PRODUCTION OF BLACK SHOE POLISH FROM CARBON BLACK DERIVED FROM WASTE CAR TYRE

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ABSTRACT

The research investigated the production of black shoe polish using carbon black obtained from waste car tyre. Waste car tyre of particle size of 2 to 4 cm was pyrolysed in a hot muffle furnace at a temperature range of 450-600 ^{o}C at a heating rate of 20 ^{o}C/min. The maximum carbon black yield 40 % was obtained at temperature of 450 ^{o}C. The pyrolysed carbon black produced was demineralized using hydrochloric acid (HCl) in order to improve its quality and to ensure its suitability in the production of black shoe polish. The proximate analysis conducted on improved carbon black revealed that it has the following values: ash content (6.28 %), moisture content (2.20 %), bulk density (0.924 g/cm^3), pore volume (0.446 cm^3/g) and porosity (0.387) respectively. The produced black shoe polish and the commercial black shoe polish were compared in terms of viscosity, pH, density and specific gravity respectively. For commercial black shoe polish, the following values were reported: viscosity = 3.67 cP, density = 0.62 g/cm^3, specific gravity = 0.87 and pH = 5.64 respectively. For black shoe polish produced, the following values were obtained: viscosity = 4.84 cP, density = 0.63 g/cm^3, specific gravity = 0.94 and pH = 6.31 respectively. Comparing both results, it can be concluded that black shoe polish produced and commercial black shoe polish have very close values in terms of viscosity. pH, density and specific gravity.
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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

The disposal of waste tyres has become an important issue worldwide in recent years and represents a major environmental problem. The tyres not only take up large amounts of valuable landfill space, but also create fire hazards and provide a refuge for disease carrying creatures. At present there are three kinds of methods for the reclamation of waste car tyres, they are retreading, recycling and pyrolysis (Teng *et al.*, 2014).

The former two methods are not the final disposal of the waste car tyres. Pyrolysis processing of waste car tyres is considered to be an environmentally acceptable and promising disposal method with its high-energy recovery and low pollution emission (Teng *et al.*, 2014).

Recently, much effort has been devoted to the thermal degradation of tyres into gaseous and liquid hydrocarbons (LHCs) and a solid char residue, all of which have the potential to be reprocessed into valuable products. The resulting HCs from thermal treatment can be used directly as fuels or added to petroleum Refinery feedstocks. As for the solid residue, the char can be used as either low-grade reinforcing filler or as carbon black (Teng *et al.*, 2014).

Most of the char as carbon black for tyres has been reported to be unsatisfactory, mainly due to the high mineral matter content, while activation of the char with steam or CO_2 to produce a high-surface area (SA) carbon has been shown to be applicable. Because of the low reaction rate between the activating agent (Steam or CO_2) and the char, a high temperature ($>800\ ^{o}C$) for activation is necessary. Under this circumstance, the energy consumed in heating the activation agent would be relatively high. The production of carbon black can also be achieved by chemical activation, which usually produces carbons with very high SA (Teng *et a.l.*, 2014).

This method consists of impregnation of the precursor with a dehydrating reagent, such as $ZnCl_2$, H_2SO_4 or potassium hydroxide (KOH), followed by carbonization in an inert environment. In comparison with activation with steam or CO_2; there are two important advantages of chemical activation. First and foremost the lower energy consumption due to the fact that heating the activation agent is not required, and the other is that tyre pyrolysis and carbon black production can be achieved in one stage.

Among the numerous chemical reagents, KOH was found to be effective in creating pores in chars derived from tyres in preliminary study, due to the difference in the activation mechanism. Recently, it has been reported that activated carbon prepared from KOH treatment have specific uses, such as the removal of SO_2 from flue gas and halogenated Hydrocarbon (HCs). Activated carbon is widely used for water purification, air purification and also in batteries and fuel cell (Teng *et al.*, 2014).

1.2 Statement of the Research Problem

Burning of several tons of waste tyres are being generated continuously, globally and annually, especially in Nigeria has given rise to many problems namely as non bio-degradable, non recyclable and emission of dangerous gases such as Carbon oxides, Nitrogen oxides and Sulphur. This has resulted into serious menace to human, plants animals and environment. There is urgent need to address these problems. Most of the methods/techniques used in disposing waste tyres are mostly inefficient because they involve open incineration or burning. Hence, burning of the waste tyres inside muffle furnance using slow pyrolysis technique is proposed to address these problems.

This is due to the fact that this method is efficient and eco-friendly. Furthermore it has the capacity to reduce and control the emission of dangerous gases to the environment. In addition, pyrolysed carbon black can be used for the production of black shoe polish.

1.3 Aim and Objectives of Research

The aim of this research is to produce black shoe polish from waste car tyres employing slow pyrolysis method.

This will be achieved by the following objectives:

i. To produce carbon black from waste car tyre by Pyrolysis of waste car tyre

ii Evaluation of the effect of temperature on the production carbon black

iii To study kinetic behaviour of waste car tyre carbon black and standard carbon black

iv. To characterize the carbon black produced

v. Production of black shoe polish from the characterized carbon black produced.

vi To compare properties of black shoe polish produced and commercial black shoe polish

1.4 Justification of the Study

The main purpose of the present work is to prepare pyrolysed carbon black from waste car tyres and conversion of this carbon black produced to black shoe polish. Carbon black was obtained as a product of slow pyrolysis of waste car tyre; it is relatively inexpensive raw material. Furthermore, tyre pyrolysis is eco-friendly with little emission, making it safer for humans, plants, animals and environment. It could be a remedy for the mass disposal problem of waste car tyres.

The demand for carbon black relates to their unique properties and low cost when compared with other inorganic adsorbents like zeolite, nano fluid and silica. Many material such as industrial sludge, charcoal and tyre, are dumped as waste causing environmental problem to the society. Carbon production from waste car tyre is a process that would result in high carbon yield and low energy consumption. The application of waste car tyres in the production of carbon black and converted to black shoe polish is of great economic importance to the nation as it will reduce the disposal of waste material into the environment.

1.5 Scope of Research

Research work was limited to the slow pyrolysed waste car tyres in the production of carbon black and conversion of this carbon black produced to black shoe polish.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 History of Shoe Polish

The shoe polish was started before the year 1900 using wax, ash and tallow. After 1900 it was replace by using different liquids and suspended solids. Various substances have been used as shoe polish for hundreds of years starting with natural substances like wax and tallow (Moral; 2017). Modern polishes formulate were introduced early in 20th Century and some of the polish produced from that era are still in use (Mohammed and Dawaki, 2013).

Wax and polish are used for many purposes they have their principal use in waterproofing; they are mainly consumed industrially as components of complex formulations, often for coatings. Most polishes depend on wax or oil for their polishing properties. Wax polishes are however more long lasting (Okanlawon, 2015).

2.2 Definition of Shoe Polish

Shoe polish is usually a waxy paste or cream used to shine, waterproof and restore the appearance of leather to make the finished leather smooth and glossy by gentle rubbing and enhancing is performance and durability (Turner, 1993; Mohammed and Dawaki, 2013). It is mostly applies on leather products to repel other solvents or dust from the film surface and impart elasticity and gloss to the film without destroying the hardness of leather (Guthrie, 2014).

It is expected also that a polish will clean the surface and prevent deterioration. Due to surface tension forces, a glossy surface is created after polishing. This will dry to give the object the required luster, the polish has to be resistant to corrosion, smooth, transparent, uniform in colour, be adhesive, glossy and also thin (Okanlawon, 2015).

2.3 Shoe Polish Content

Shoe polish consists of a waxy colloidal emulsion, a substance composed of a number of partially immiscible liquids and solids. It is usually made from ingredients such as water, naphtha, lanoline, turpentine, wax, gum arabic, ethylene glycol required a colorant such as carbon black or azo-dye. Typically it has a specific gravity 0.8, it is negligibly soluble in water and is made of between 65 and 77% volatile substance, which helps black shoe polish to dry out and harder after application while retaining its shine (Hilditch, 2012).

Lanoline, hydrophilic grease from wool bearing, animals such as sheep or goats, acts as both water proofing wax and a bonding agent, giving the black shoe polish its greasy feel and texture, it prevents the naphtha from evaporating until the polish has been spread and buffed into a thin film on the leather surface (De Bussy, 2014).

An essential ingredient in black shoe polish manufacture is thickener, without this the polish will be too runny making it difficult to use. Gum Arabic is a substance which commonly used to increase the viscosity of the product. Water acts as a solvent while different dyes can be used to give the coloration. Shoe polishes contain chemical substance which can be absorbed through the skin or inhaled, during application; one should ideally wear gloves and stay in a well-ventilated area while applying it and will cause irritation to the eye if there is direct contact (Mohammed and Dawaki, 2013).

2.4 Types of Black Shoe Polish

Basically there are two types of polish:

i. Waterless

The paste polished in non-aqueous and clear or translucent.

ii. Water based.

The emulsion polish is milky in appearance and aqueous. Oil polishes are easy to apply but the polished surface easily attracts dust and finger marks. However, wax polishes are more difficult to apply on the surface and are more reliable in that little or on dust is attracted and no finger marks are shown. Nevertheless, it is better to use wax polish on shoes rather than oil polishes (Kirk and Othmer, 2011).

A number of companies that manufacture shoe care products also sell a liquid shoe polish in a squeezable plastic bottle, with a small sponge applicator at the end to decrease its viscosity. Bottled polish usually has very low wax content (Kirk and Othmer, 2011).

2.5 Properties of Shoe Polish

i. Gloss: forms the basis for the decorative and protective properties of polish.

ii Quick-Drying: the precipitation of dust on the polished surface occurs when there is low drying rate.

iii. Thin-Layer formation: this serves as a barrier between the polished surface and the moisture filled environment. This give shoes smart look and inhibits corrosion

iv Decorative: the polish should look smart and nice (Hans-George, 2013).

2.6 History of Carbon Black

Soot, which is similar to carbon black, was used for writing letters on papyrus in ancient Egypt and on bamboo strips in ancient china carbon black production became a type of Cottage industry about the time when the paper production method was established in the Second century. It then became widely used in industries after it was produced with the channel process in 1892 and with the oil furnace method in 1947. (Mitsubishi Chemical).

Carbon black is produced from “sour” gas-natural gas that contains more than 1.5 grain of hydrogen sulfide or more than two grains of sulfur per hundred standard cubic feet. Although J.K Wright, a Philadelphia ink matter, discovered the process of manufacturing carbon black (CB) in 1864, it was little used until improved technology in the twentieth century reduced the high cost of production. After 1915 CB became widely used as a reinforcing agent in the production of automobile types

In early 1923, the first Texas plant for manufacturing carbon black by burning residue gas from gasoline plants were constructed in Stephens County. Two other plant were erected in the same county later year, together the three annually produced 2,633,013 pounds of CB valued at $184,306 CB production was limited to Stephens and Eastland counties until March 11, 1926, when the Railroad commission permitted the Philips petroleum company to build a plant in the panhandle for the casing head gasoline plants in Carson and Hutchinson counties. This plant, initially run by the western carbon company, was later owned and operated by the Columbia carbon firm (Houston and Gulf, 1998).

By 1926, there were seven CB plants in Stephens county and two in Eastland county, as well as the one in Hutchinson county; that year Texas produced 20 percent of the nation's output of CB in 1928 the cabot carbon company established the first of several plants' near pampa, and in 1931 a plant was erected at Big lake, such corporations as coltexo, Texas. EIF carbon continued to expand and sometimes established their own company towns in more remote areas to house employees and their families. In 1931 thirty-one plants in Texas produced. 210,878,000 pounds of carbon black, 75 percent of the nation's output. In 1937 forty Texas plants, thirty-three of them in the panhandle, produced 82 percent of the nation's CB, the panhandle plants alone yielded 405,247,000 pounds plants were also operating in winkler and ward counties during the late 1930s and 1940s (Taylor *et al.*, 2017).

By the close of World War 11 there were forty-two CB plants in the state, including one at Bunavista, west of Borger, built shortly after the Japanese bombing of Pearl Harbor. During the 1950s, when eighty-billion cubic feet of gas were burned annually to produce CB Texas retained its position as the nation's leading CB producer. In 1954 thirty Texas plants with the total daily capacity of three million pounds were located in eighteen counties and produced 65 percent of the nation's total CB. Rubber companies absorbed most of the total production; smaller quantities were used as pigments in ink and paint. Production continued to be concentrated in the panhandle, although some carbon black plants were built along the Gulf coast. Major locations included five plants (four furnace type and one channel type) at Borger, two furnace type plants at Big spring, and two plants (one furnace –type and one channel type) at seagraves, other plants were located at Skellytown, Baytown, and Aransas pass (Taylor *et al*., 2017).

Of the two methods of production, channel and furnace, the lather was becoming more popular by the 1960s. In 1964 the industry recovered 1,165,593,000 pounds of CB valued at $86,494,000. Thirty-nine plants employed 1,954 persons and had a value added by manufacturing of $29,957,000. The total daily capacity of Texas CB plants had increased by that year to 3,945,300 pounds (Taylor *et al*., 1985).

By 1969, Texas CB production was valued at $110,816,000 The 1970s and 1980s saw a general decline in the number of CB plants, due mainly to the decrease in output of natural gas. This was particularly true of the panhandle, where by the 1980s only a few plants near pampa and Borger remained in operation. Even so, Texas remained the large producer of CB in 1973 the state produced, 1,511,127,000 pounds of CB, valued at $128,144,000. By 1981 only 3, 213, 8999 cubic feet, or about, 05 percent of all the natural gas in Texas, went to produce CB; in 1984 CB was manufactured from, 456,809 cubic feet, or 04 percent of Texas natural gas (Taylor *et al*., 1985).

2.7 Disposal Technology

Disposal Technology is a technical methods used for decomposing waste material in to value added product, methods such as incineration, pyrolysis, open burning and land filling

2.7.1 Incineration

Incineration of waste car tyres has a history than other disposal methods because of its simplicity; however, incineration may produce environmental problems due to the emission of air pollution from the burning process. If the environmental problem is controlled adequately, this method may be the best for mass of waste car tyres. Waste car tyres are excellent fuel source, with an estimated heating value ranging from 12,000 to 16,000 Btu/lb (EPA, 1991), compared to coal and municipal waste values of 12,000 to 12,600 Btu/lb and 2,500 to 8,500 Btu/lb, respectively (Beckman, 1974). According to Ahmed and Lovell, (1992), proven technology exists to efficiently burn whole, shredded or granulated tyres. While all applicable pollution control codes. In 1990, 10 percent of the total waste cars tyres generated, about 25.9 million tyres, were burn for energy production. The use of tyres and tyre-derived fuel (tdf) can be accomplished in various combustion facilities such as power plants, tyre manufacturing plants, cement kilns, pulp and paper plants and small package steam generators (EPA, 1991).

2.7.2 Pyrolysis

The pyrolysis of waste tyres is rapidly developing and spreading technology, pyrolysis is a method of decomposing tyres by a cooking process in order to break down the rubber into saleable by-products. Tyre pyrolysis yields approximately 55 % oil, 25 % carbon black, 9 % steel, 5 % fiber and 6 % gas (Roy *et al*., 1990). The yield can be carryout depending on the operation conditions such as temperature and pressure. High temperature (that is, 900 ^{o}C), pyrolysis yields larger quantities of residues, which are called pyrolyzed carbon black, steel and ashes. Lower temperature pyrolysis yields larger quantities of oil, mostly olefins, aromatics, and naphtenes (OECD, 1981).

Destructive distillation and carbon black recovery are the two main operations in the pyrolysis of tyres. As many as 5,000 waste tyres can be processed in a day by a single facility (Cindy *et al*., 1990). The products recovered in pyrolysis can be re-processed for the manufacturing industry and for the construction industry. This is often done in order for the method to be effective and economical method (Roy *et al*., 1990).

Whole tyres should be used as feedstock rather than shredded tyres. The plant operation should be supported by a high-quality control laboratory that can be operated by low-level technicians. In addition, it is necessary that constant steady markets exists for the carbon black and other residues, which otherwise need to be land-filled (Roy *et al*., 1990).

2.8 Definition of Carbon Black

2.8.1 Carbon

Carbon is a chemical element with symbol C and atomic number 6. As a member of group IV in the Periodic Table, it is non-metallic and tetravalent making for electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, with 12C and 13C being stable. While 14C is radioactive, decaying with a half-life of about 5700 years. Carbon is one of the elements known to man since antiquity. The name “carbon” comes from Greek word carbon, coal, and in Romans language, the word carbon can refer to both as the element and coal. It is fourth most abundant element in the universe by mass after hydrogen, helium and oxygen. It is present in all known life forms and in human body; carbon is the second most abundant element by mass (about 18.5%) after oxygen. This abundance, together with the unique diversity of organic compounds and their unusual polymer-forming ability at the temperatures commonly encountered on earth, make this element the chemical basis of all known life (Ababio, 2010).

2.8.2 Carbon Black

Carbon Black (CB) is a black, powder or granular substance made by burning hydrocarbons in a limited supply of air. This produces a black smoke containing extremely small carbon black particle which can be separated from the combustion gases to form a fluffy power of intense blackness. Carbon black is composed of fine particles consisting mainly of carbon; various features of CB are controlled in production by partial combustion of oil or gas. Carbon black is widely used in various applications mostly as a reinforcing agent for rubber. The largest use of CB is in the manufacture of automotive tyres. It is also used to colour printing ink, painting, paper, and plastics. Over two thirds of the carbon black is used as a reinforcing agent by the tyre industry (Ramakrishnan, 1916).

According to Roster *et al*. (1977) until 1919, most of the automobile tyres were white or red and lasted only 5,000 miles. However, due to the use of CB in the tyre industry. Practically all tyres were black and 15,000 miles to 20,000 miles by 1929. Today, tyres may last for beyond 20,000 miles.

