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# A Review and Discussion of Waste Tyre Pyrolysis and Derived Products

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***Abstract*—This paper reviews and discusses the waste tyre pyrolysis process and the applications of the derived products. The primary and secondary applications of oil, char, gas and steel wires are discussed. The paper also reviews the influence of operating parameters such as feed size, temperature and residence time. An analysis of the pyrolysis products market is also given. The study objectives were achieved through a triangulation procedure comprising of literature analysis, site visits and as well as personal and telephonic interviews. The paper concludes by discussing the successes and failures of the pyrolysis process.**

***Index Terms*—Process parameters, product markets, pyrolysis, triangulation procedure, waste tyre**

## I. INTRODUCTION

PPROLYSIS has been applied in the past to carbonaceous materials such as coal or wood. The ancient Egyptians practiced wood distillation by collecting tars and pyro ligneous acid for use in their embalming industry [1]. Pyrolysis of wood to produce charcoal was a major industry in the 1800s, supplying fuel for the industrial revolution. Charcoal was used for the smelting of metals and it is still used today in metallurgy [2]. For thousands of years charcoal has been a preferred heating fuel until it was replaced by coal. In the late 19th century and early 20th century wood distillation was still profitable for producing soluble tar, pitch, creosote oil, chemicals, and non-condensable gasses often used to heat boilers. The wood distillation industry declined in the 1930s due to the advent of the petrochemical industry and its lower priced products. However, pyrolysis of wood to produce charcoal for the charcoal briquette market and activated carbon for water purification is still practiced in the United States of America (USA) [2]. Over the last 20–30 years, several laboratory, pilot-plant and even commercial attempts have been made to establish economical units for pyrolysis of such materials for example; Kobe Steel in Japan, Tosco in the USA, Tyrolysis in the United Kingdom (UK), Ebenhausen in Germany and many more [3].

Pyrolysis is an endothermic process that induces the thermal decomposition of feed materials without the addition of any reactive gases, such as air or oxygen. The thermal efficiency of this process is approximately 70%, and can increase to 90% with the use of pyrolysis products as fuel [4]. The use of tyre chips instead of whole tyres may also increase the efficiency of the process by 20-30% [5]. The thermal energy used to drive the pyrolysis reaction is applied indirectly by thermal conduction through the walls of the containment reactor. Pyrolysis generally occurs at temperatures between 400 and 800°C [6]. As the temperature changes, the product distribution (or the phase of the products) are also altered. Lower pyrolysis temperatures usually produce more liquid products while higher temperatures favour the production of gases.

The speed of the process and rate of heat transfer also influences the product distribution. Slow pyrolysis (carbonization) can be used to maximize the yield of solid char. This process requires a slow pyrolytic decomposition at low temperatures. Rapid quenching is often used to maximize the production of liquid products, by condensing the gaseous molecules into liquid. In some pyrolysis processes, a product up to 80% liquid by weight can be produced [3].

Hydrogen or steam can also be used in the pyrolysis process to change the makeup of the product distribution. Hydrogen can be used to enhance the chemical reduction and suppress oxidation by means of the elemental oxygen in the feedstock. Steam can also be used as a pyrolyzing medium, allowing pyrolysis to occur at lower temperatures and higher pressures. The use of water as a pyrolyzing media also allows the feedstock to be introduced into the reactor in an aqueous form. An additional advantage of water or steam is that the resulting char has a relatively high surface area and porosity that is similar in nature to activated charcoal [2]. Nitrogen gas can be supplied to maintain the inert atmosphere in the reactor and also to sweep away the pyrolyzed vapour product to the condensers. Furthermore, purging the system with nitrogen assists to minimise secondary reactions in the hot zone [2].

Some of the problems related to the process are the high cost of the plant and residue treatment [5]. Fig. 1. shows the pyrolysis process pathway.

