Beneficiation of Pyrolitic Carbon Black

Jefrey Pilusa, Edison Muzenda

***Abstract*—**This research investigated treatment of crude carbon black produced from pyrolysis of waste tyres in order to evaluate its quality and possible industrial applications. A representative sample of crude carbon black was dry screened to determine the initial particle size distribution. This was followed by pulverizing the crude carbon black and leaching in hot concentrated sulphuric acid for the removal of heavy metals and other contaminants. Analysis of the refined carbon black showed a significant improvement of the product quality compared to crude carbon black. It was discovered that refined carbon black can be further classified into multiple high value products for various industrial applications such as filler, paint pigment, activated carbon and fuel briquettes.

***Keywords*—**Activated Carbon, Briquettes, Fuel, Filler, Pyrolysis.

I. INTRODUCTION

CARBON black is a generic term for an important family of products that is used principally for the reinforcement of rubber, as a black pigment and because of its electrical conductive properties [1]. It is an extremely fluffy fine powder with a large surface area and is composed essentially of elemental carbon. Carbon black is one of the most stable chemical products. In general, it is the most widely used nano-material and its aggregate dimension ranges from tens to a few hundred nanometers [2].

Plants for the manufacture of carbon black are strategically located worldwide to supply the rubber tyre industry, which consumes 70% of the carbon black produced. About 20% is used for other rubber products and 10% is used for a variety of non-rubber applications. World capacity in 2005 was estimated at more than 10 million tons [3].

Over 40 grades are used by the rubber industry alone. Many additional grades are marketed for non-rubber applications [4]. Carbon black demand from the tyre sector is projected to increase 3.7 percent per year through 2013 to 6.9 million metric tons. The non-tyre rubber carbon black market is expected to expand by 4.8 percent per year through 2013 to 3.6 million metric tons. South Africa generates approximately 0.12% of the global new tyre production [3]. Carbon black grades are determined according to an international ASTM classification. The major multinational tyre companies account for in excess of 80% of the carbon black consumption in South Africa. Non-rubber applications (e.g. pigments in plastics, inks and paints) account for only around 5% of the market. The average market price for high-grade carbon black is in the order of $661/ton and low grade at $273/ton based on the historical import market [4].

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A. Waste Tyre Pyrolysis

Pyrolitic carbon black is produced as a solid by-product of waste tyre pyrolysis process after the gaseous fraction have been recovered and condensed into liquid fuels. For every 1 ton of tyres processed, 366 kg of crude carbon black is produced as a by-product. Pyrolysis has since been a solution to some as an environmentally friendly solution of producing products with high market value such as gas, oil and high tensile steel as presented in Fig. 1 [3].

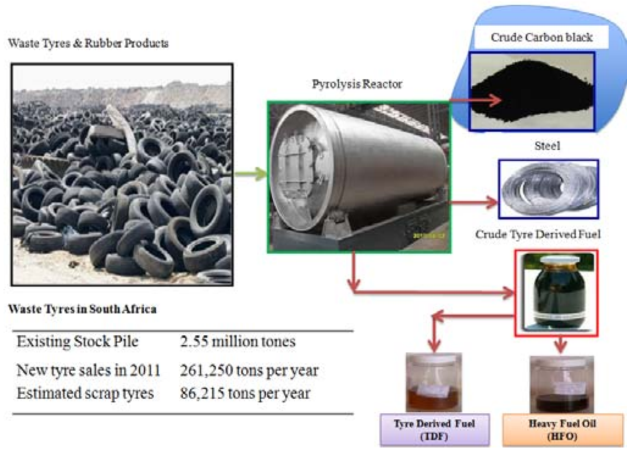

Fig. 1 Process Flow Diagram of Waste Tyre Pyrolysis [5]

B. Carbon Black Particle Size

Particle sizes of commercially used carbon black are very small compared to pyrolytic carbon black, particle sizes of carbon black are especially important because it is used to characterize carbon black by grades. The average particle size of commercially available rubber type carbon black grades ranges from about 10 to 500 nanometers [6], [3]. Small particle size of carbon black is favoured in the reinforcement industry because the reinforcement strength increases with decrease in particle sizes.

TABLE I
EFFECT OF PARTICLE SIZE ON REINFORCEMENT [7]

Particle size nm	Strength
1000-5000	Small reinforcement
<1000	Medium reinforcement
<100	Strongest reinforcement

Carbon black may be used as reinforcing filler in rubber for automotive tyre manufacturing as shown in Table I, or as activated carbon because of its high carbon content [8]. Activated carbon was used mainly for the purification of products of different industries as well as for purification of drinking water [8]. Jha [8] classified various sizes fractions of activated carbon black as presented in Table II.