2.9 Physical Structure of Carbon Black

The void volume of a carbon black expressed as a function of applied pressure, W, is a carbon black structure property. Structure is a generic term that is a function of the shape irregularity and deviation from sphericity of CB aggregates. The greater a CB resists compression by having substantial aggregate irregularity and non-sphericity, the greater the compressed volume and void volume. Also, the more that a CB resists compression, the greater the energy required to compress the sample per unit void volume (George *et al*., 2009).

Structure, traditionally measured by OAN (Test method D2414) and COAN (Test method D3493), is a property that strongly influences the physical properties developed in CB elastomer compounds for use in tyres, mechanical rubber goods, and other manufactured rubber products. Several studies within D24 have demonstrated that void volume data can be used to estimate OAN and COAN numbers of CB using mathematical models derived from void volume-pressure data and oil absorption data (George *et al*., 2009).

2.10 Characterization of Carbon Black

Characterization of carbon black is very important in terms of their specific uses. Fundamentally: Carbon black is characterized by physical and chemical properties. According to the Guo and Luo (2003) stated that the characteristic of carbon black depends on the physical and chemical properties of the raw material. Properties of carbon black such as ash content, sieve residue, structure surface area and surface activity can affect the use of a granular CB and render them either suitable or unsuitable for specific applications (Guo and Luo, 2003).

2.10.1 Properties of carbon black

Carbon black broadly can be defined as very fine particulate aggregates of carbon processing an amorphous of quasi-graphitic molecular structure. The most significant areas of distinction between a thermal black and a furnace black are particle size and structure. Most carbon black are classified and assigned a grade number based on surface area and structure measurements (Smith *et al*., 2018).

2.10.2 Sieve residue

Sieve residue refers to non-dispersible contaminants (such as coke, refractory, water soluble salts and metal oxides) and is expressed as a percentage of the carbon black by weight. 75µm sieve is used for this test. The resulting grit can cause blemishes and may affect the appearance and performance of some rubbers and plastic products. The 75µm grit is also tested for magnetic content (Smith *et al*., 2018).

2.10.3 Surface area

Surface area measurements give an indirect characterization of carbon black particle size. There are two methods in use for surface area determination. Iodine absorption (expressed in mg/g of carbon) measures the amount of iodine which can be absorbed on the surface of a given mass of carbon black. Nitrogen surface area is a measurement of the amounts of nitrogen which can be absorbed on a given mass of carbon black (Smith *et al*., 2018).

Both tests have a good correlation for most rubber grades of furnace black, both toluene extractable on the surface of thermal blacks interfere with the aqueous iodine-potassium of the system iodine absorption method, making nitrogen surface area a more suitable test. Accordingly, the American Society for Testing and materials (ASTM) does not recommend iodine absorption for surface area measurements of thermal blacks (Smith *et al*., 2018).

Based on surface area , thermal black is classified as an N900 series black while furnace black fall within the N100 and N700 series. (N) denotes normal curing material. Thermal black has the largest particle size (mean diameters of 240 -320 nm) of any CB and hence has the lowest surface area 7-11m^2/g). In contract, furnace black particle sizes are approximately three to twenty times smaller (mean diameters 15-80 nm) providing surface area from 27-145 m^2/g. (Smith *et al*., 2018).

2.10.4 Structure

Measuring structure or morphology of carbon black is a more difficult task. The current industry index test is the dibutyl phthalate absorption number (DBPA). Dibutyl phthalate absorption measures the relative structure of carbon black by determining the amount of DBP a given mass of CB can absorb before reaching a specified viscous paste. Thermal blacks have the lowest DBPA numbers (32-47 ml/100g) of any CB, indicating very little particle aggregation or structure (Smith *et al*., 2018).

Electron micrographs of thermal black show a number of individual spherical carbon particles. At the same time, aggregates are very limited and consist of no more than fused particles. Furnace blacks on the other hand do not consist of individual spheres of carbon but exhibit a rather wide range of particle aggregations in which carbon particles are fused into grape-like clusters and/or reticulate chain or branches. Even the lowest structure furnace blacks can be considered as having moderate structure (DBPA: 65 ml/100 g). High structure furnace black has the greatest of amount reticulation (Smith *et al*., 2018).

2.10.5 Ash content

Ash level is highly dependent on the amount of inorganic impurities present in the cooling water. It consists primarily of sodium, magnesium and calcium, but also contains minute amounts of other metals (Raahbar *et al*., 2019).

2.10.6 Heat loss

The heating loss of carbon black is very important in determining its moisture content. The amount of moisture content present is related to: the surface area of the black, relative humidity, ambient temperature and the time for which the material is exposed. Thermal black have the lowest surface per unit's mass of all carbon blacks and therefore absorb an insignificant amount of moisture. The heat loss determination is at 110 ^{o}C (Raabhar *et al*., 2019).

2.10.7 Surface activity

Unfortunately there is no direct method for measuring carbon black surface activity. The ipo8terms refer to the chemical reactivity of the surface. Surface activity is influenced by the graphic plane orientation as well as the number and type of organic side groups. On a molecular level, carbon black is composed of amorphous graphite layer planes created from the condensation of aromatic rings. The edges of such planes have unsatisfied carbon bond which can act as chemical reaction sites. The reaction time for the production of thermal black is long in comparison to the furnace black process. Long reaction times combined with the high temperature require for the thermal decomposition of natural gas feed stock (1300) allows the graphite layer plane edges are exposed and therefore no potential reaction sites for elastomer interaction are present in thermal black. Conversely, the shorter reaction times used in making furnace black produce layer planes at the surface which are less ordered, resulting in numerous sites for chemical with elastomers.

Recent scanning tunneling electron microscope (STM) studies, which are characterize the surface of carbon black, clearly support the fact that layer particle size CBs like thermal black tend toward a more organized surface structure with fewer active sites. The formation of thermal black occurs in the absence of flame or while furnace black is generally the product of incomplete combustion of petroleum refinery residues. As a result, furnace black contain numerous types of organic functional groups such as hydroxyls, phenols, lactones and quinones which are also contribute to the level of surface activity. The same organic functional groups are virtually absent from thermal black.

Carbon black with a high amount of surface activity often provides high reinforcement. While thermal black does impart some degree of reinforcement to elastomers it is most often referred to as an inactive or non-reinforcing black.

The influence of carbon black on rubber can best be described in terms of processing and vulcanization properties. In choosing carbon black for an elastomer formulation, the degree of CB and the degree of loading must be taken into consideration. The general effects of carbon black on any given rubber property can be summarized according to surface area (particle size), structure and loading level. (Smith *et al.*, 2018).

2.11 Process of Carbon Black

Carbon black (also known as acetylene black, channel black, furnace black, lamp black or thermal black) is a material produced by the incomplete combustion of heavy petroleum products such as, fuel catalytic cracking (FCC) tar, coal tar, ethylene cracking tar and a small amount from vegetable oil. Carbon black is a coke or carbonaceous matter produced from the burning of conversion oil and fuel gas. There are about five a half-dozen manufacturing processes, just about all carbon black in the world is produced by one or two methods as follow: (a) the thermal black process, or (b) the furnace black process. Both processes involve essentially the same steps, but the furnace black process uses heavy aromatic oil as the feedstock (Ralph, 1991).

The feedstock is introduced as micro-droplets (atomized) into an intensely hot combustion chamber or reactor maintained under controlled conditions of temperature and pressure, with the reaction rate being controlled by the injection of water or steam. The feedstock pyrolysis, produces carbon black particles which are cooled and removed from process gas stream using bag-filters and may then be palletized and bagged for transportation, or further processing to achieve certain qualities (Ralph, 1991).

The thermal black process uses natural gas as feedstock, these in turn uses two furnaces that alternate every five minutes between pre-heating and production, with the carbon black particles produced being then quenched and captured in bag-filters, followed by further processing to remove impurities, palletized, screened, and packaged for transportation (Ralph, 1991).

Studies have shown that a pure gum vulcanized of styrene-butadiene rubber (SBR), or synthetic rubber, which has a tensile strength of less than 2.5 Mpa with almost non-existent abrasion resistance, if compounded with 50 percent by weight of carbon black, has much higher tensile strength and wear resistance. Grade chosen for a given compound can greatly influence the properties of the compound, as well as have a large impact on the methods used to process the compound (Ralph, 1991).

The two processes especially impacted by the CB grade are mixing and extrusion. Effective mixing or "dispersion" of the carbon black in the polymer matrix is important, as mixing time can be major bottleneck in the tyre manufacturing process (Ralph, 1991).

While large particles produce good dispersion relatively quickly, finer particles can be difficult and may require more than one pass through the mixer, when the rubber stock is extruded through a die, it exhibits "elastic memory," a phenomenon that produces swelling (Ralph, 1991).

2.12 Method Available for Carbon Black Characterization

A large selection of characterization method is available for quantification of physical and chemical properties that affect dispersibility of carbon blacks (Contescu and Ridge, 2005).

2.12.1 Electron Microscopy

Electron Microscopy is used to visualize the aggregate shape and to characterize the average size and morphology of primary particles. The ASTM method D 3849-04 covers the morphological characterization of carbon black primary aggregate based on transmission electron microscopy, image processing software is used to derive the mean particle and aggregate size of carbon black in a dry state (Contescu and Ridge, 2005).

2.12.2 Nitrogen Adsorption

Nitrogen Adsorption measurements at liquid nitrogen temperature are used to characterize the total surface area based on the Brunauer Emmett and Teller (BET) theory of multilayer gas adsorption. Additional information include evaluation of external surface area based on the statistical thickness method, evaluation of the total volume of micropores (pore with widths smaller than 2 nm) based on adsorption potential theories, and the pore size distribution based on the density functional theory (DFT) method The ASTM method D 6556-04 covers only the determination of total and external surface area by nitrogen adsorption. The other determinations are available in commercial software packages from all manufacturers advanced gas adsorption equipment in the market (Contescu and Ridge, 2005).

A method for structure characterization of carbon black is based on determination of the oil absorption number (OAN), and is covered by ASTM D 2414-05. It is based on detecting the volume of paraffin oil or dibuthylphthalate that, by incorporation to carbon black powder, suffices to change the state from free power to a semi plastic agglomerate state. The oil absorption number is related to processing and vulcanization properties of rubber compound containing carbon black. High OAN values correlate roughly with high structure aggregates. The method is specific for characterization of carbon black additives for rubber industry, and requires the use of special equipment (absorptometer). We have not used the OAN method in the study (Contescu and Ridge, 2005).

Chemical methods for characterization of carbon blacks comprise methods for measuring impurity content and methods for characterization of surface chemistry (Contescu and Ridge, 2005).

Several methods are available for element analysis of impurities in carbon. The analysis of sulfur, oxygen and nitrogen content in carbon black is possible using combustion techniques (for S) and inert gas fusion techniques (for O and N) available on commercial instruments equipped with infrared gas analyzers. Analysis of other impurities in carbon black and of elements present in trace concentration is possible by high resolution glow discharge mass spectrometry (HR-GDMS). In this method the solid sample is atomized by sputtering in low pressure DC plasma and extracted into the mass analyzer for separation and detection. (Contescu and Ridge, 2005)

The X–ray photoelectron spectroscopy (XPS) method also known as electron spectroscopy for chemical analysis (ESCA) is a powerful method for elemental analysis of the surface layer (0-10nm) of inorganic materials. The method is based on surface excitation of the sample's surface with monochromatic X-Rays and energy analysis of photoelectrons ejected from the sample. High resolution XPS could also be used to identify bonding or oxidation states of specific elements (Contescu and Ridge, 2005).

The use of infrared (IR) spectra for identification of chemical groups is well established as a chemical detection method. However, the applicability of Fourier transforms infrared spectrometer (FTIR) for analysis of surface groups on carbons is limited by the very high absorption of infrared radiation by carbons. This can be circumvented by using highly diluted carbon samples in an inert matrix, but this drastically lowers the signal/noise ratio and the quality of IR spectra (Contescu and Ridge, 2005).

A Chemical method for identification and quantification of acid-base groups on carbons is based on potentiometric titration in an aqueous electrolyte. The pH-volume titration data are converted into a proton binding isotherm that relates the amount of protons bound (or released) to (From) the surface as a function of pH, this is by itself a measure of surface charge evolution on carbon as a function of solution pH. One more step of data processing allows for the derivation of the continuous spectrum of acidity constants (or pka spectrum) of the carbon surface. The assignment of surface chemical groups is based on comparison with known acid strengths of the main organic functions (Contescu and Ridge, 2005). Methods of characterization are briefly introduced in Section 2.12.3.

2.12.3 Thermo gravimetric Analysis (TGA)

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled atmosphere. Thermo gravimetric analysis is a technique in which, upon heating a material, its weight increases or decreases. A sample TGA concept to remember: TGA measures a sample's weight as it is heated or cooled in a furnace (Yaowen *et al.*, 2020).

A Thermo gravimetric Analysis consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. Perkin Elmer offers two types of Thermo gravimetric Analysis (TGA), a top-loading TGA 4000^{tm} and a bottom-loading or hang down, TGA 4000 supports the sample pan above the balance via a "stem" support rod. The TGA 8000 supports the sample pan via a "hang down" below the balance. Both styles take advantage of gravity to obtain very accurate and reproducible measurements (Yaowen *et al.*, 2020).

These instruments can quantify loss of water, loss of solvent, loss of plasticizer, decarboxylation , pyrolysis, oxidation, decomposition, weight percent % filler, amount of metallic catalytic residue remaining on carbon nanotubes, and weight percent % ash. All these quantifiable application are usually done upon heating, but there are some experiments where information may be obtained upon cooling. Both the TGA 800 and the TGA 4000 are controlled by Perkin Elmer's proprietary thermal software, Pyris Software, and have auto-sampler accessories for unattended operation. Both Thermo gravimetric Analysis can be used for evolved gas analysis incorporated into a hyphenated analytical system (Yaowen *et al.*, 2020).

Two most common used TGA are: Thermo gravimetric Analysis TGA 8000 – IR, MS or GC/MS and Thermo gravimetric Analysis TGA 4000 – IR or MS (Yaowen *et al.*, 2020).

2.12.4 Fourier Transform Infrared Spectroscopy

Fourier Transform infrared spectroscopy, also known as Fourier transform infrared analysis or Fourier transform infrared spectroscopy, is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials, the Fourier transform infrared analysis method uses infrared light to scan tests samples and observe chemical properties (Pradhan, 2011).

The Fourier transform infrared instrument sends infrared radiation of about 10,000 to 100 cm through a sample, with some radiation absorbed and some passed through. The absorbed radiation is converted into rotational and/or vibrational energy by the sample molecules. The resulting signal at the detector presents as a spectrum, typically from 4000cm^{-1} to 400cm^{-1} representing a molecular fingerprint of the sample. Each molecule or chemical structure will produce a unique spectral fingerprint, making Fourier transform infrared analysis a great tool for chemical identification (Pradhan, 2011).

2.12.4.1 Uses of Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy is an established technique for quality control when evaluating industrially manufactured material, and can often serve as the first step in the material analysis process. A chance in the characteristic pattern of absorbed bands clearly indicates a change in the composition of the material or the presence of contamination. If problems with the product are identified by visual inspection, the origin is typically determined by Fourier transform infrared microanalysis. This technique is useful for analyzing the chemical composition of smaller particles, typically 10–50 microns, as well as larger area on the surface (Pradhan, 2011).

Fourier transform infrared analysis is used to: (i) identify and characterize unknown material (for instance, films, solid, powders, or liquids), (ii) identify contamination on or in a material (for example, particles, fibers, powders, or liquids), (iii) identify additives after extraction from a polymer matrix and (iv) identify oxidation, decomposition, or uncured monomers in failure analysis investigation (Sindhu and Pandey, 2015).

2.13 Adsorption Mechanism

The process by which such a surface concentration fluid molecules by chemical and/or physical force is known as adsorption whereas, absorption is a process whereby fluid molecules are taken up by a liquid or solid or solid and distributed throughout that liquid or solid.

In the physical adsorption process, molecules are held by the carbon's surface by weak forces called Van der Waals forces resulting from intermolecular attraction. The carbon and the adsorbate are thus unchanged chemically. However, in the process known as chemisorption molecules chemically react with the carbon's surface and are held by much stronger forces-chemical bonds.

In general terms, to affects adsorption it is necessary to present the molecules to be adsorbed to a pore of comparable size, in this way the attraction forces couple with opposite wall effect will be a maximum and should be greater than the energy of the molecule.

Maximum adsorption capacity is determined by the degree of liquid packing that can occur in the pores. In very high vapor pressures, multilayer adsorption can lead to capillary condensation even in mesopores (25A).

If adsorption capacity is plotted against pressure (for gases) or concentration (for liquid) at constant temperature, the curve so produced is known as an isotherm. Adsorption increases with increased pressure and also with increasing molecular weight, within a series of a chemical family. Thus, methane (CH_4) is less easily adsorbed than propane (C_3H_8). This is a useful fact to remember when a particular system has a number of components.

After equilibrium, it is generally found that, all else being equal; the higher molecular weight species of a multi-components system are preferentially adsorbed. Such a phenomenon is known as competitive or preferential adsorption–the initially adsorbed low molecular weight species desorbing from the surface and being replaced by higher molecular weight species.

Physical adsorption in the vapor phase is affected by certain external parameters such as temperature and pressure. The adsorption process is more efficient at lower temperatures and higher pressures since molecular species are less mobile under such conditions. Such an effect is also noticed in a system where moisture and an organic species are present. The moisture is readily accepted by the carbon surface but in time desorbs as the proffered organic molecules are selected by the surface. This usually occurs due to differences in molecular size but can be also attributable to the difference in molecular charge.

Generally speaking, carbon surfaces dislike any form of charge–since water is highly charged (ionic) relative to the majority of organic molecules the carbon would prefer the organic to be adsorbed. Primary amines possess less charge on the nitrogen atom than secondary amines that in turn have less than tertiary amines (Anthony *et al*., 2001).