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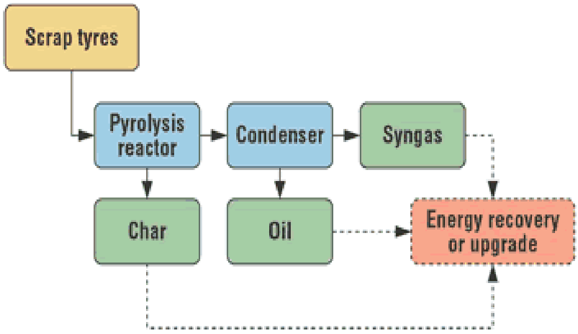

Fig. 1. Pyrolysis pathway [7]

## II. INFLUENCE OF OPERATING PARAMETERS ON YIELD

The pyrolysis process yields a gaseous fraction of mainly non-condensable gases, a solid fraction mainly composed of carbon, metal and others inert material as well as an oily fraction mainly composed of organic substances condensable at ambient temperature and pressure. The composition of the pyrolysis products is influenced by the process operating conditions such as, feed size, operating temperature and pressure, residence time, heating rate and as well as the presence of catalytic medium.

### *A. Feed Size*

Smaller feed size particles provide more reaction surface, giving high heating rate and rapid decomposition of rubber. The oil product vapours comparatively get enough time for secondary reactions in the reactor and this consequently increases gas yield and reduces liquid and char yields [3]. On the other hand, the heating rate in whole tyre feed is low due to its lower thermal conductivity, in addition heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller pieces. Thus, the rubber core of the larger pieces becomes carbonized and/or cannot be decomposed completely resulting in increased char yield and decreased liquid and gas yield. Fig. 2. shows the effect of feed size on product yield.

### *B. Temperature*

The increase in gas yield with a corresponding reduction in liquid yield with increase in temperature is due to vapour decomposing into permanent gases, and secondary re-polymerization as well as carbonization reactions of oil hydrocarbons into char [3]. It is also a result of char loss and thermal cracking. Thus, gas yields dominate at higher temperatures, Fig. 3.

### *C. Residence time*

An increase in vapour residence time decreases liquid and char yields while the gas yield increases slightly. This is due to the decomposition of some oil vapour into secondary permanent gases. Primary vapours are first produced from tyre pyrolysis at optimum temperature, the primary oil vapours then degrade into secondary gases. For instance: oil vapours→ heavy hydrocarbons + light hydrocarbons ($CH_4$ + $C_2H_4$ + $C_3H_6$ +……) + ($CO$ + $CO_2$ + $H_2$) [3] leading to less oils and more gaseous products. In addition, longer contact time of the volatiles and char leads to another parallel secondary pyrolysis reaction: $C + CO_2 \rightarrow 2CO$ which reduces the char yield [3] Fig. 4. Table 1 shows a typical tyre composition. There are many different manufacturers with various tyre formulations. Hence, the yield and composition of waste tyre pyrolysis depend on the source and grade of tyres [3].

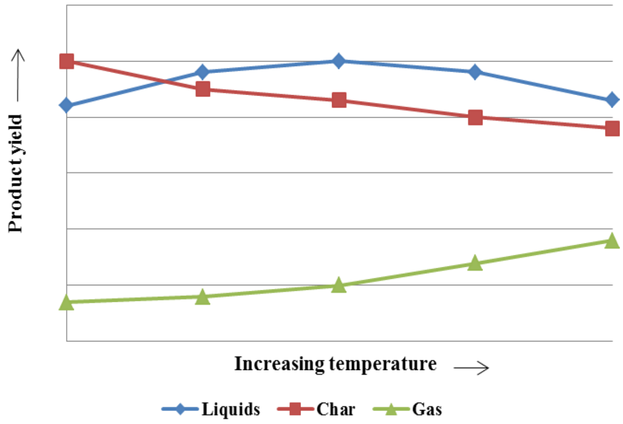

Fig. 2. Effect of feed size on product yield [8].