TABLE II
CLASSIFICATION OF ACTIVATED CARBON BLACK BY SIZE [8]

Particle Size	Type of Activated Carbon
1-150 µm	Powdered activated carbon
0.5-4 mm	Granular activated carbon
size 0.8-4 mm	Extruded activated carbon

A carbon black with a high degree of aggregation is said to have a high 'structure'. Structure is determined by the size and shape of the aggregated primary particles, the number of primary particles per aggregate and their average mass [9].

The particle size of a carbon black particle is very important; carbon black is produced by incomplete combustion by using the Pyrolitic process [10]. These particles may be categorized into 3 size ranges. The primary particles have the smallest size, which are typically 13–100 nm in diameter depending on the parameters set in carbon black processing [11]. Such primary particles fuse and form in the furnace reactor, a second larger level of structure or aggregates having size in the range 200–1000nm. The morphologies of these aggregates can vary from linear, branched to completely compact and roughly spherical domain [12]. Further, these carbon aggregates may percolate and form agglomerates, which have the largest size (exceeding 1000nm) [13]. The easy formation of aggregate of the furnace carbon is due to the high inter particular forces, while agglomerates result from weakly bound aggregates, and might be broken down into aggregates by micro-milling.

C. Properties of Carbon Black

Carbon black consists of aggregates, defined as the smallest dispersible units, which are composed of partially fused, reasonably spherical primary particles. Surface area increase as primary particle size is reduced [14]. The aggregates, in turn, are held together by attractive van der Waals forces to form agglomerates. These forces increase as the size of the primary particle is reduced and agglomerate density is increased.

Characterization of the surface properties of carbon black in terms of surface activity has been difficult compared to the other fundamental properties. However, surface activity has been evaluated in terms of oxygen content and/or moisture adsorption rate [15]. For polar carbon black surfaces, oxygen content and acidity are important measures of the effective surface activity [14].

Sulphur is one of the most common impurities in carbon black. It can be introduced with the tyre rubber feedstock. Inorganic contaminants in carbon black, such as Si, Al, and Cu can also be introduced with the rubber feedstock in the form of trace metals, cracking catalyst residues, and from the carbon black reactor [16]. It is necessary to obtain surface chemical states of these elements in terms of surface element distribution /concentration and chemical structure for the surface chemistry information on carbon black [17].

D. Applications of Carbon Black

Traditionally, carbon black has been used as a reinforcing agent in tyres. Today, because of its unique properties, the uses of carbon black have expanded to include pigmentation, ultraviolet (UV) stabilization and conductive agents in a variety of everyday and specialty high performance products, including:

1. Tyres and Industrial Rubber Products

Carbon black is added to rubber as both filler and as a strengthening or reinforcing agent. For various types of tyres, it is used in inner liners, carcasses, sidewalls and treads utilizing different types based on specific performance requirements

2. Plastics

Carbon blacks are now widely used for conductive packaging, films, fibres, mouldings, pipes and semi-conductive cable compounds in products such as refuse sacks, industrial bags, photographic containers, agriculture mulch film, stretch wrap, and thermoplastic moulding applications for automotive, electrical/electronics, household appliances and blow-moulded containers.

3. Electrostatic Discharge (ESD) Compounds

Carbon blacks are carefully designed to transform electrical characteristics from insulating to conductive in products such as electronic packaging, safety applications, and automotive parts.

4. High Performance Coatings

Carbon blacks provide pigmentation, conductivity, and UV protection for a number of coating applications including automotive (primer basecoats and clear coats), marine, aerospace, decorative, wood, and industrial coatings.

5. Toners and Printing Inks

Carbon blacks enhance formulations and deliver broad flexibility in meeting specific colour requirements.

6. Activated Carbon

Carbon black exhibits high iodine absorption number making it a potential adsorbent for water purification and gold recovery.

7. Solid Fuel

Carbon black has higher calorific value, fixed carbon and low sulphur and ash content; it can be potentially used as high quality fuel either in granules or briquettes.

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II. MATERIAL AND METHOD

A. Experimental System

A representative sample of crude carbon black with an average top size of 4000µm was dry screened to determine the initial particle size distribution. This was followed by pulverizing the crude carbon black for 3 minutes and leaching in concentrated sulphuric acid for the removal of heavy metals and other contaminants. The treated carbon black sample was dried for further analysis.