Thus, it was found that primary amines are more readily adsorbed than tertiary amines. High levels of adsorption can be expected if the adsorbate is a reasonably large bulky molecule with no charge, whereas a small molecule with high charge would not be expected to be easily adsorbed (Anthony *et al*., 2001).

Molecular shape also influences adsorption but this is usually of minor consideration. In certain situation, regardless of how the operating conditions can be varied, since species will only be physically adsorbed to a low level. Examples are ammonia, sulfur dioxide, hydrogen sulfide, and methyl iodide. In such instances, the method frequently employed to enhance a carbon's capacity is to spread it with a particular compound that is chemically reactive towards the species required to be adsorbed. Since carbon possesses such a large surface (a carbon granule the size of a "quarter" has a surface area in the order of ½ square miles!) Coating of this essentially spreads out the impregnation over a vast area. Thus, therefore, greatly increases the chance of reaction since the adsorbate has a tremendous choice of reaction sites. When the adsorbate is removed in this way the effect is known as chemisorption (Anthony *et al*., 2001).

Unlike physical adsorption the components of the system are changed chemically and the changed adsorbate chemically held by the carbon's surface and desorption in the original from is nonexistent. This principle is applied in many industries. Particularly in the catalysis field, where with the ability of a catalyst it can be greatly increased by spreading it over a carbon surface (Anthony *et al*., 2018).

2.14 Factors Affecting Adsorption

The extent of adsorption depends on physical parameters such as temperature, PH of the solution, nature of the adsorbent, surface area of the adsorbent and solubility of the adsorbent. A thermodynamic description of adsorption quantifies the driving force for adsorption in terms of this parameter. An important quantity that can be defined in this regard is the Gibbs free energy of the surface, that is, the surface free energy (Anthony *et al*., 2018). For a one component system, surface free energy is also called surface tension. Factors that affect adsorption include:

i.) Nature of the adsorbent: The physiochemical nature of the adsorbent can have effect on both the rate and capacity for adsorption. Each type of process of carbon black definitely has some unique properties. Also other adsorbents like Nano fluid, Silica gel and Zeolite, also have properties relative to adsorption rate. For instance, temperature sensitivity of various adsorbent varies. Carbon rapidly loses working capacity at above 120f while Zeolite can withstand higher temperature (Anthony *et al*., 2018).

ii.) Solubility of the adsorbent: the rate of adsorption of solute is relatively proportional to its stability in the solvent. The greater the solubility, the stronger the solute-solvent bond and therefore the smaller the extent of the rate of adsorption. This theorem is referred to as the Lundelius rule (Anthony *et al*., 2018).

2.15 Adsorption Equilibrium

Adsorption equilibrium is dynamic concept achieved when the rate of molecules Adsorb onto a surface is equal to the rate at which they desorbed. The physical chemistry involved may be complex and no single theory of adsorption has been put forward which satisfactorily explains all system. Most theories have been developed for gas-solid system because the gaseous state is better understood than the liquid state. Statistical theories are being developed, which should apply equally well to gas-solid and liquid-solid equilibrium, through these are not yet at a stage when they can be applied easily and confidently to the design of equipment (Anthony *et al*., 2018).

The capacity of all adsorbent for a particular adsorbate involves the interaction of three properties, the concentration (C) of the adsorbent in the fluid phase, the concentrations (Cs) of the adsorbent in the solid phase and temperature (T) of the system. If one of these properties is kept constant, the other two may be graphed to present the equilibrium. The commonest practice is to keep the temperature constant ant plot C against T which is known as adsorption isotherm. In gas-solid systems, keeping the pressure constant and plotting Cs against T gives adsorption isobars (Anthony *et al*., 2018).

2.16 Development of Adsorption Isotherm

The amount of the adsorbate that can be taken by an adsorbent is a function of both the characteristics and concentration of the adsorbate and the temperature. The characteristics of the adsorbate that are of importance include: solubility, molecular structure. Generally the amount of material adsorbed is determined as a function of the concentration at a constant temperature and the resulting function are called an adsorbent (http://www.carbonsuppliers.com)

CHAPTER THREE

3.0 MATERIALS AND METHOD

Summarized list of materials and equipment used throughout this research work, procedures and experimental description are stated in this section.

Table 3.1: List of Materials and their Sources

Material	Manufacturer	Sources	Quantity
Waste car tyre	Beijing, China	Vulcanizer, by Idi Junction Esso road Bida, Niger State, Nigeria	1000g
Distilled water	NCRI, Bida	NCRI, Bida, Niger State, Nigeria	5Liters
Hydrochloric acid	Avondate Laboratory England	Chemical engineering Department, FUT, Minna, Nigeria	300ml
Methylene blue	-	Biochemistry Department, FUT, Nigeria	250ml
Paraffin Wax	Nigeria	Chemical Shop, Bida, Niger State, Nigeria	48.05g
Paraffin Oil	Nigeria	Chemical Shop, Bida, Niger State, Nigeria	77.5ml
Gum Arabic	NCRI, Bida	NCRI, Bida, Niger State, Nigeria	150g

Table 3.2: List of Equipment used

Equipment	Manufacturer	Source	Model
Oven	Gallenkamp	Chemical Engineering Dept., FUT, Minna, Nigeria	
England	Department		
Sieve	SETHI	Chemical Engineering Dept., FUT, Minna, Nigeria	
Magnetic Stirrer	Gallenkamp	National Cereal Research Institute, Badeggi, Niger State, Nigeria	
Hotspot Muffle Furnace	Gallenkamp, England	Chemical Engineering Department, FUT, Minna, Nigeria	
Ultra Violente Visible Spectrophotometer	Unico, USA	National Cereal Research Institute, Badeggi, Niger State, Nigeria	
Measuring Cylinder	Pyrex, England	National Cereal Research Institute, Badeggi, Niger State, Nigeria	
Beakers	Pyrex, England	National Cereal Research Institute, Badeggi, Niger State, Nigeria	
Desiccators		National Cereal Research Institute, Badeggi, Niger State, Nigeria	

Conical flask	Danaplast	National Cereal Research Institute, Badeggi, Niger State, Nigeria
Filter paper	Whatman	National Cereal Research Institute, Badeggi, Niger State, Nigeria
Funnel		National Cereal Research Institute, Badeggi, Niger State, Nigeria
Mortar and pestle	Bida, Nigeria	Chemical Engineering Department, FUT, Minna, Nigeria
Hacksaw	Beijing, China	Carpenter, Bida, Niger State, Nigeria
Container	Minna, Nigeria	Chemical Engineering Department, FUT, Minna, Nigeria
Thermogravimetric Analyzer	Perkin-Elmer 4000	Step B (FUT, Minna, Niger State, Nigeria)
Scanning Electron Microscopy	Japan	A.B.U. Zaria, Kaduna State, Nigeria
Fourier Transform	Pyrex England	Step B (FUT, Minna, Niger State, Nigeria)

Infrared Spectroscopy		
Brunauer Emmet Teller	Pyrex England	Step B (FUT, Minna, Niger State, Nigeria)

3.3 Preparation of Carbon Black

The prescription processes of production of carbon black are as follows:

i.) Waste car tyre was first cut with hacksaw to a size of 2 to 4cm long, then washed manually with water

ii.) Samples were dried after washing under sun for 3 days so as to remove the moisture in the sample

iii.) After drying, the pyrolysis process was performed at different temperature of 450 °C-600 °C at every 50 °C elevation. 200g of sample was weighed into a container and placed in a closed muffle furnace at temperature of 450 °C at a heating rate of 20 °C/min for 1 hour at 1 atmospheric pressure. The experiment was repeated for temperature of 500 °C, 550 °C and 600 °C

iv.) After pyrolysis, samples were removed from the furnace and cooled in the desiccators for 30 minute and then pulverized with mortar and pestle. Pulverization provided smaller particle size with increased in surface area

v.) And then sieved, after sieving the samples were demineralized to removed impurities and residual inorganic matter. After demineralization black shoe polish was formulated in accordance to the process earlier on, used in the production of shoe polish from carbon black (Gumel, 2005). 48.05g, paraffin wax was melted at temperature of 90 °C to give a fine solution. The temperature was lower to 60 °C, 150g gum arabic was added to the sample and stirred for 10 minutes with further lowering of temperature to 40 °C, 77.5ml paraffin oil was added and stirred for 15 minutes then carbon black was added, then it cooled for about 30 minutes respectively.

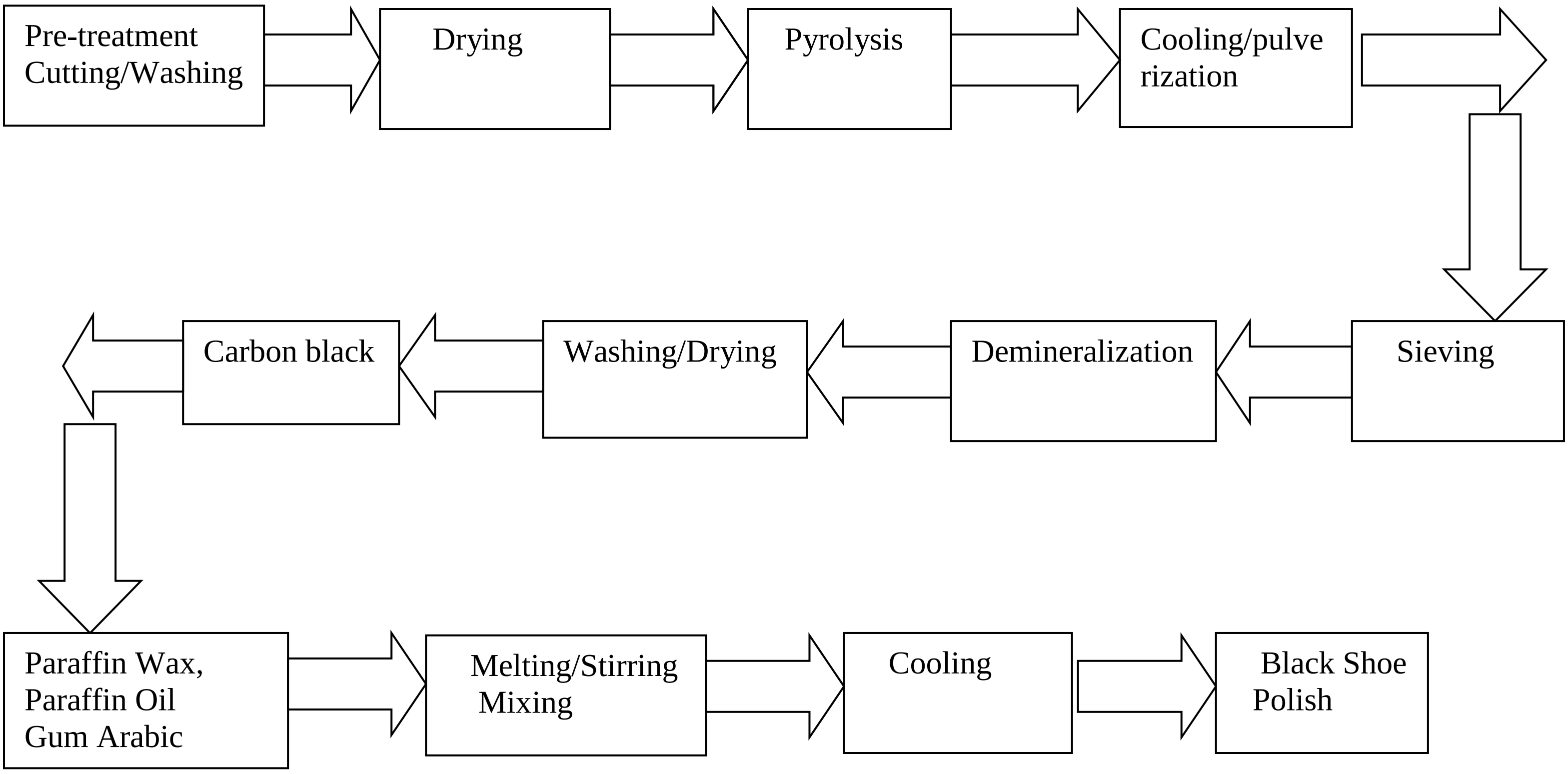


Figure 3.1: Block diagram for the production of Carbon black from waste car tyre

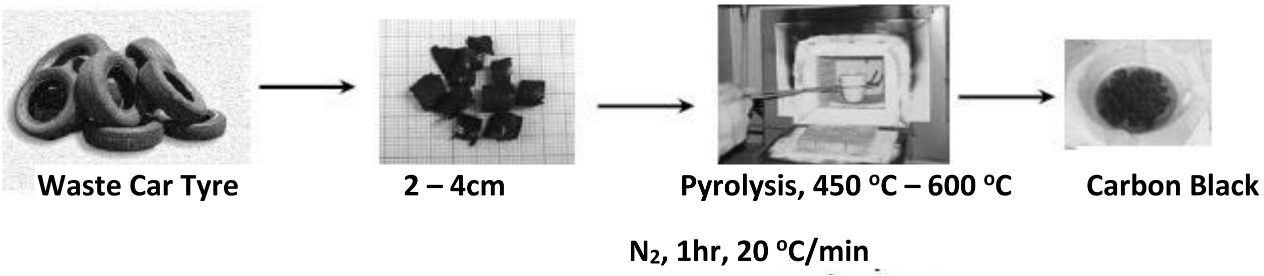


Figure 3.2: Schematic Diagram for the Pyrolysis Set-up

3.4 Characterization of Carbon Black

3.4.1 Acid Demineralization

Acid demineralization was performed to remove undesirable ash content as well as decrease the inorganic impurities from carbon black. 5g of each sample with 50 cm^3 of hydrochloric acid were used for the acid demineralization. The samples were demineralized for a period of 24 hours. After 24 hours the samples were filtered and thoroughly rinsed with 100 cm^3 of distilled water to remove the residual acid, and then dried in an oven at 110 ^oC for 4 hours.

3.4.2 Percentage yield of carbon black

The yield of char is the ratio of amount of carbon black produced in gram to the amount of precursor sample taken for pyrolysis in gram. The percentage yield gives an idea about the amount of substance that has left during production of the samples

$$\text{Percentage yield of carbon black} = \frac{M_1}{M_o} \times 100\%$$

M_o = mass of original Sample

M_1 = mass after pyrolysis

3.4.3 Ash Content

Ash contents were carried out in a closed muffle furnace. 5g of samples were weighed into a container and placed in a furnace at a temperature of 600 ^oC for 2 hours at a heating rate of 20 ^oC/min. The mass of the samples before and after heating were used to determine the amount of Ash content present in the samples. During experiment, the quantity of residual substance that remained is equal to Ash present in the samples.

$$\text{Percentage of Ash Content} = \frac{M_{ash}}{M_o} \times 100\%$$

M_o = mass of pyrolytic carbon black sample

M_o = mass of ash

3.4.4 Moisture Content

Moisture contents were carried out in an oven. 5g of samples were weighed into the beaker and heated at 110 ^oC for 4 hours in an oven. The mass of the samples before and after heating were determined. This specifies the amount of moisture contents present in the samples.

$$\text{Percentage of Moisture Content} = \frac{M_o - M_1}{M_o} \times 100\%$$

M_o = mass of sample before heating

M_1 = mass of sample after heating

3.4.5 Bulk Density

Bulk density was carried out in accordance with that of laid down procedure reported in ASTM D2854 (1987). 5g of samples were weighed and poured into 100 cm^3 measuring cylinder. 50 cm^3 of distilled water was poured into the measuring cylinder and allowed to settled down for 30-minutes; the levels of displacement of the water were noted for all the samples.

$$\text{Bulk density} = \frac{M_o}{M_m}$$

M_o = mass of sample

M_m = mass of equal volume of water

3.4.6 Pore volume

The pore volume was performed in accordance with (Smith, 1981). 5g of the samples were weighed into the beaker and the mass of both the samples and beakers were noted and recorded. 50 cm^3 of distilled water was poured into the beaker containing the dry samples and the mixtures were boiled for 30 minutes. After the air in the pores had been displaced, the masses were recorded.

$$\text{Pore volume} = \frac{M_f - M_i}{M_f} \div \text{density of water}$$

M_f = final mass of sample

M_i = initial mass of sample

3.4.7 Porosity

The porosity or void fraction was calculated according to (Smith, 1988), thus:

Porosity = bulk density × pore volume

3.4.8 Adsorption study

The adsorption studies were undertaken on raw and acid treated carbon black. Methylene blue was employed as the adsorbate in the adsorption studies. Concentration of 10mg/dm^3 was prepared by mixing an appropriate amount of methylene blue with distilled water. Adsorption studies were carried out by placing 0.5g of the carbon black and 50ml of the distilled water in a 250 cm^3 conical flask. The flasks were agitated for about 30mins until the equilibrium was attained. The solutions were filtered and finally there concentrations of the filtrate were measuring using a UV-Visible spectrophotometer at wave lengths of 630 nm. The equilibrium adsorption capacities (Q_e) at different methylene blue concentrations were determined according to the mass balance on the adsorbate (Shah *et al*., 2006).

$$Q_e = (C_i - C_e) \times V/M$$

Where, C_i is the initial concentration, C_e is the equilibrium concentration, V is the volume of the liquid phase and M is the mass of the carbon black.

3.4.9 Thermo gravimetric Analysis

The Thermo gravimetric Analysis (TGA) was performed to show decomposition behaviour during heating, it is defined as a thermal analysis method which investigates the mass change of sample as a function of temperature and time. The sample was heating from 55.20 ^{o}C to a final temperature of 600 ^{o}C at a heating rate of 20^{o}C/min.

3.4.10 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed to observe the morphology (surface structure) of a pyrolysed carbon black at a temperature of 600 ^{o}C.