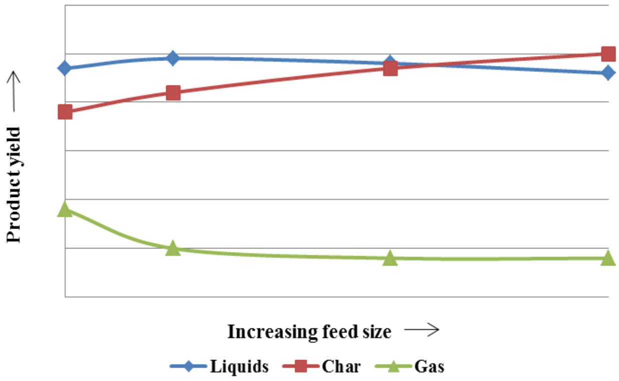

Fig 3. Effect of temperature size on product yield [8].

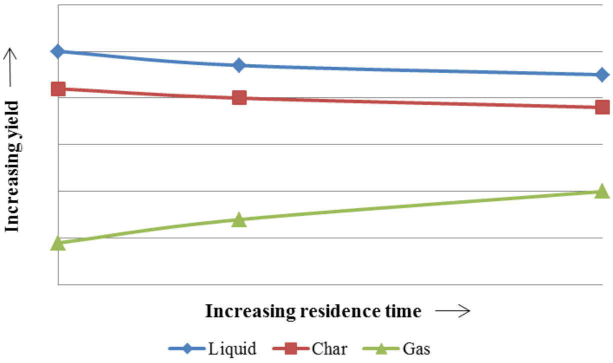

Fig. 4. Effect of temperature size on product yield [8].

## III. PYROLYSIS PRODUCTS

### *A. Pyrolysis Gas*

The approximate yield of gas from waste tyre pyrolysis is about 10-30% by weight [2] and it increases with increasing pyrolysis temperature. The pyrolysis derived gas has a calorific value of approximately 30-40MJ $N/m^{-3}$ [9] and can be sufficient to provide the energy required for a small scale process plant. The carbon oxide components ($COx$) are mostly derived from the oxygenated organic compounds in tyres, such as stearic acid and extender oils. $H_2S$ is a product of the sulphur links vulcanized rubber structure decomposition and its concentration is low. $C_4$ and $>C_4$

gases are the most predominant products and these result from the depolymerisation of styrene-butadiene-rubber (SBR), usually the main constituent of automotive tyres [3]. Table II shows the gaseous constituents produced during the pyrolysis of tyres. The components of the gas obtained from tyre pyrolysis at 400, 500, 600 and 700°C is shown by Fig. 5. The gaseous product mixture is made of shorter aliphatic chains than SBR due to rubber cracking and subsequent reactions to form lighter gases.

TABLE I
COMPOSITION OF WASTE TYRES

| | |
|---|---|
| Rubber | 38% |
| Fillers (Carbon black, silica, carbon chalk) | 30% |
| Reinforcing material (steel, rayon, nylon) | 16% |
| Plasticizers (oils and resins) | 10% |
| Vulcanisation agents (Sulphur, zinc oxide, various chemicals) | 4% |
| Antioxidants to counter ozone effect and material fatigue | 1% |
| Miscellaneous | 1% |
| Elementary Composition | |
| Carbon | 86% |
| Hydrogen | 8% |
| Nitrogen | 1% |
| Sulphur | 2% |
| Oxygen | 3% |
| Proximate Analysis | |
| Volatiles | 62% |
| Fixed carbon | 30% |
| Ash | 7% |
| Moisture | 1% |

### B. *Pyrolysis Oil*

There is need for greener fuel alternatives due to fossil fuel depletion, increasing oil prices and emission challenges. Tyre pyrolysis liquids production pathways with their wide range of potential applications are as shown in Fig. 6.

The waste tyre pyrolytic liquid is an oily organic compound, dark brown in colour and with a strong acrid smell. This oil should be handled carefully as it reacts easily with human skin, leaving permanent yellowish brown marks and an acrid smell for a few days, and this is difficult to remove by detergents. The tyre derived oil is composed mainly of alkylated benzenes, naphthalenes, phenanthrenes, n-alkanes from $C_{11}$ to $C_{24}$, and alkenes from $C_8$ to $C_{15}$, with small quantities of nitrogen, sulphur and oxygenated compounds [10]. The pyrolysis oil has a high calorific value of about 44 MJ/kg compared to that of waste tyres, 33 MJ/kg [10]. The calorific value of the oil is also higher than that of bituminous coal, 28 MJ/kg [11] and wood charcoal, 30 MJ/kg [12]. Pyrolytic oils can be used as liquid fuels for industrial furnaces, power plants and boilers. The oil has a relatively low ash content and residual carbon as shown in Table III.