1. Carbon Black Leaching

Treatment of pyrolitic CB was investigated using concentrated sulphuric acid (70wt. %), reaction temperatures of 60ºC, and reaction time 90 minutes. The reaction was carried out in a 500ml beaker placed on a hotplate magnetic stirrer maintained at 60ºC. Initial XRF analysis showed a high concentration of zinc oxide, iron oxide and sulphur in the crude carbon black. Concentrated sulphuric acid at elevated temperatures can react with the focus compounds to form water soluble salts and gaseous compounds that can be easily isolated from the solid phase. After the reaction the mixture was left to cool and pressure filtered while washed with de-ionised water to neutralise the solids, the solids were dried at 110^{o}C for 24 hours.

2. Analysis

Pyrolitic carbon black was pelletized and analysed for the presence of inorganic components using Rigaku X- ray fluorescence (XRF). Proximate, Ultimate and bomb calorimeter methods were also used for determination of critical properties such as elemental composition, moisture, calorific value and iodine absorption.

3. Particle Size distribution Analysis

Carbon black was dry screened using a series of shaking laboratory sieves 4000µm and 38µm. The minus 38µm material was re-combined and put through a spinning riffle to obtain a reasonable representative sample of the ultra-fine fraction. A laser particle analysis method was applied to measure the particle size of the ultra fine particles using Malvern particle size analyser.

III. RESULTS AND DISCUSSION

Commercial carbon black favours small particles of carbon black; it is for this reason that pyrolytic Carbon black was reduced in size so that it may have the particle size of those used in the rubber industry as presented in Tables I and II. Characterization of carbon black aggregates critically influences their commercial uses [5].

Analysis of the refined carbon black showed a significant improvement of the product quality compared to crude carbon black. Crude carbon black initially consisted of coarser particles with approximately 24.3wt. % of particles larger than 425µm and 0.2wt% for particles below 38µm in size. Pulverizing the material for 90 seconds improved the surface area significantly and 64wt. % of the product was below 38µm. This process assisted in liberating the heavy metals and other contaminants to be extracted. A high concentration of silica was identified amongst other contaminants in the feed, hence pulverising was chosen over milling since the bond work index of silica is higher than that of carbon black. This makes it easier to separate the silica from carbon black by size fraction after grinding. Tables III and IV summarise the particles size distribution of the feed and ground products.

TABLE III
PARTICLE SIZE OF CARBON BLACK BEFORE PULVERIZING

Screen Size (µm)	Passing Size (-µm)	Mass (g)	Mass Fraction	Cum. Fraction
-4000 + 2800	4000	0.1	0.001	0.999
-2800 + 2000	2800	1.9	0.01	0.989
-2000 + 1400	2000	10.4	0.05	0.939
-1400 + 1180	1400	16.1	0.08	0.859
-1180 + 1000	1180	9	0.046	0.813
-1000 + 850	1000	16	0.08	0.733
-850 + 710	850	14.9	0.076	0.657
-710 + 500	710	17.4	0.088	0.569
-500 + 425	500	47.9	0.243	0.326
-425 + 355	425	20	0.1	0.226
-355 + 300	355	16.1	0.08	0.146
-300 + 212	300	8.6	0.04	0.106
-212 + 150	212	8.9	0.045	0.061
-150 + 106	150	5	0.025	0.036
-106 + 75	106	2.3	0.012	0.024
-75 +38	75	2.2	0.011	0.013
-38	38	0.5	0.002	0
Total		197.3	1	

TABLE IV
PARTICLE SIZE OF CARBON BLACK AFTER PULVERIZING

Screen Size (µm)	Passing Size (-µm)	Mass (g)	Mass Fraction	Cum. Fraction
-4000 + 2800	4000	0.2	0.001	0.999
-2800 + 2000	2800	0.4	0.002	0.997
-2000 + 1400	2000	2.4	0.01	0.987
-1400 + 1180	1400	3.5	0.02	0.967
-1180 + 1000	1180	3.4	0.02	0.947
-1000 + 850	1000	3.7	0.02	0.927
-850 + 710	850	5.3	0.03	0.897
-710 + 500	710	4.4	0.02	0.877
-500 + 425	500	0.4	0.003	0.875
-425 + 355	425	0.8	0.005	0.87
-355 + 300	355	2.5	0.01	0.86
-300 + 212	300	2.5	0.01	0.85
-212 + 150	212	2.5	0.01	0.84
-150 + 106	150	3.6	0.03	0.81
-106 + 75	106	13.4	0.075	0.735
-75 +38	75	16.4	0.09	0.654
-38	38	113.8	0.64	0
Total		179.2	1	