3.4.11 Brunauer Emmett Teller

The Brunauer Emmett Teller (BET) was performed to carryout surface area of produced carbon black and demineralized carbon black at a temperature of 550^{o}C and 600^{o}C to compare the results in other to known which has more pore size or active site than the other. This is shown in Table 3.3.

Table 3.3: Show the Procedure of Brunauer Emmett Teller (BET)

Produced Carbon Black	Demineralized Carbon Black
Temperature	Temperature
550^{o}C	550^{o}C
600^{o}C	600^{o}C

3.5 Properties of Black Shoe Polish

3.5.1 Viscosity

Using viscometer (Digital Rotothinner SH455N) at 40 ^{o}C the rotor was lowered into the sample by putting the handle down to 77.5ml of the sample, then the digital reading in poise was noted on the display.

3.5.2 pH

The instrument (Jenwayi, 3505 pH meter) was calibrated using pH = 7 buffer solution. Then the electrode was immersed in distilled water and dried very well. After that the electrode was immersed into the samples and the results were recorded when the reading was stabilized.

3.5.3 Specific Gravity

The density cup was weighed when it was empty using electronic balance, then it was filled with the samples of the black shoe polish after that the lid was placed on the cup. The cup was weighed after it was filled with the sample then the weights were divided by the volume to determine the specific gravity.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

Product distribution was obtained from pyrolysis of waste car tyre sample for temperature range of 450 – 600 °C; this occurred at every 50 °C elevation in temperature for an average feed size as 2–4cm. Figure 4.1 shows the effect of pyrolysis temperature on the yield of carbon black. It was observed from Figure 4.1 that as the temperature increases the carbon black yield decreased. Carbon black yield was higher at lower temperature; this observation may be attributed to the fact that increases in temperature led to decrease in the yield of carbon black. The increase of oil yield with increasing temperature was most probably due to the secondary reaction. The maximum char yield was obtained at a temperature of 450 °C. This may be most probably due to the fact that the lower temperature was not sufficiently high enough for complete pyrolysis to take place (that is, complete devolatilization reaction). Similar result was reported by (Cunliffe *et al.*, 2010) which is in accordance with results reported by other researchers (Rofiquel *et al.*, 2004; Li *et al.*, 2004; Helleur *et al.*, 2001; Mui *et al.*, 2010).

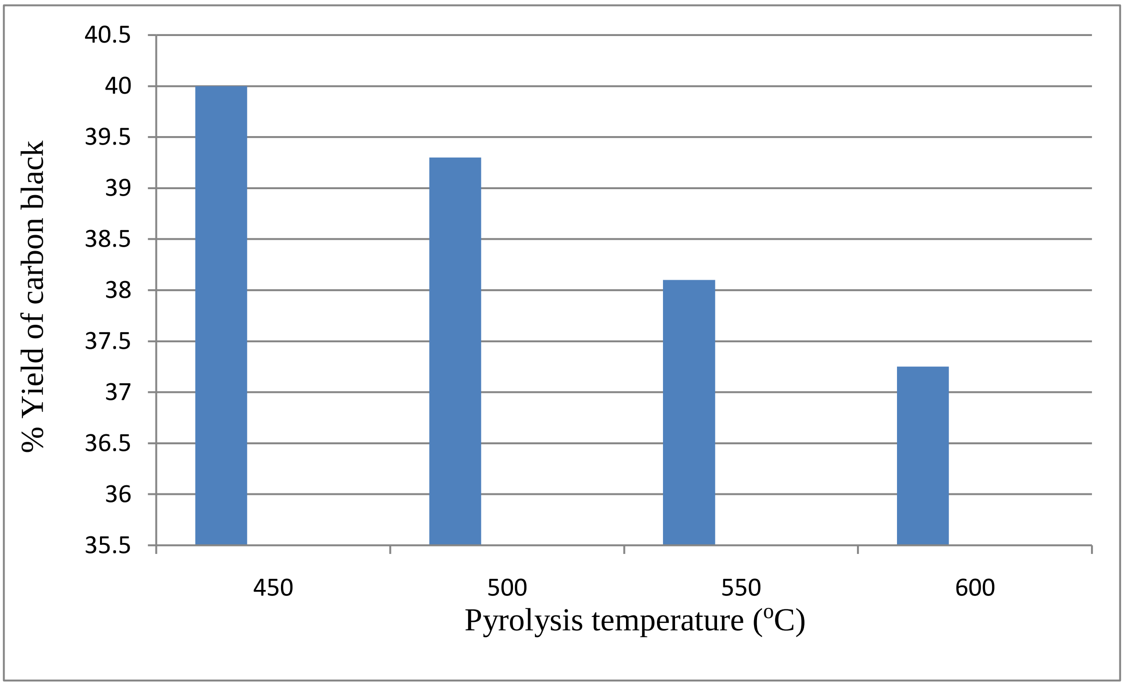


Figure 4.1: Effect of pyrolysis temperature on carbon black yield

Therefore, 600 ^{o}C was observed to be the optimum temperature for recycling waste car tyre by pyrolysis, since decomposition is complete at this temperature. It was also observed that with increase in temperature, reaction time decreases. This may be so because, at low temperature, various compounds (constituents) present in waste car tyre require more time to pyrolyze. During the process of production there are some gases that burn off like carbon monoxide (CO), Carbon dioxide (CO_2), Sulphur (IV) oxide (SO_2), and Nitrogen (IV) oxide (NO_2) were given-off/evolved, which may constitute serious environmental problem. These gases are the major sources of the depletion of ozone layer. Furthermore, they cause serious damages to humans, plants, animals and environment. Examples of serious health problems caused by these gases include: blood poisonous, brain damage and suffocation.

Table 4.1 shows the effect of temperature on yield of carbon black and their physicochemical characteristics. Again as observed earlier, the percentage yield decreasing with increasing temperature, bulk density and ash content increase as the temperature of its production increase as well, whereas moisture content, pore volume and porosity decreasing as the temperature of its production increasing. From characterization study, it may be concluded that the waste car tyre has high volatile content, which is suitable for pyrolysis conversion of organic solid wastes to liquid product. Moisture content is low which favors for liquid fuel production. Similar result has been obtained by (ICME2003-TH-31).

Table 4.1: Effect of pyrolysis temperature on yield of carbon black and their physicochemical characteristics.

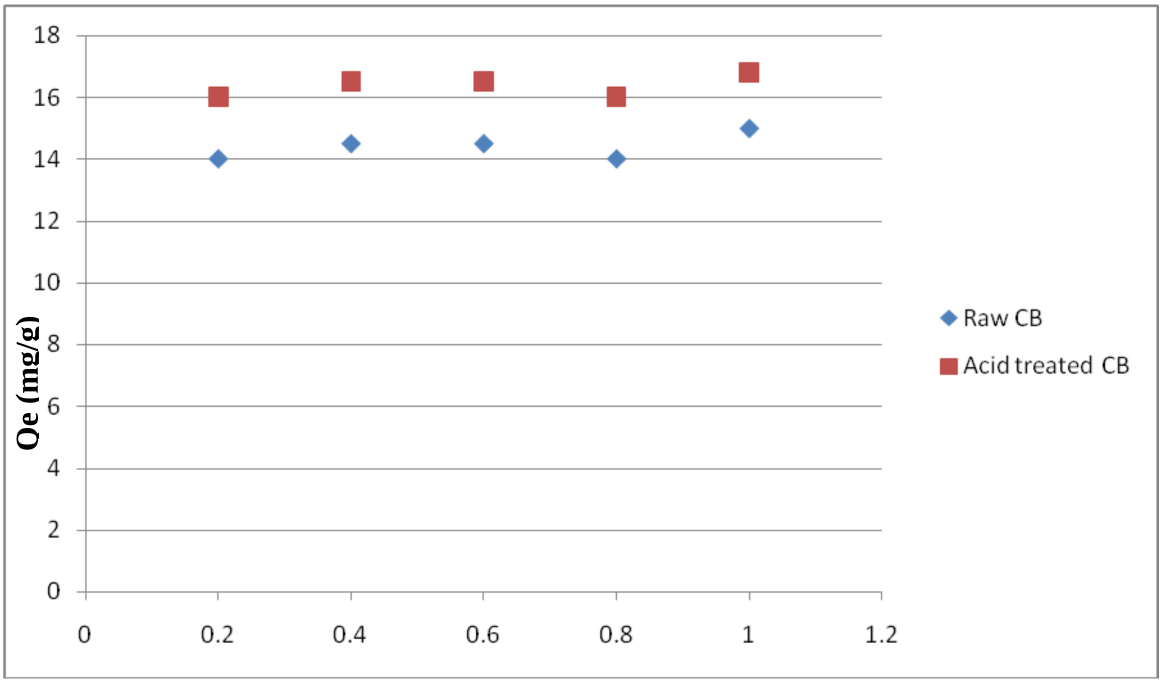
Pyrolysis Temperature (^0C)	Yield of Carbon (%)	Yield of Volatile (%)	Ash Content (%)	Moisture Content (%)	Bulk Density (g/cm^3)	Pore Volume (cm^3/g)	porosity
450	40.00	60.00	5.19	2.80	0.868	0.446	0.387
500	39.30	60.70	5.47	1.80	0.910	0.374	0.340
550	38.10	61.90	6.02	1.60	0.934	0.263	0.246
600	37.25	62.75	6.28	1.20	0.924	0.161	0.149

4.1 Acid Demineralization

In the acid demineralization process the feed samples contain 5g each. After the application of acid treatment of samples, the concentration of carbon black was increased significantly, indicating the removal of non-carbon black phases with acid. The highest carbon black concentration achieved with hydrochloric acid treatment was 92.6%. It can be observed that inorganic elements such as sodium and calcium appear to be completely removed and hydrogen gas which has a pop sound goes up. The results of hydrochloric acid demineralization show that the process has potential for the production of a high carbon concentration.

4.2 Adsorption Capacity for Methylene Blue

Methylene blue adsorptions were studied and compared on pyrolysed and demineralizsd carbon black. The demineralizes and pyrolysed carbon black were employed to adsorb methylene blue for the purpose of comparison. The adsorption capacity of methylene blue onto the pyrolysed and demineralizwd carbon black was shown in Figure 4.2. The adsorption capacities are sharp and the plateaus are relatively horizontal for both. The amounts of methylene blue adsorbed increased considerably with acid treated and raw carbon black.



Ce (mg/dm^3)

Figure 4.2: Comparison of adsorption capacity for methylene blue on pyrolysed and demineralized carbon black.

4.3 Thermo gravimetric (TGA) Analysis

Figures 4.3–4.6 present Thermo gravimetric (TGA) curves at a temperature of 450 ^{o}C and 600 ^{o}C. Weight percent was plotted against temperature and time. From the thermo-gravimetric analyses provided by different researchers (Leung and Wang, 2012; Yang *et al*., 2019; Berrueco *et al*., 2019), they observed that more than one degradation temperature was responsible for rubber pyrolysis region they reported. Based on these results shown in Figures 4.3 – 4.6, it was observed that there was no constant decomposition of weight from the beginning of the pyrolysis to the end. Figure 4.3 and 4.4 Present TGA curved obtained by pyrolysis of waste car tyre at a temperature of 450 ^{0} C. Weight percent were plotted against temperature and time while Figure 4.5 and 4.6 present TGA curved obtained by pyrolysis of waste car tyre at a temperature of 600^0 C were plotted against temperature and time.

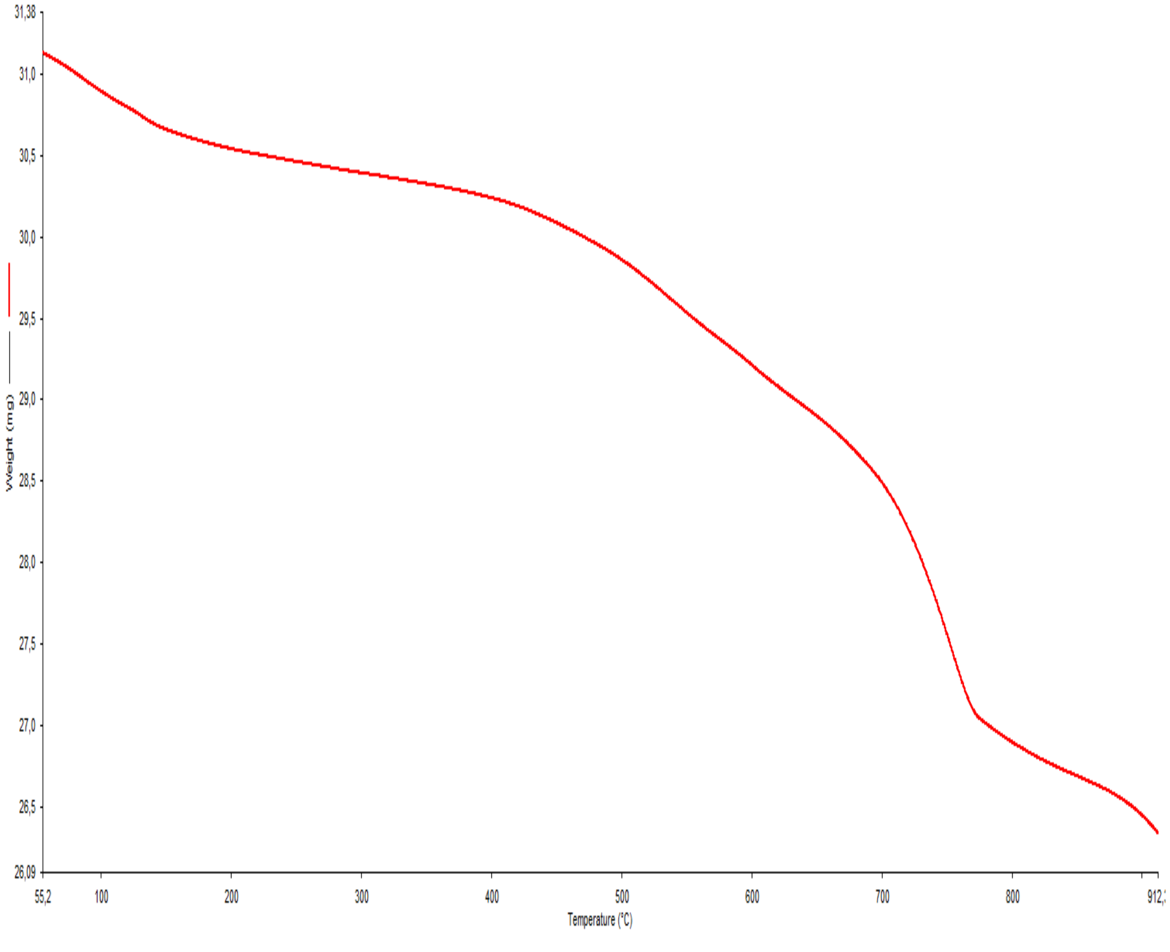


Figure 4.3: TGA curve obtained by pyrolysis of waste car tyre at a temperature of 450 °C weight percent against temperature: residence time: 43 mins.

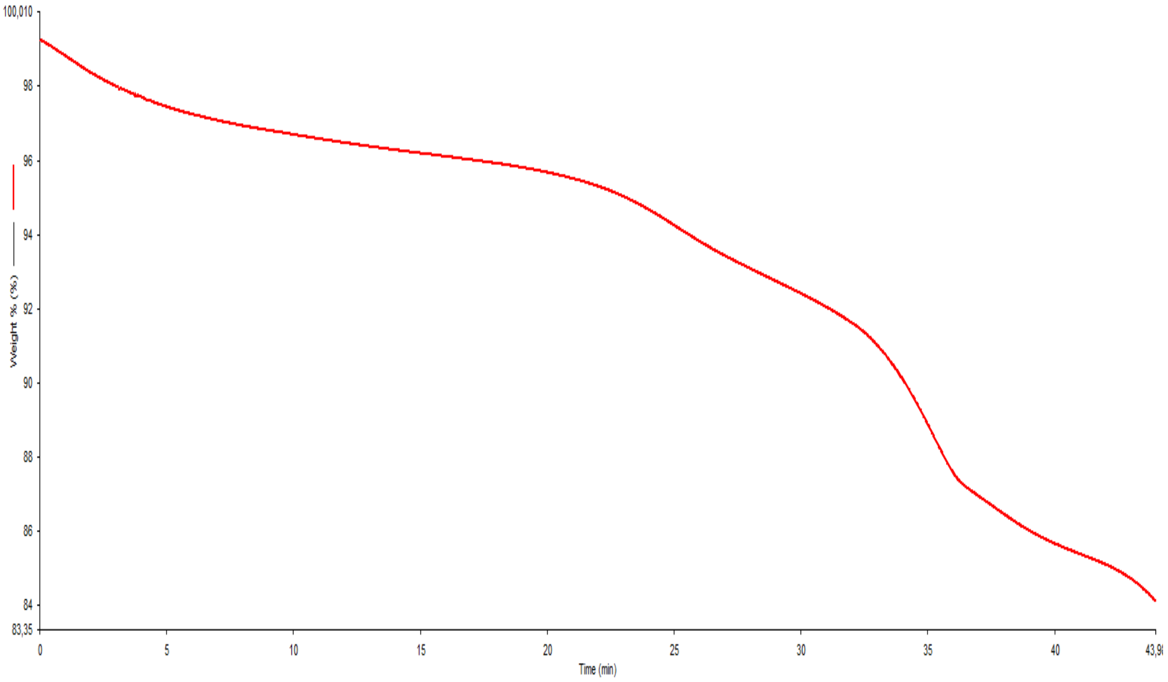


Figure 4.4: TGA curve obtained by pyrolysis of waste car tyre at a temperature of 450 °C, weight percent against time: residence time: 43 mins.

