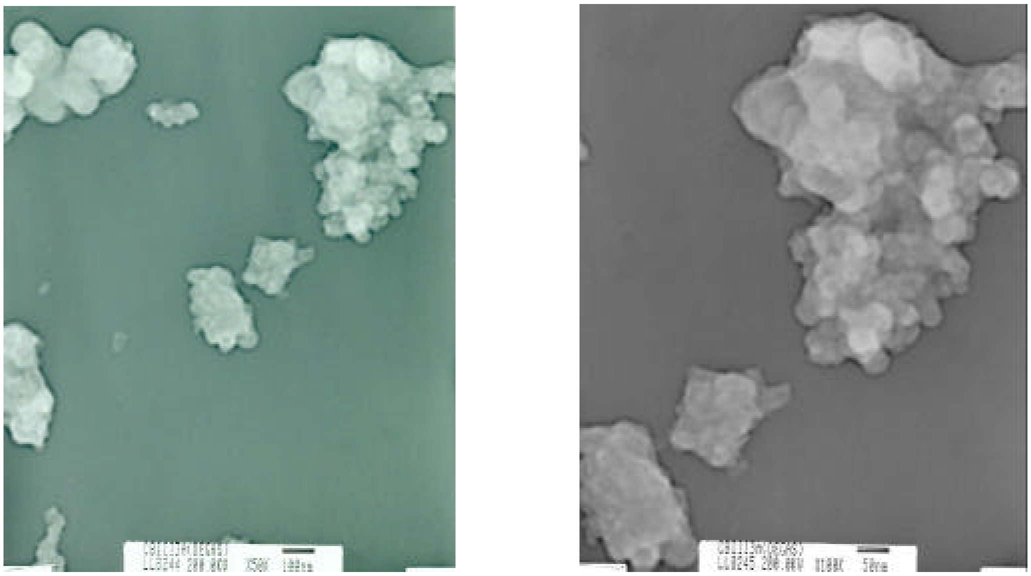
X50K X100K

Figure B-12 Carbon black recovered from Run III-13 – magnified 50,000 and 100,000 times respectively.



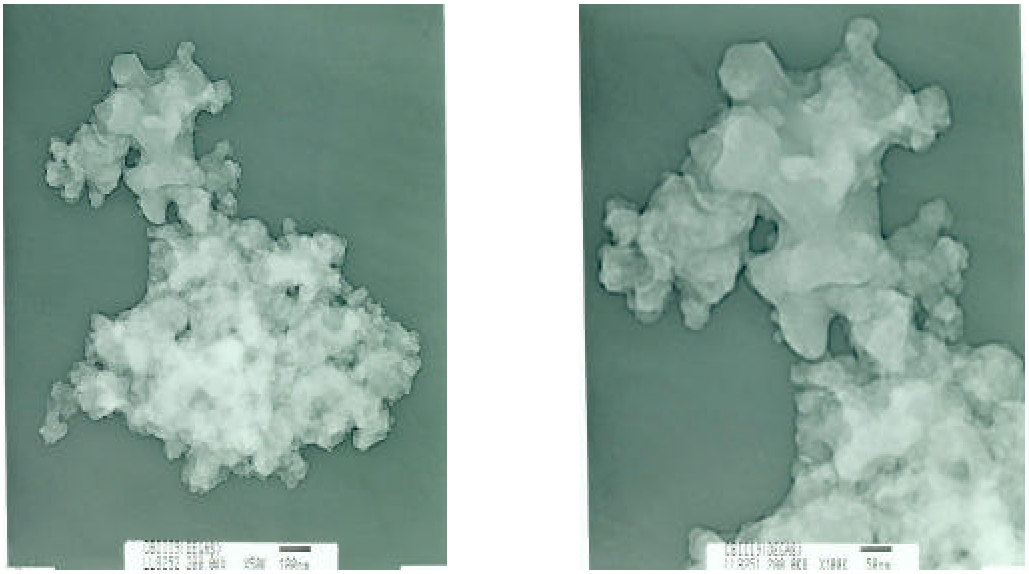
X50K X100K

Figure B-13 Recovered carbon black sample: III-02B (degassed)– magnified 50,000 and 100,000 times respectively.



X50K X100K

Figure B-14 Recovered carbon black sample: III-03A (degassed)– magnified 50,000 and 100,000 times respectively.



X50K X100K

Figure B-15 Recovered carbon black sample: III-09 (degassed)– magnified 50,000 and 100,000 times respectively.

VITA

Lan Liang was born in Wuwei, Gansui province, P.R. China on June 11, 1973. She graduated from Jining No. 1 High School in Jining, Shangdong province, China, in July of 1991. In July of 1995, she received a B.S. degree in Chemical Engineering from Dalian University of Technology, China. Upon graduation, she continued her study at Tianjin University as a graduate student and a research assistant as well. In August of 1999, she enrolled in the Ph.D. program in the Chemical Engineering Department of Texas A&M University. She can be reached through her father, Mr. Dongzheng Liang, at 173 Taibailou West Road, Jining city, Shangdong Province, 272121, P.R.China.