Table V shows the particle size distribution of ultrafine treated (minus 38µm). Approximately 90% of the ground product after leaching and drying was below 33.88µm in size with 10% below 532nm. By interpolation, 17.34% of the particles are below 5000nm is size which means they can be used as small reinforcement as per specifications outlined in Table I. Majority of this fraction is suitable for medium reinforcement application. According to Table II, there is a wide range of particle size specifications for activated carbon. This material will require grinding and treatment for the removal of contaminants prior re-granulation for activated carbon application. Since the resultant distribution is largely dependent upon residence time in the pulverizer, the feed is an important tool in controlling this residence time, and subsequently the resulting PSD. This size was desirable here so that it would be further analysed by particle size. The analytical test confirms weather the grade of commercial carbon black was obtained by pulverizing.

TABLE V
PSD FROM MALVERN PARTICLE ANALYZER OF CARBON BLACK (<38 MICRONS)

Distribution type: Volume		Mean Diameters (µm)	
Concentration	0.0430%vol.	D(v,0.1)	0.532
Density	1.000g/cub.	D(v,0.5)	25.12
Specific Surface Area	0.5939 sq. m/g	D(v,0.9)	33.88

Analysis on acid treated carbon black was performed to determine whether removal of sulphur and heavy metal by concentrated sulphuric acid at elevated temperature was efficient enough. Table VI shows the composition of focus contaminant in both crude and treated carbon black as a percentage of the total stream. Removal of these contaminants will increase the carbon content.

The reduction in contaminants of over 91.7% was observed across the board. It is evident that hot concentrated sulphuric acid is efficient for removing most contaminants in pyrolitic carbon black. Zinc oxide reacts with sulphuric acid to yield water soluble zinc sulphate that can be isolated from the solid phase likewise ferric sulphate and other salt resulting from this reaction. The sulphur is oxidized into gaseous sulphur dioxide which is also isolated from the solids phase. Other hard material such as silica are removed by size fraction since carbon black has a lower bond work index and can be ground by less input energy.

TABLE VI
COMPOSITION OF CONTAMINANTS IN CRUDE AND TREATED PYROLITIC CARBON BLACK

Major Contaminant (wt. %)	Crude	Treated
Zinc(Zn)	2.435	0.0651
Silica(Si)	1.189	0.098
Iron(Fe)	0.879	0.0043
Sulphur(S)	1.664	0.0453
Others	0.9983	0.0083

TABLE VII
PROPERTIES OF COAL AND TREATED PYROLITIC CARBON BLACK

Parameter	Anthracite Coal	Pyrolitic Carbon Black
Inherent Moisture:ISO589,2008	8.7	1.56
Ash Content: ISO1171	7.3	1.30
Total Sulphur	2.1	0.05
Volatile Matter: ISO562	10.9	3.67
Fixed Carbon	71	93.42
Oxygen	7.4	3.6
Hydrogen	4.3	2.4
Carbon	81.4	94.32
Gross Calorific Value : ASTM D3286	29.56	31.23
Iodine absorption (mg/kg)	_	897mg/kg

Proximate analysis of dry treated pyrolitic carbon black and anthracite coal were conducted. Ultimate analysis was also carried out to determine other important parameters. Pyrolitic carbon black contain 93.42% fixed carbon, 3.67% volatile matter, 1.56% moisture and 1.30% ash as per proximate analysis. The bomb calorimeter tests have shown the carbon black yielding a gross calorific value of 31.23MJ/kg. The iodine absorption number of 897mg/kg un-activated was measured, indicating that a higher value can be achieved when carbon black is activated. The higher iodine absorption number suggests that activated pyrolitic carbon black at specified particle size range can be potentially used as activated carbon.

IV. CONCLUSIONS

Pyrolitic carbon black can be used for industrial applications as a reinforcement, activated carbon and alternative fuel. Size reduction and acid treatment is an efficient method for liberation of the contaminants for extraction and increases the surface area of carbon black. Hot concentrated sulphuric acid is efficient for the removal of contaminants. The Ultimate, proximate and XRF results reveal that the quality of crude carbon black has significantly improved after treatment. Approximately 64% of carbon black can be transformed into high value product as 10% of this fraction is below 0.5µm in size and majority of industrial re-enforcement products are derived using this specific size fraction. The higher fixed carbon, calorific value and low sulphur and ash content of coarser fraction suggests that it can be used as high quality clean fuel briquettes. It was also observed that the un-activated carbon black has an iodine absorption number of 897mg/kg which suggests its excellent adsorption characteristics which could be improved by thermal or chemical activation.

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