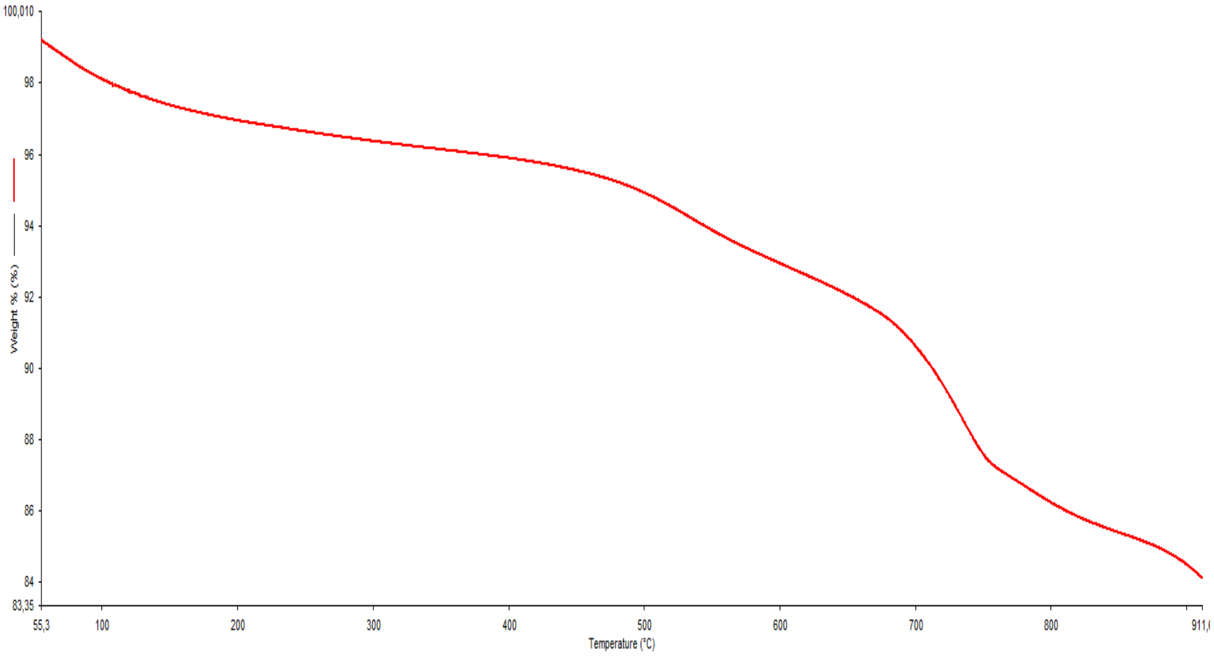


Figure 4.5: TGA curve obtained by pyrolysis of waste car tyre at a temperature of 600 °C, weight percent against temperature: residence time: 43 mins.

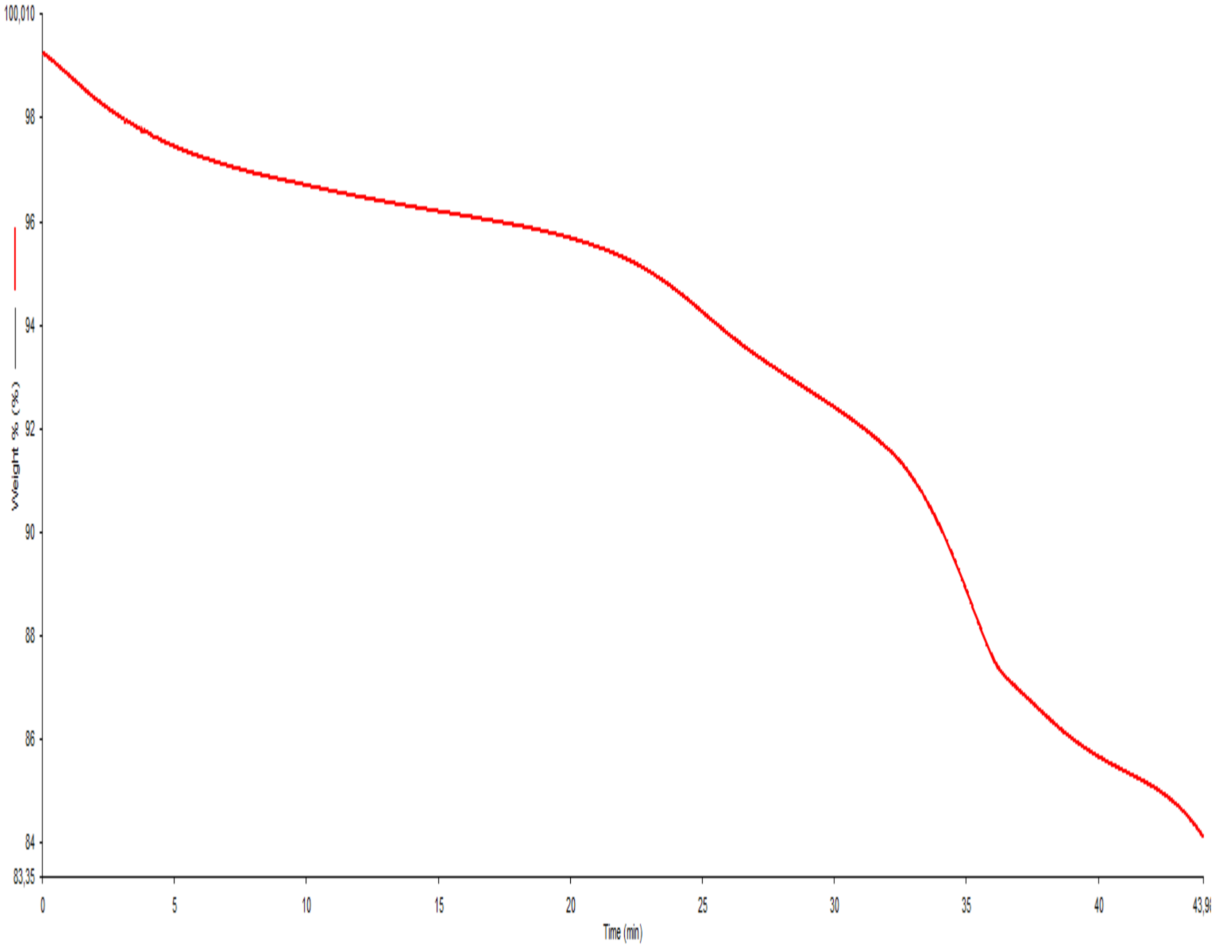


Fig 4.6: TGA curve obtained by pyrolysis of waste car tyre at a temperature of 600 °C, weight percent against time: residence time: 43 mins.

TGA results were explained in Table 4.2. Both standard carbon black and waste car tyre carbon black is stable at temperature lower 100 ^{o}C. The initial decomposition of waste car tyre carbon black start at 105^{o}C the maximum was at 519 ^{o}C and completed at 737 ^{o}C while for standard carbon black the initial decomposition started at 450 ^{o}C, reach maximum at 643 ^{o}C and completed at 740 ^{o}C. Base on this analysis the carbon black content is about 83.35 wt. % for waste car tyre carbon black and 97.7w.t% carbon black for standard carbon black.

This can most probably be attributed to the higher inert filler or ash content present in waste car tyre carbon black is about 16.65 wt. % higher when compared to 2.3 wt. % for standard carbon black. From this result showed that the waste car tyre carbon black contains impurities with the inert filler or ash content. From the thermal kinetic study the physical properties of waste car tyre carbon black started to decompose at lower temperature and not stable at a temperature of 480 ^{o}C when compared with the standard carbon black.

Table 4.2: Thermal kinetic decomposition of standard carbon black and waste car tyre carbon Black

Temperature °C	Standard Carbon Black (wt %)	Waste Car Tyre Carbon Black (wt %)
55	100	100
100	100	98.40
295	100	97.24
483	100	96.10
580	89.4	94.62
676	35.9	18.85
737	2.3	16.65
757	2.3	16.65
1000	2.3	16.65

4.4 Scanning Electron Microscopy (SEM)

Figure 4.7 presents scanning electron microscope (SEM) images. Temperature at 600 °C for 2 h at a heating rate of 20 °C/mins was analyzed. Showing the micrograph of a carbon black exhibits a slightly porous morphology structure with small pores of various shapes and sizes. It also observed that wide varieties of pores were present in the carbon black.

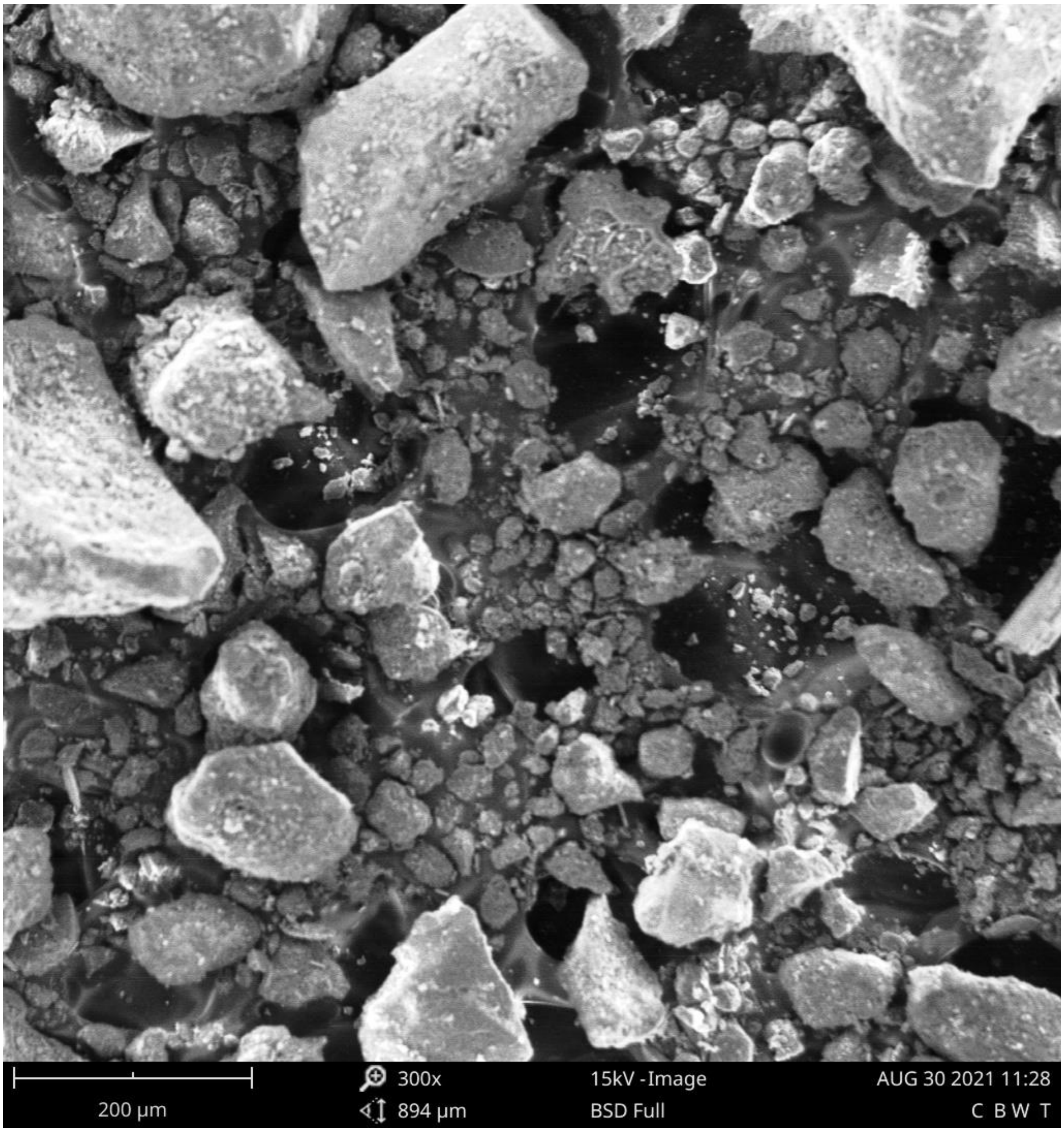


Figure 4.7: SEM image of carbon black at a temperature of 600 °C at 300X

4.5 Fourier Transforms Infrared Spectroscopy (FTIR)

The Fourier transforms infrared (FTIR) spectroscopic study of the produced carbon black is shown in Figure 4.9. The sample showed four major bands at 2664.8cm^{-1}, 2325.9cm^{-1}, 2109.7 and 1990.4cm^{-1} in addition to a small band at 1684.8cm^{-1}. A wide band with two peaks can be notice at 2664.8cm^{-1} to 2325.9cm^{-1}. The band at 2664.8cm^{-1} is due to the stretching mode of hydroxyl group while band at 2325.9cm^{-1} is attributed to C–H interaction with the surface of the carbon. However, it should be indicated that bands between 2664.8cm^{-1} to 2109.7cm^{-1} was attributed to the hydrogen–bonded OH group of alcohols and phenols. In the region of 1990.4cm^{-1}, amides were distinguished on the surface of carbon black which has larger peak. The bands at 1990.4cm^{-1} were associated either C–O symmetric and asymmetric stretching vibration (–C–O–C– ring). The band at 1684.8cm^{-1} was associated with the in plane and out of plane aromatic ring deformation vibration. These spectra were also suggested to be due to alkaline groups' cyclic ketones.

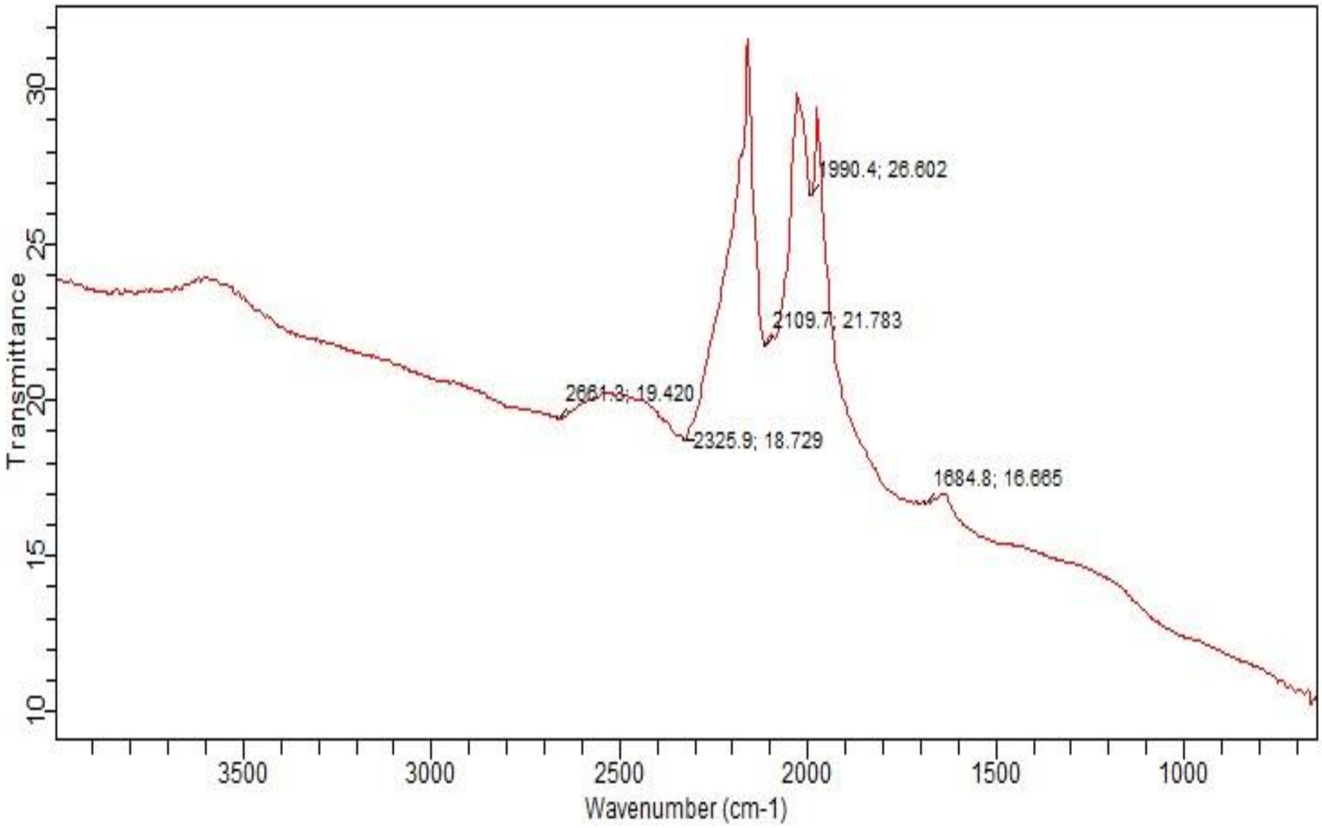


Figure 4.9: Fourier Transforms Infrared Spectroscopy (FTIR) of Carbon Black

4.6 Surface Area Determination using Brunauer Emmett Teller (BET)

Dr. Method were used to discussed the result of surface area determined using Brunauer Emmett Teller (BET). It was observed that in produced carbon black the surface area increases as the temperature of the sample increases, and also with increases in temperature of the sample there also increases in pore volume and pore diameter. In demineralized carbon black the same thing was observed as the temperature increases surface area, pore volume and pore diameter increases as well. Comparison of the produced carbon black to demineralized carbon black, observed that demineralized carbon black has larger value and therefore it has increase in pore size as well as larger active site or more surface area than the produced carbon black. These results are presented in Tables 4.3 and 4.4.