The liquids are very complex mixtures, containing aliphatic and aromatic compounds with their total concentration of 49.54% and 16.65%, respectively [2]. The aliphatic compounds mainly consist of alkanes and alkenes with alkenes being the predominant group, 43.23%. The aromatic compounds are mainly single ring alkyl aromatics. The aromatic nature of the waste tyre pyrolytic oils is due to aryl chain fragments from SBR aromatic rings splitting and ciclation of olefin structures through dehydrogenation reaction [8], Fig. 7.

TABLE II
PYROLYSIS GAS CONSTITUENTS

| Component | Chemical formula |
|---|---|
| Carbon monoxide | $CO$ |
| Carbon dioxide | $CO_2$ |
| Hydrogen sulphide | $H_2S$ |
| Methane | $CH_4$ |
| Ethane | $C_2H_6$ |
| Ethene | $C_2H_4$ |
| Propane | $C_3H8$ |
| Propene | $C_2H_6$ |
| Butane | $C_4H_{10}$ |
| Butene | $C_4H_8$ |
| Butadiene | $C_4H_6$ |
| Pentane | $C_5H_{12}$ |
| Pantene | $C_5H_{10}$ |
| Hexane | $C_5H_{14}$ |
| Hexene | $C_6H_{12}$ |

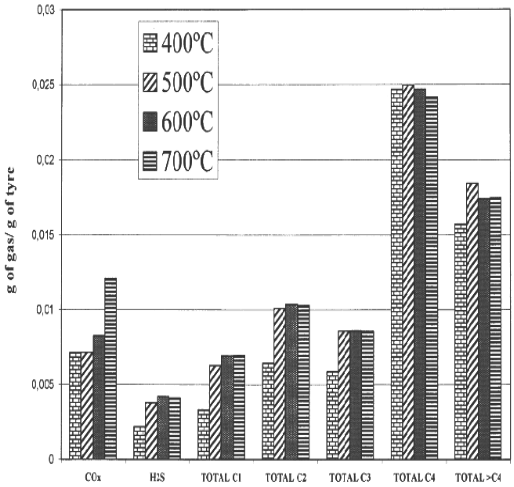

Fig.5. Gaseous products distribution with temperature [3]

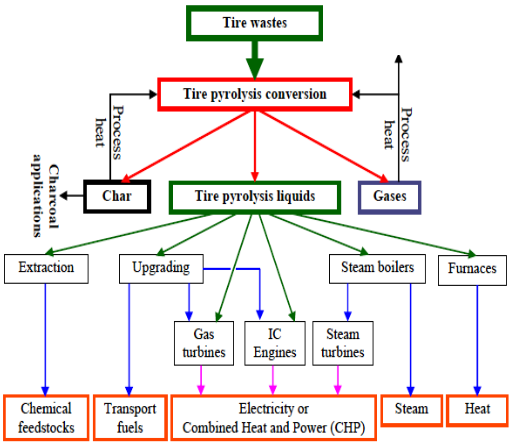

Fig. 6. Tyre pyrolysis conversion and products applications [4]

TABLE III[11]
CHARACTERISTIC OF VACUUM PYROLYSIS WASTE TYRE DERIVED OIL

| | |
|---|---|
| Gross calorific value (MJ:kg) | 43.8 |
| Water content (wt.%) | 1.6 |
| Sulphur content (wt.%) | 1.5 |
| Chlorine content (ppm) | 180 |
| Carbon Conradson residue | 1.8 |
| Ash content (wt.%) | traces |

Nitrogen and nitro-sulphureted compounds originate from the thermal degradation of accelerators used in tyre compounding and these are usually sulphur and/or nitrogen based organic compounds [8]. The oils have higher carbon content, leading to the production of high value carbon materials for various applications. They are also contaminated with little metallic elements. The olefinic composition of the waste tyre pyrolytic oil is similar to that of condensates from petroleum residues cracking and thermal steam cracking of gasoline [5]. Hence, pyrolytic oil may be blended with these condensates and subjected to the same thermal treatment.