Table 4.3: Properties of Produced Carbon Black

Property	Produced Carbon Black	
Temperature °C	550	600
Surface Area m^2/g	380.5	503.7
Pore Volume cc/g	13.53	17.90
Pore Diameter mm	0.042	0.181

Table 4.4: Properties of Demineralized Carbon Black

Property	Demineralized Carbon Black	
Temperature °C	550	600
Surface Area m^2/g	525.7	903.5
Pore Volume cc/g	18.65	34.95
Pore Diameter mm	0.435	3.066

4.7 Comparison between Black Shoe Polish Produced and Commercial Black Shoe Polish

From the result it can be observed that the viscosity of black shoe polish produced is slightly higher when compared with that of commercial black shoe polish due to the viscous oil which is the paraffin oil and also the gum arabic has it is role to increase the value of the viscosity. pH of the black shoe polish was 6.41 and that of commercial black shoe polish was 5.67 which is in accordance to the elaboration of standards of international organization (ISO) has noted that the value of the pH for the shoe polish specification has to be in the range from 6.5 to 9. The value of specific gravity of black shoe polish produced is higher when compared by the value obtained in commercial black shoe polish, however the amount of the paraffin wax used in this study was larger (48.05 g), so it can be said that the difference in the specific gravity on the two shoe polish may be due to the use of gum arabic. Gum Arabic increased the density of the droplets through steric stabilization and reduced water and oil. As it has been shown in Table 4.5 the properties for the produced black shoe polish is higher than commercial black shoe polish such as viscosity, specific gravity and although density is almost the same.

Table 4.5 Comparison between black shoe polish produced and commercial black shoe polish

Properties	Black Shoe Polish Produced	Commercial Black Shoe Polish
Viscosity cp	4.84	3.67
pH	6.31	5.64
Density g/cm^3	0.63	0.62
Specific gravity	0.94	0.87

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

(1) The results of slow pyrolysed of waste car tyre in the hot muffle furnace at a temperature of 450 ^{o}C – 600 ^{o}C at a very 50 ^{o}C elevation. Maximum char yield of 40 % obtained at a temperature of 450 ^{o}C with heating rate of 20 ^{o}C/min. (2) The effect of temperature on the yield of carbon black revealed that decomposition was incomplete at a temperature of 450 ^{o}C, with high char yield and low liquid and gas product. Acid treatment was used to demineralize and increase the concentration of the carbon black as well as increase the surface area. The demineralized carbon black was characterized using equipment such as: FTIR, TGA, SEM and BET. Demineralized carbon black was also used for production of black shoe polish.

5.2 Recommendations

Based on the findings from the present study, few recommendations are suggested for future work and they are listed below:

(1) It is recommended that more sophisticated equipment such as: FESEM-EDX, XRD and XPS . should be used to improve on the findings from this research work.

(2) Further research should be carried out using other types of waste tyres including: Tractor tyres, Bicycle tyres, motorbike tyres and Trailer tyres.

(3) It is also strongly recommended that carbon's exact physical characteristics should be performed with more relevant in depth analyses.

5.3 Contribution to Knowledge

The Following are my Contribution to Knowledge

1 Conversion of 800g of slow pyrolysed waste car tyre to 100g improved carbon black used with other ingredients to produce high quality black shoe polish. In order word, conversion of waste to wealth

2 Production of black shoe polish from waste car tyre, leads to prevention of the nuisance and serious health

3 Characterization results obtained from improved carbon using TGA, BET, FTIR and SEM revealed that it possess desirable properties which in conjunction with other ingredients used to produce high quality black shoe polish

4 Comparing produced black shoe polish with the commercial black shoe polish. It was observed that desired properties and qualities compared very well.

REFERENCES

Ababio O.Y, (2011). New School chemistry 5th Edition . African Publisher, Nigeria pp.108-113.

Abdullahi A., (2010). production of black shoe polish using spent carbon black photocopier: Federal University of Technology, Minna, Niger state, Nigeria.

Ali, B. H., Ziada A., Blunden G., (2009). Biological effects of gum Arabic: A review of some recent research. In: *Food and Chemical Toxicology* 47 (1):

Allen, J. L.; Gatz, J. L.; Eklund, P. C., (2011). Application for Activated Carbons from Used Tyres: Butane Working Capacity; Carbon1999, 37, 1485.

Ameh Ch. U., (2011). *Thermodynamic properties of shoe polish manufactured from pure water Sachet*; River State University of Science and Technology, Nigeria.

Bianchi, M. G, Bortolani, M., Cavazzoni C., (2014). Preliminary design and numerical analysis of a scrap tyre pyrolysis system, *Energy Procedia*, vol. 45, pp. 111–120,

Cunliffe A. M., Williams P. T., (1998). Composition of oils derived from the batch pyrolysis of tyres. *Journal of Analytical and Applied Pyrolysis.* 44. 131-152.

Debussy J.H (2014). Other carbonization product materials and Technology. Vol.2, 1 Edition Longman Group Limited London 189-193

Haydary, J.,. Korenova, Z., Jelemensky, L.,.Markos, J., (2008). Thermal decomposition of waste polymers, in *ThermoPhysics*, pp. 62– 68,

Hsisheng T., Yu-chuan L., Li-Yeh H., (2000). Production of activated carbons from pyrolysis of waste tyre impregnated with potassium hydroxide, journal of the air and waste management association 50; 1940-1946.

Hu, H. Y., Fang, H. Liu L., (2014). The fate of sulfur during rapid pyrolysis of scarp tyres, *Chemosphere*, vol. 97, pp. 102–107.

Islam, M. R., Parveen M., Haniu, H., Sarker R. I., (2013). Innovation in Pyrolysis Technology for management of scrab tyre, a solution energy and environmental. *International Journal of Environmental and Development.*

Jasmin S. M., Raul J. F., Mabood S., (2006). Conversion of waste tyres. carbon black and their utilization as dsorbent, 53, 1085 – 1089.

Juma, M. Z., Korenova, J., Markos, J. A., Jelemensky, L., (2006). Pyrolysis and combustion of Scrap tyre, *Petroleum & Coal*, vol. 48, no. 1, pp. 15–26,

Karthikeyan, S. C., Sathiskumar, Moorthy, S. R., (2012). Effect of process parameters on tire pyrolysis: a review, *Journal of Scientific and Industrial Research*, vol. 71, no. 5, pp. 309–315,

Martinez, J. A., Veses, A. M.., Mastral B., (2014). Co-pyrolysis of biomass with waste tyres: upgrading of liquid to bio-fuel," *Fuel Processing Technology*, vol. 119, pp. 263–27S. Frigo, Mastral, A. M.; Murillo, R.; Callen, M. S., Garcia, T., (2004). Resour. Conserv. Recycl. 2000, 29, 263-

Miguel G. S., Fowler G. D., Dall, O. M., Sollars C. J., (2001). Porosity and surface characteristics of carbon black produced from waste tyre rubber. *Journal of chemical Technology and Biotechnology,* 77, 1-8.

Mohammed A. Dawaki M.(2013). Formulated Black shoe Polish from Activated carbon using Cum arabaic. Federal University of Technology, Minna Niger State, Nigeria.

Pradham D. Singh B.K (2011). Thermal pyrolysis of bicycle waste tyre using batch reactor. *International Journal of Chemical Engineering and application,* Vol 2. Pp332-336

pyrolysis of Bangladeshi bicycle/rickshaw Tyre wastes. *Journal of Analytical and Applied Pyrolysis,* 82, 96-109.

Quek A., Balasubramanian, R., (2013). Liquefaction of waste tyres by pyrolysis for oil and Chemicals—a review, *Journal of Analytical and Applied Pyrolysis*, vol. 101, pp. 1–16,.

Rofigul I. M., Tushar M. S. H. K., Haniu H., (2008). Production of liquid fuels and chemicals from

Roy, C., (2006). Recovery of Commercially Valuable Products from Scrap tyres; US patent No. 5229, 1993,099.[21]. Shah, G. *Journal of Chinese Chemical, Soc.,* Vol. 53, 5.

Seggiani, M., Puccini, and S. Vitolo, (2014). Liquid fuel production from waste tyre pyrolysis and its utilization in a diesel, fuel vol. 116 pp. 399 – 408.

Shama M. Ahmed A. (2018). Formulation of a shoe polish using activated charcoal and Gum arabic, Sudan University of Science and technology.

Taylor D.T William, P.T Besier S. (2017). The pyrolysis Scrap automative tyres, the influence of temperature and heating rate on Product composition fuel 1474-1482.

Teng H., Lin Y., and Hsu L.,(2014). Production of Activated Carbons from Pyrolysis of Waste, Tyre impregnated with potassium hydroxide, *Journal of air and management, 50.*

Undri, A. L., Rosi, M., Frediani, Frediani, P., (2014). Upgraded fuel from microwave assisted pyrolysis of waste tyre,” *Fuel*, vol. 115, pp. 600–608.

Williams, P. T., (2013). Pyrolysis of waste tyres: a review, *Waste management*, vol. 33, pp. 1714–1772.

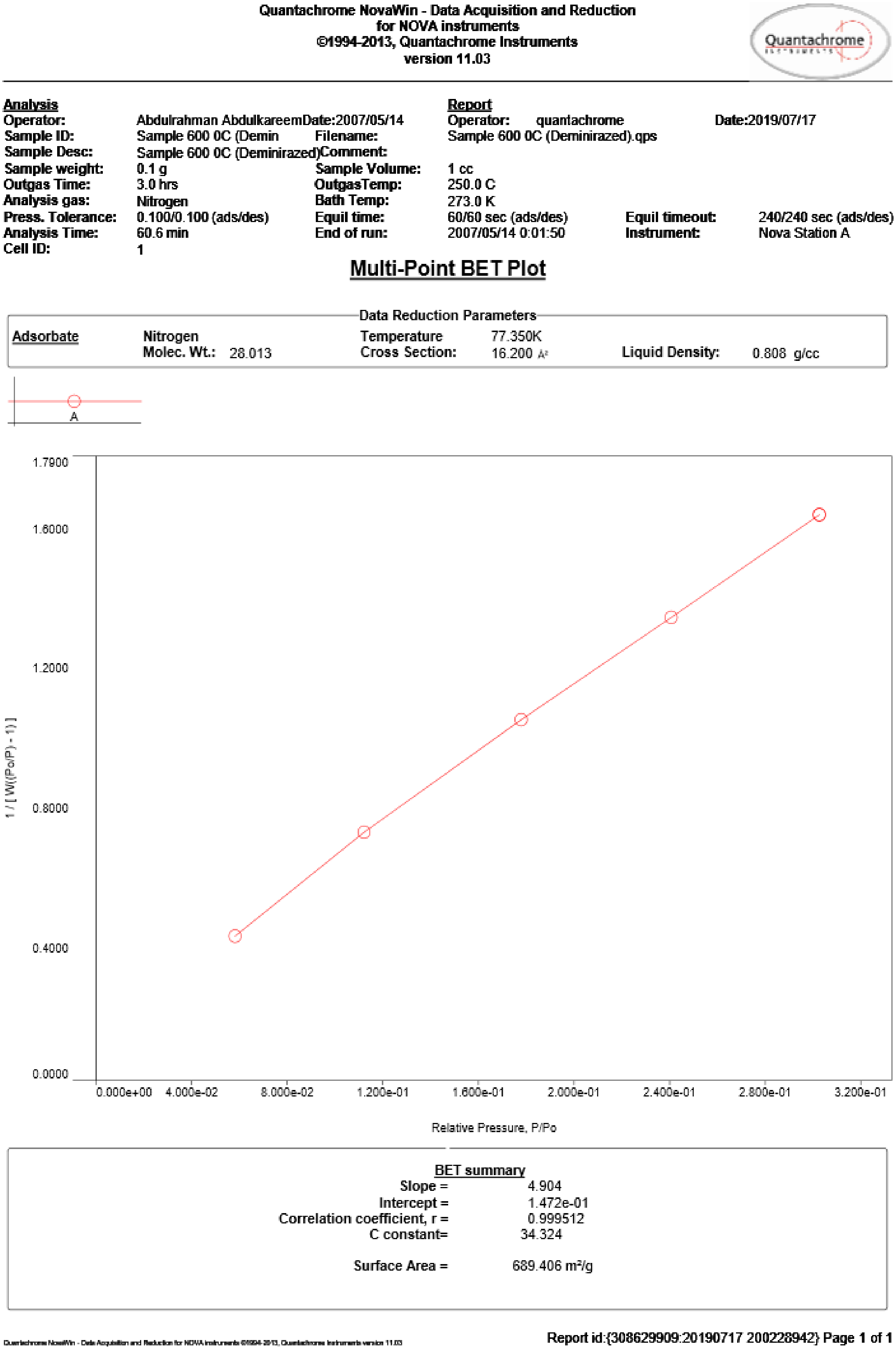
Williams, P. T., Brindle, A. J., (2003). Anal. Application Pyrolysis. 67, 143-164 (2003).

Yang Y. R., Lu J., Chem. B. C., (2002). Surface characteristics of carbon black produced by pyrolysis of used tyres (Chinese). Acta Scientiae Circumstantiae, 22, 637-640.

APPENDIX

Results obtained from the analyses performed on the demineralized carbon black using DR Method available in Brunauer Emmett Teller (BET)

Section 4.7 presents the results obtained from the analyses performed on demineralized carbon black to determined: surface area, pore diameter, pore volume and pore size distribution respectively using DR method available in Brunauer Emmett Teller (BET) to verify how suitable and compliance were the values obtained for the production of high quality black shoe polish.



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Outgas Time: 3.0 hrs **OutgasTemp:** 250.0 C
Analysis gas: Nitrogen **Bath Temp:** 273.0 K
Press. Tolerance: 0.100/0.100 (ads/des) **Equil time:** 60/60 sec (ads/des) **Equil timeout:** 240/240 sec (ads/des)
Analysis Time: 60.6 min **End of run:** 2007/05/14 0:01:50 **Instrument:** Nova Station A
Cell ID: 1

Report
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Sample 600 0C (Deminirazed).qps

Multi-Point BET Plot

Data Reduction Parameters

Adsorbate Nitrogen
Molec. Wt.: 28.013
Temperature 77.350K
Cross Section: 16.200 Å²
Liquid Density: 0.808 g/cc

BET summary
Slope = 4.904
Intercept = 1.472e-01
Correlation coefficient, r = 0.999512
C constant= 34.324

Surface Area = 689.406 m²/g

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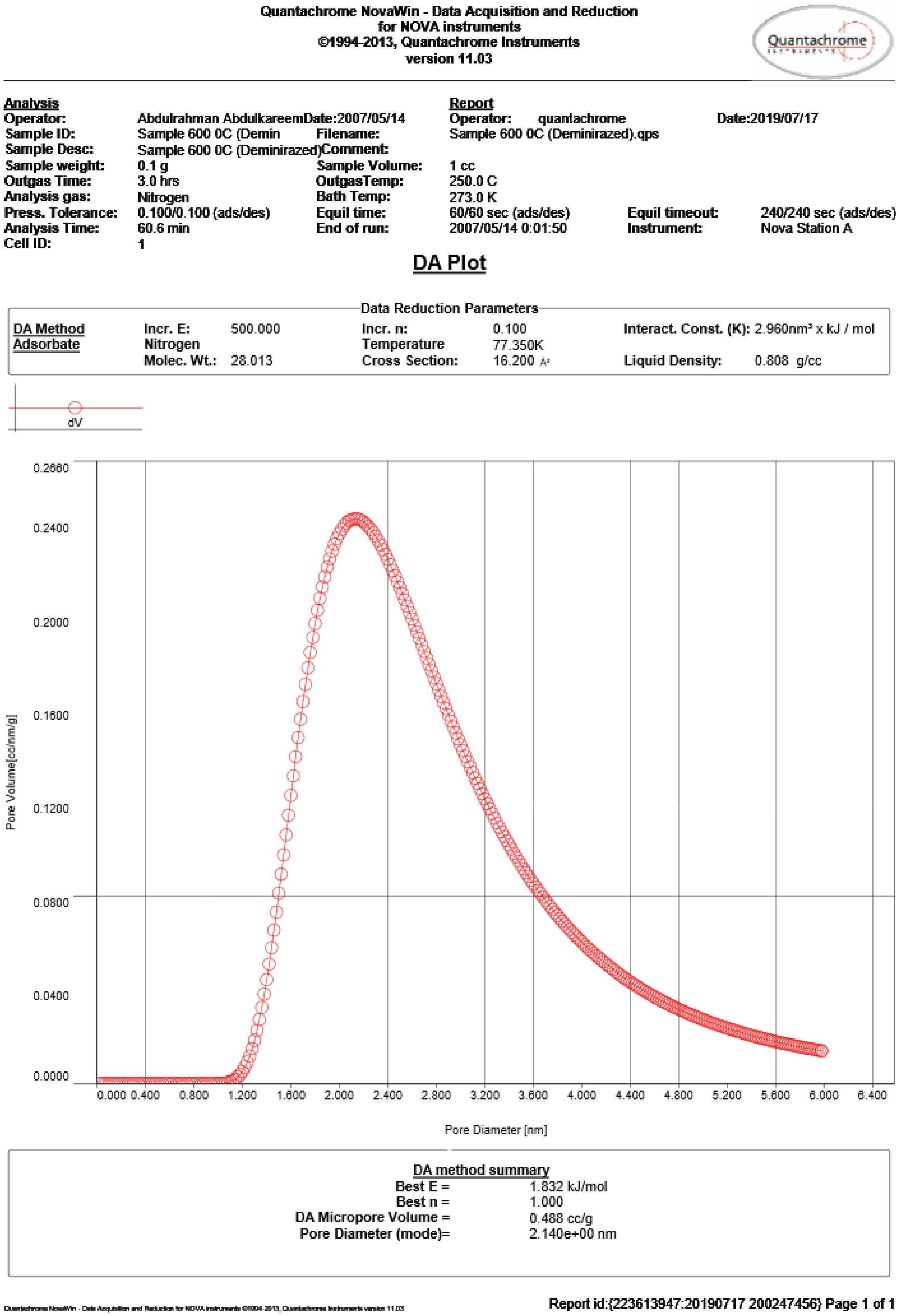