Monoterpene [1-methyl-4-(1 methylethenyl)cyclohexene], also known as limonene constitutes about 30% [2] of pyrolytic liquids. *dl*-Limonene (dipentene) is produced from the thermal decomposition of poly-isoprene or natural rubber. It has extremely fast growing and vast industrial applications including formulation of resins and adhesives; dispersing agent for pigments; fragrance in cleaning products and an environmentally acceptable solvent [4]. It also has applications in the cosmetic industry [13].

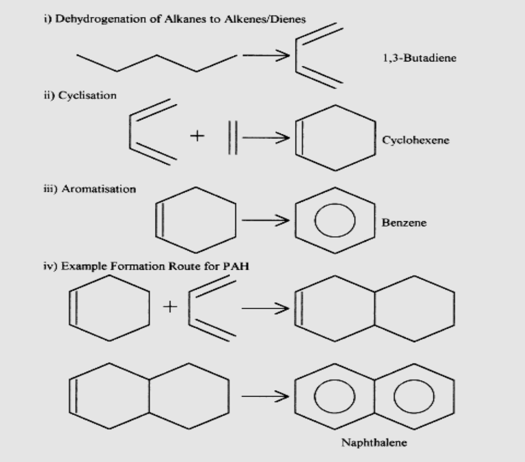

Fig. 7 Formation of polycyclic aromatic hydrocarbons in scrap tyre [14].

### *C. Activated Carbon*

Activated carbon from pyrolytic char can be used for water purification and air purification, as well as in batteries and fuel cells. Pyrolytic char has a calorific value comparable to high-grade coal and may therefore be used as fuel either in pulverized or briquetted form. The application of pyrolytic char as low grade carbon black for the manufacturing of thermoplastics and a low cost adsorbents for the treatment of industrial effluents has also been suggested [15]. The potential of the tyre carbon black product as possible adsorbents for various pollutants has been assessed and found to be successful, thus stimulating a huge research interest [16]. Active carbon can be used to adsorb phenols, basic dyes, metals, p-chlorophenols, butane and natural gas. The production, characterization and uses of carbon black as printing inks bases and recycled tyre fillers have been studied [16]. To enhance the commercial value of waste tyre pyrolytic carbon black and increase its potential application as activated carbon, further treatment such as chemical activation is required. This allows both pyrolysis and activation to be integrated into a single, relatively lower temperature process in the absence of oxygen. Demineralization of carbon black with acid (sulphuric and hydrochloric acid) followed by activation at high temperature, normally 900ºC, in a furnace is common [17].

Commercial activation of carbon black is usually conducted at temperatures above 800ºC in a mixture of steam and carbon dioxide. There is general agreement that steam is a more reactive agent than carbon dioxide [18] Activation increases the surface area while decreasing the concentration of contaminants or non-carbon material. Table IV shows the characteristics of acid treated and activated carbon black. Steam-activated carbon black present greater capacities for the adsorption of small and medium size species such as phenol and methylene blue, while carbon dioxide-activated adsorb larger molecular size compounds such as textile dye Procion Red more effectively [18]. Carbon black characteristics are influenced by the nature of activation and process temperature to a lesser extent.