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Analysis gas: Nitrogen **Bath Temp:** 273.0 K
Press. Tolerance: 0.100/0.100 (ads/des) **Equil time:** 60/60 sec (ads/des) **Equil timeout:** 240/240 sec (ads/des)
Analysis Time: 60.6 min **End of run:** 2007/05/14 0:01:50 **Instrument:** Nova Station A
Cell ID: 1

Report
Operator: quantachrome **Date:**2019/07/17

DA Plot

Data Reduction Parameters

DA Method Incr. E: 500.000 Incr. n: 0.100 Interact. Const. (K): 2.960nm³ x kJ / mol
Adsorbate Nitrogen Temperature 77.350K
Molec. Wt.: 28.013 Cross Section: 16.200 Å² Liquid Density: 0.808 g/cc

DA method summary
Best E = 1.832 kJ/mol
Best n = 1.000
DA Micropore Volume = 0.488 cc/g
Pore Diameter (mode)= 2.140e+00 nm

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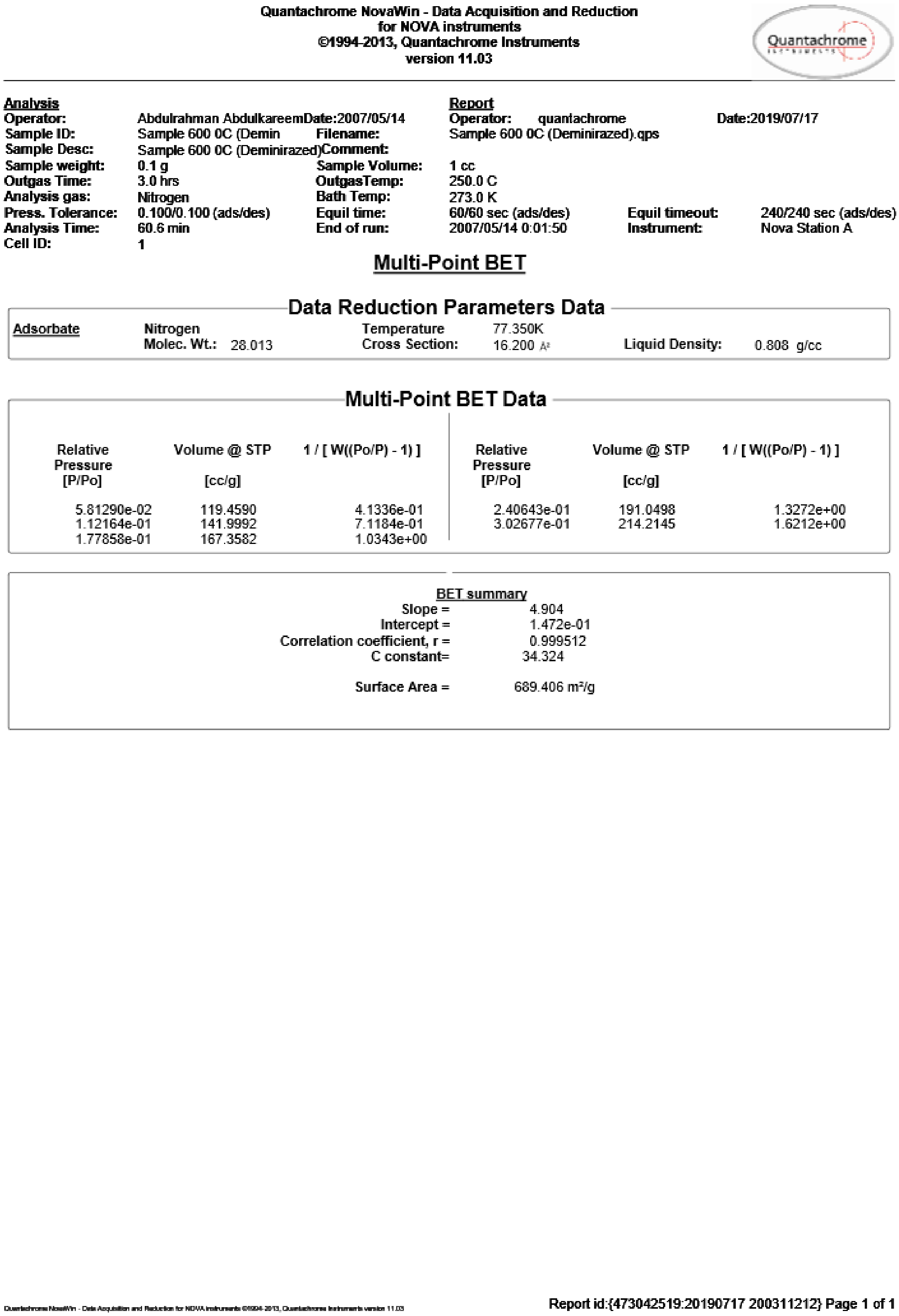

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Sample Desc:	Sample 600 0C (Deminirazed)	**Comment:**			
Sample weight:	0.1 g	**Sample Volume:**	1 cc		
Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C		
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K		
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/des)
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A
Cell ID:	1				

Multi-Point BET

Data Reduction Parameters Data

Adsorbate	Nitrogen	Temperature	77.350K		
	Molec. Wt.: 28.013	Cross Section:	16.200 Å²	Liquid Density:	0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
5.81290e-02	119.4590	4.1336e-01	2.40643e-01	191.0498	1.3272e+00
1.12164e-01	141.9992	7.1184e-01	3.02677e-01	214.2145	1.6212e+00
1.77858e-01	167.3582	1.0343e+00			

BET summary

Slope = 4.904
Intercept = 1.472e-01
Correlation coefficient, r = 0.999512
C constant= 34.324

Surface Area = 689.406 m²/g

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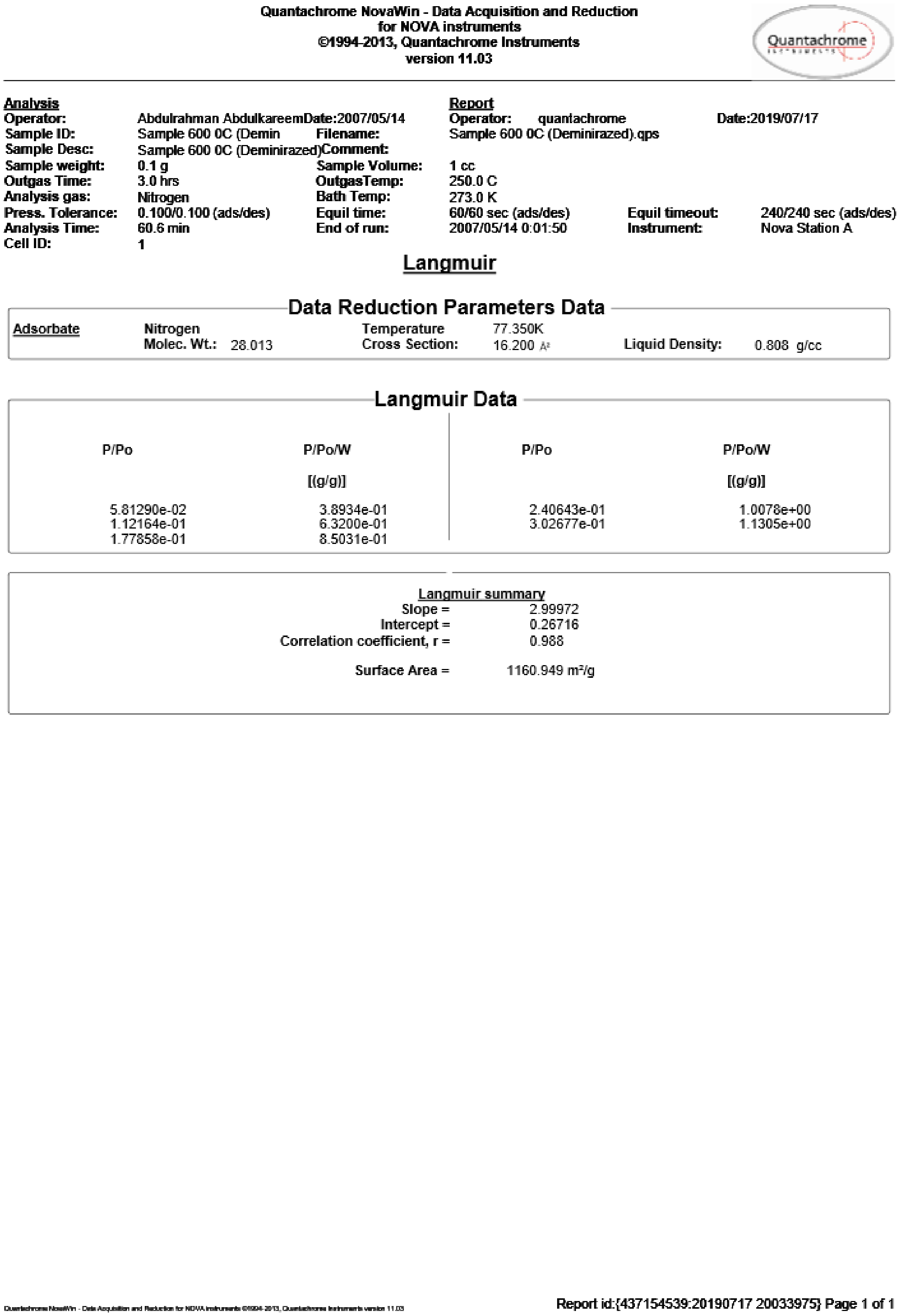

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Quantachrome

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Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C				
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K				
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/des)		
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A		
Cell ID:	1						

Langmuir

Data Reduction Parameters Data

Adsorbate — Nitrogen — Temperature 77.350K
Molec. Wt.: 28.013 — Cross Section: 16.200 Å² — Liquid Density: 0.808 g/cc

Langmuir Data

P/Po	P/Po/W [(g/g)]	P/Po	P/Po/W [(g/g)]
5.81290e-02	3.8934e-01	2.40643e-01	1.0078e+00
1.12164e-01	6.3200e-01	3.02677e-01	1.1305e+00
1.77858e-01	8.5031e-01		

Langmuir summary

Slope = 2.99972
Intercept = 0.26716
Correlation coefficient, r = 0.988

Surface Area = 1160.949 m²/g

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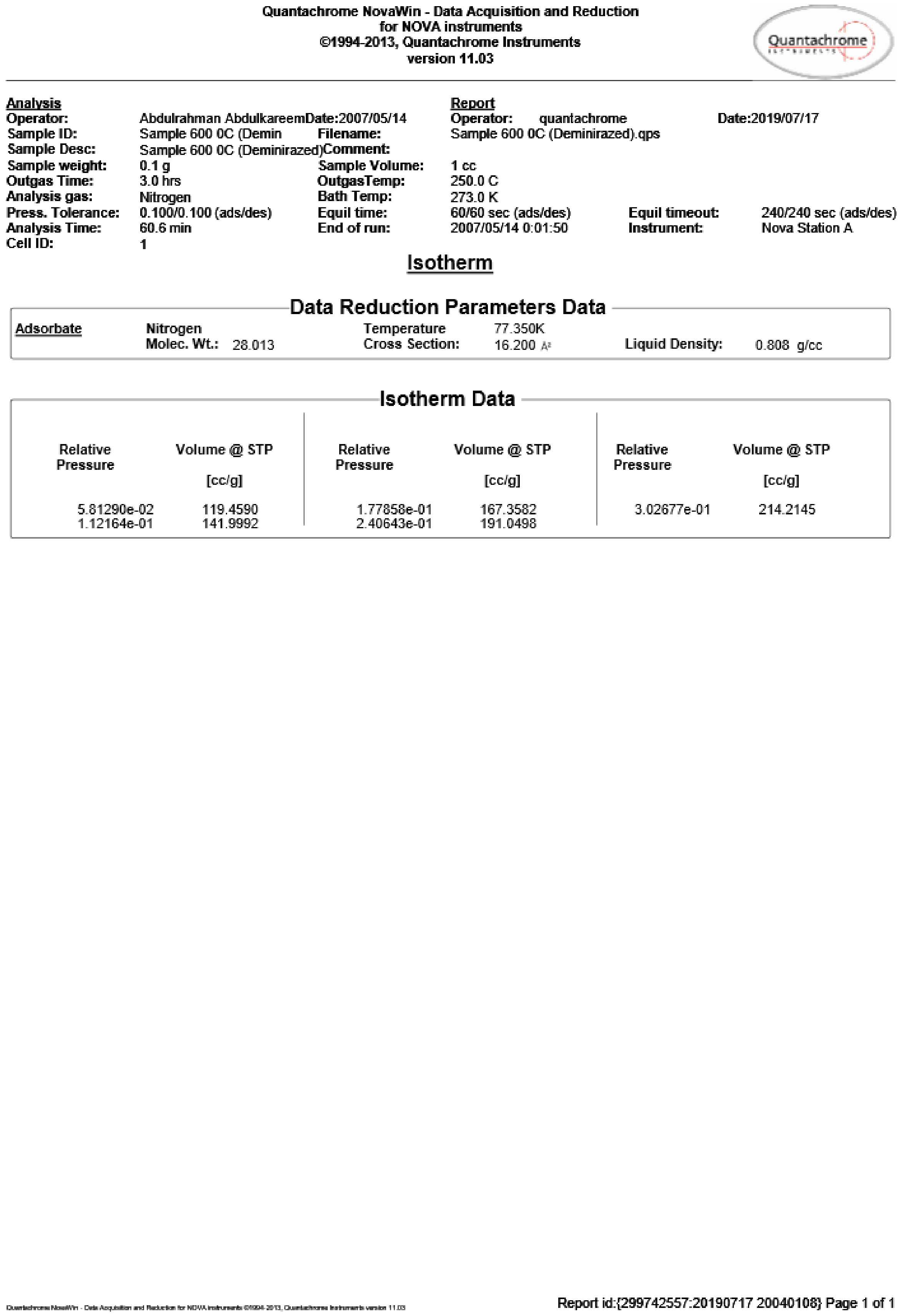

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Sample weight:	0.1 g	**Sample Volume:**	1 cc		
Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C		
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K		
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/des)
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A
Cell ID:	1				

Isotherm

Data Reduction Parameters Data

Adsorbate	**Nitrogen**	**Temperature**	77.350K		
	Molec. Wt.: 28.013	**Cross Section:**	16.200 Å²	**Liquid Density:**	0.808 g/cc

Isotherm Data

Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]
5.81290e-02	119.4590	1.77858e-01	167.3582	3.02677e-01	214.2145
1.12164e-01	141.9992	2.40643e-01	191.0498		

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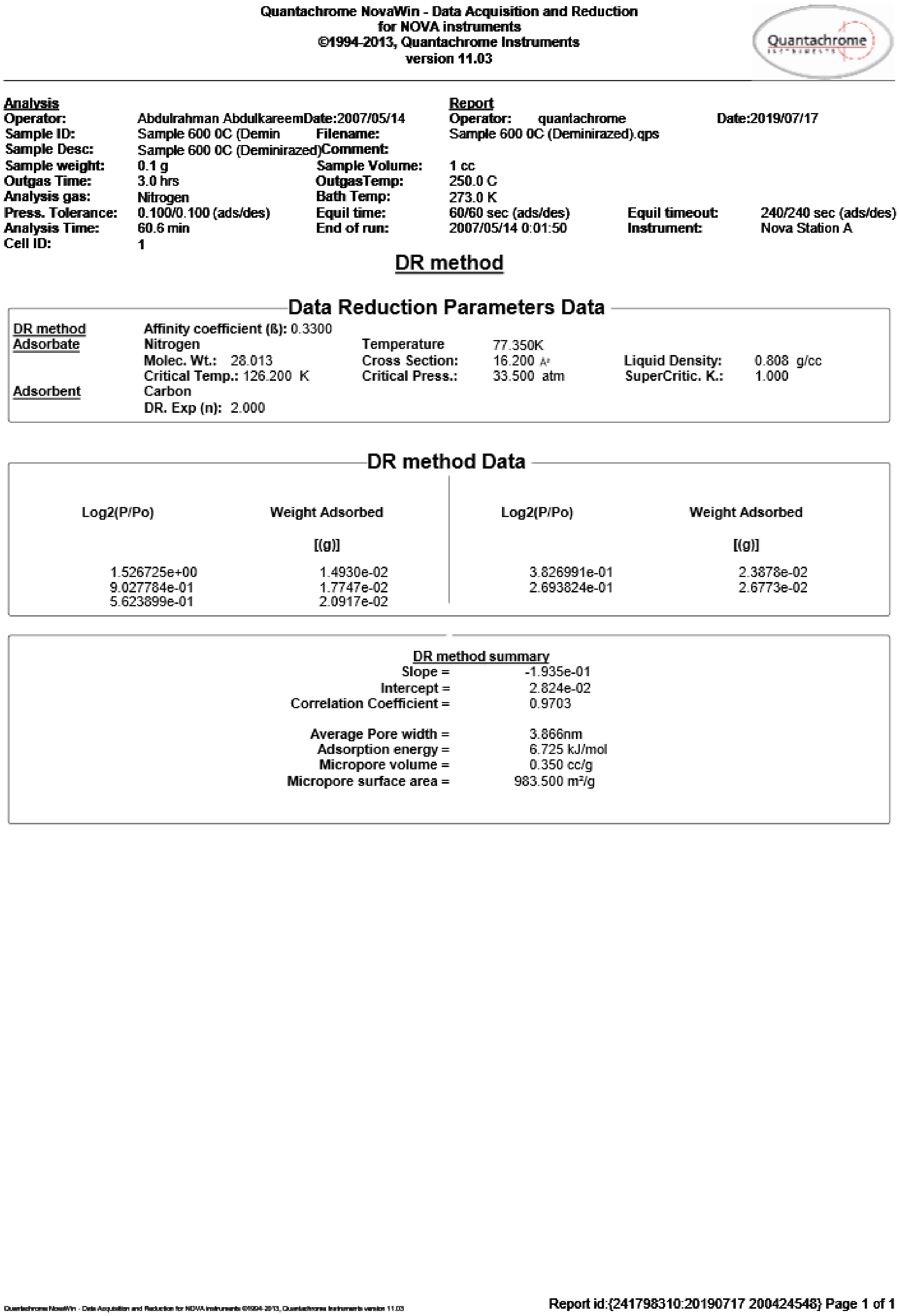

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Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C		
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K		
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/des)
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A
Cell ID:	1				

DR method

Data Reduction Parameters Data

DR method	**Affinity coefficient (ß):** 0.3300					
Adsorbate	Nitrogen	Temperature	77.350K			
	Molec. Wt.: 28.013	Cross Section:	16.200 A²	Liquid Density:	0.808 g/cc	
	Critical Temp.: 126.200 K	Critical Press.:	33.500 atm	SuperCritic. K.:	1.000	
Adsorbent	Carbon					
	DR. Exp (n): 2.000					

DR method Data

Log2(P/Po)	Weight Adsorbed [(g)]	Log2(P/Po)	Weight Adsorbed [(g)]
1.526725e+00	1.4930e-02	3.826991e-01	2.3878e-02
9.027784e-01	1.7747e-02	2.693824e-01	2.6773e-02
5.623899e-01	2.0917e-02		

DR method summary

Slope = -1.935e-01
Intercept = 2.824e-02
Correlation Coefficient = 0.9703

Average Pore width = 3.866nm
Adsorption energy = 6.725 kJ/mol
Micropore volume = 0.350 cc/g
Micropore surface area = 983.500 m²/g

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Report id:{241798310:20190717 200424548} Page 1 of 1

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Sample ID: Sample 600 0C (Demin **Filename:**

Report
Operator: quantachrome **Date:**2019/07/17
Sample 600 0C (Deminirazed).qps

DA Method Micropore Analysis Data continued

Diameter [nm]	dV(d) [cc/nm/g]
4.66000e+00	3.53097e-02
4.68000e+00	3.47666e-02
4.70000e+00	3.42334e-02
4.72000e+00	3.37099e-02
4.74000e+00	3.31960e-02
4.76000e+00	3.26913e-02
4.78000e+00	3.21958e-02
4.80000e+00	3.17092e-02
4.82000e+00	3.12314e-02
4.84000e+00	3.07622e-02
4.86000e+00	3.03013e-02
4.88000e+00	2.98488e-02
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4.92000e+00	2.89677e-02
4.94000e+00	2.85388e-02
4.96000e+00	2.81176e-02
4.98000e+00	2.77038e-02
5.00000e+00	2.72973e-02
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5.08000e+00	2.57415e-02
5.10000e+00	2.53693e-02
5.12000e+00	2.50037e-02
5.14000e+00	2.46443e-02
5.16000e+00	2.42912e-02
5.18000e+00	2.39442e-02
5.20000e+00	2.36032e-02
5.22000e+00	2.32680e-02
5.24000e+00	2.29386e-02
5.26000e+00	2.26147e-02
5.28000e+00	2.22964e-02
5.30000e+00	2.19835e-02
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5.38000e+00	2.07840e-02
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5.44000e+00	1.99362e-02
5.46000e+00	1.96629e-02
5.48000e+00	1.93943e-02
5.50000e+00	1.91300e-02
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5.54000e+00	1.86145e-02
5.56000e+00	1.83632e-02
5.58000e+00	1.81159e-02
5.60000e+00	1.78727e-02
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5.66000e+00	1.71665e-02
5.68000e+00	1.69387e-02
5.70000e+00	1.67145e-02
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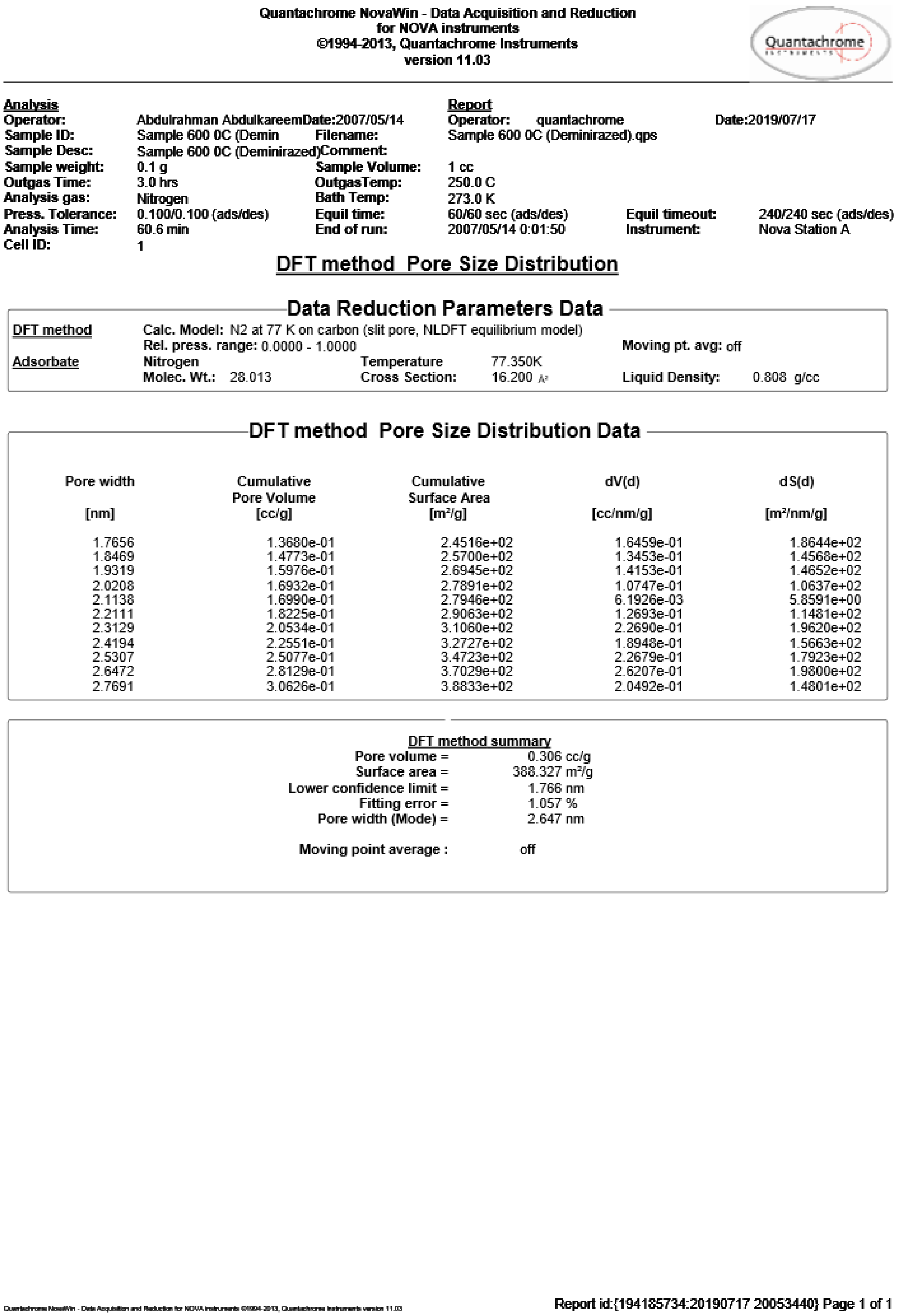
5.74000e+00	1.62770e-02
5.76000e+00	1.60635e-02
5.78000e+00	1.58534e-02
5.80000e+00	1.56467e-02
5.82000e+00	1.54432e-02
5.84000e+00	1.52430e-02
5.86000e+00	1.50459e-02
5.88000e+00	1.48520e-02
5.90000e+00	1.46610e-02
5.92000e+00	1.44731e-02
5.94000e+00	1.42881e-02
5.96000e+00	1.41060e-02
5.98000e+00	1.39268e-02

DA method summary

Best E = 1.832 kJ/mol
Best n = 1.000
DA Micropore Volume = 0.488 cc/g
Pore Diameter (mode)= 2.140e+00 nm



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Analysis
Operator: Abdulrahman Abdulkareem **Date:**2007/05/14
Sample ID: Sample 600 0C (Demin **Filename:** Sample 600 0C (Deminirazed).qps
Sample Desc: Sample 600 0C (Deminirazed) **Comment:**
Sample weight: 0.1 g **Sample Volume:** 1 cc
Outgas Time: 3.0 hrs **OutgasTemp:** 250.0 C
Analysis gas: Nitrogen **Bath Temp:** 273.0 K
Press. Tolerance: 0.100/0.100 (ads/des) **Equil time:** 60/60 sec (ads/des) **Equil timeout:** 240/240 sec (ads/des)
Analysis Time: 60.6 min **End of run:** 2007/05/14 0:01:50 **Instrument:** Nova Station A
Cell ID: 1

Report
Operator: quantachrome **Date:**2019/07/17

DFT method Pore Size Distribution

Data Reduction Parameters Data

DFT method
Calc. Model: N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)
Rel. press. range: 0.0000 - 1.0000
Moving pt. avg: off

Adsorbate
Nitrogen
Molec. Wt.: 28.013
Temperature 77.350K
Cross Section: 16.200 Å²
Liquid Density: 0.808 g/cc

DFT method Pore Size Distribution Data

Pore width [nm]	Cumulative Pore Volume [cc/g]	Cumulative Surface Area [m²/g]	dV(d) [cc/nm/g]	dS(d) [m²/nm/g]
1.7656	1.3680e-01	2.4516e+02	1.6459e-01	1.8644e+02
1.8469	1.4773e-01	2.5700e+02	1.3453e-01	1.4568e+02
1.9319	1.5976e-01	2.6945e+02	1.4153e-01	1.4652e+02
2.0208	1.6932e-01	2.7891e+02	1.0747e-01	1.0637e+02
2.1138	1.6990e-01	2.7946e+02	6.1926e-03	5.8591e+00
2.2111	1.8225e-01	2.9063e+02	1.2693e-01	1.1481e+02
2.3129	2.0534e-01	3.1060e+02	2.2690e-01	1.9620e+02
2.4194	2.2551e-01	3.2727e+02	1.8948e-01	1.5663e+02
2.5307	2.5077e-01	3.4723e+02	2.2679e-01	1.7923e+02
2.6472	2.8129e-01	3.7029e+02	2.6207e-01	1.9800e+02
2.7691	3.0626e-01	3.8833e+02	2.0492e-01	1.4801e+02

DFT method summary

Pore volume = 0.306 cc/g
Surface area = 388.327 m²/g
Lower confidence limit = 1.766 nm
Fitting error = 1.057 %
Pore width (Mode) = 2.647 nm

Moving point average : off

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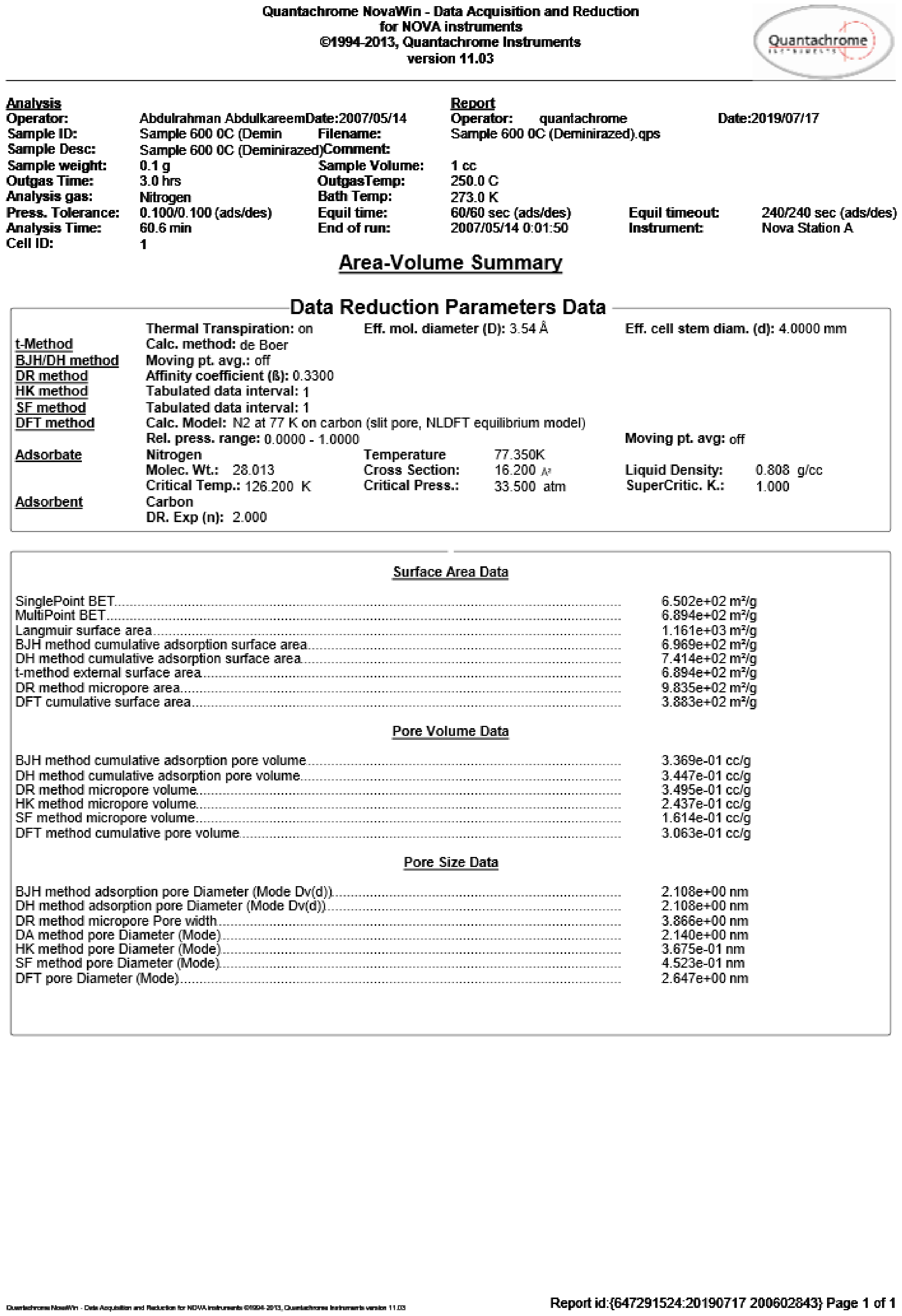

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Analysis			**Report**		
Operator:	Abdulrahman Abdulkareem	**Date:**2007/05/14	**Operator:** quantachrome		**Date:**2019/07/17
Sample ID:	Sample 600 0C (Demin	**Filename:**	Sample 600 0C (Deminirazed).qps		
Sample Desc:	Sample 600 0C (Deminirazed)	**Comment:**			
Sample weight:	0.1 g	**Sample Volume:**	1 cc		
Outgas Time:	3.0 hrs	**OutgasTemp:**	250.0 C		
Analysis gas:	Nitrogen	**Bath Temp:**	273.0 K		
Press. Tolerance:	0.100/0.100 (ads/des)	**Equil time:**	60/60 sec (ads/des)	**Equil timeout:**	240/240 sec (ads/des)
Analysis Time:	60.6 min	**End of run:**	2007/05/14 0:01:50	**Instrument:**	Nova Station A
Cell ID:	1				

Area-Volume Summary

Data Reduction Parameters Data

	Thermal Transpiration: on	**Eff. mol. diameter (D):** 3.54 Å	**Eff. cell stem diam. (d):** 4.0000 mm
t-Method	**Calc. method:** de Boer		
BJH/DH method	**Moving pt. avg.:** off		
DR method	**Affinity coefficient (ß):** 0.3300		
HK method	**Tabulated data interval:** 1		
SF method	**Tabulated data interval:** 1		
DFT method	**Calc. Model:** N2 at 77 K on carbon (slit pore, NLDFT equilibrium model)		
	Rel. press. range: 0.0000 - 1.0000		**Moving pt. avg:** off
Adsorbate	**Nitrogen**	**Temperature** 77.350K	
	Molec. Wt.: 28.013	**Cross Section:** 16.200 Å²	**Liquid Density:** 0.808 g/cc
	Critical Temp.: 126.200 K	**Critical Press.:** 33.500 atm	**SuperCritic. K.:** 1.000
Adsorbent	**Carbon**		
	DR. Exp (n): 2.000		

Surface Area Data

SinglePoint BET	6.502e+02 m²/g
MultiPoint BET	6.894e+02 m²/g
Langmuir surface area	1.161e+03 m²/g
BJH method cumulative adsorption surface area	6.969e+02 m²/g
DH method cumulative adsorption surface area	7.414e+02 m²/g
t-method external surface area	6.894e+02 m²/g
DR method micropore area	9.835e+02 m²/g
DFT cumulative surface area	3.883e+02 m²/g

Pore Volume Data

BJH method cumulative adsorption pore volume	3.369e-01 cc/g
DH method cumulative adsorption pore volume	3.447e-01 cc/g
DR method micropore volume	3.495e-01 cc/g
HK method micropore volume	2.437e-01 cc/g
SF method micropore volume	1.614e-01 cc/g
DFT method cumulative pore volume	3.063e-01 cc/g

Pore Size Data

BJH method adsorption pore Diameter (Mode Dv(d))	2.108e+00 nm
DH method adsorption pore Diameter (Mode Dv(d))	2.108e+00 nm
DR method micropore Pore width	3.866e+00 nm
DA method pore Diameter (Mode)	2.140e+00 nm
HK method pore Diameter (Mode)	3.675e-01 nm
SF method pore Diameter (Mode)	4.523e-01 nm
DFT pore Diameter (Mode)	2.647e+00 nm

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