TABLE IV [11]
CHARACTERISTICS OF VACUUM PYROLYSIS WASTE TYRE DERIVED CARBON BLACK

| | Surface area ($m^2/g$) | C | O | Si | S | Z | Ca |
|---|---|---|---|---|---|---|---|
| Carbon black (not treated) | 85 | 83 | 6 | 1.6 | 2.6 | 4.2 | 2.4 |
| Carbon black (HCl treated) | 870 | 93 | 5.1 | 0.4 | 0.9 | 0.6 | |
| Carbon black activated (HCl treated) | 940 | 94 | 4.3 | 0.4 | 0.8 | 0.6 | |
| Carbon black ($H_2SO_4$) | 800 | 87 | 5.9 | 0.6 | 1.8 | 2.9 | 1.8 |
| Carbon black activated ($H_2SO_4$ treated) | 910 | 30 | 4.4 | 0.6 | 1.2 | 2 | 1.8 |
| Activated carbon (commercial) | 990 | 96 | 2.9 | | 0.3 | | |

-- Liquid-phase applications: Activated carbon has been used in the removal of both organic and inorganic species from industrial effluents [18]. Due to the high surface area, 164 to 1260 $m^2/g$ and pore volumes of up to 1.62 $cm^3/g$ [19], tyre carbon black is considered to be a potential adsorbent in water treatment particularly for the removal of organic pollutants such as phenol and *p*-chlorophenol. Potassium hydroxide (KOH) activated waste tyre pyrolytic carbon black can be used to remove halogenated hydrocarbons and pesticides from drinking water. Tyre-derived carbon may also be used to remove chromium, lead, copper, dyes and phenol from industrial waste waters.

-- Gas-phase applications: Activated carbon from waste tyres provides an effective means for gas-phase applications such as the separation, storage and catalysis of gaseous species. One example is the storage of natural gas for automobiles in which natural gas is adsorbed on tyre carbons under high pressure. It can also be used for the transportation of flammable gases such as acetylene [20], [21] and [22]. Pyrolytic carbon black may be used in the treatment of industrial gaseous effluents. For example, it was found to have a similar sulphur dioxide ($SO_{2)}$ adsorption rate to commercial lignite-based carbon [20]. It was also found to be superior in the adsorption of mercury [20].

### *D. Steel Wires*

The pyrolysis derived steel wire marketing depends on the cleanliness, quantity, and packaging of the product. The cleanliness of recovered is measured by the degree of rubber contamination. Steel with less than 10% rubber is considered acceptable in the market [20]. Thermal processing of scrap tyres can be used to recover steel with minimum or zero rubber contamination. The quality is also influenced by the pyrolytic process. For a batch process, the separation of steel and carbon black from pyrolytic oil is fairly simple. This is complex for continuous pyrolysis, gasification and liquefaction process where tyres are usually ground into chips. In addition, the recycling of the recovered steel in the manufacturing of steel products is hindered by the burning of residual sulphur [20]. The waste tyre market is influenced by the business cycle. During off peak, the processors may give away the steel for free or pay markets for collection. Bailing is difficult for steel recovered from shredded tyres. The added cost of transportation and storage reduces the income from this waste stream. However, this may be cheaper than paying a tipping fee for disposal.

## IV. PYROLYSIS PRODUCT MARKETS

In order for the pyrolysis to be successful and sustainable, a market for the derived products should exist. The primary products (oil, char and gas) can be further processed to value added products. Product upgrade is expected to significantly improve the economics of scrap tyre pyrolysis. This can significantly improve the commercial viability of waste tyre pyrolysis.

### *A. Oil*

Fuel oil is classified into six classes, fuel oil 1 to 6, according to boiling point, composition and purpose. The boiling point ranges from 176 to $600^{o}$C. Oil derived from the tyre PGL process is similar to No. 6 fuel oil. This is also regarded as residual oil as it contains various impurities including 2% water and 0.5% mineral soil [23].

No. 6 fuel oil is a thick, syrupy, black, tar-like liquid. It smells like tar, and may even become semi-solid in cooler conditions. It is also known as bunker oil or black liquor and consists of a complex mixture of hydrocarbons with varying boiling points [20]. It is used as fuel for steam boilers and power generators. It is generally bought in large quantities and stored in large tanks, either above or below the ground [21]. Heating is required before application to increase flow ability, reduce pump demands and promote burning performance. Cool or cold No. 6 fuel oil is quite stable with a flashpoint of about $65^{o}$C [23]. However, the oil also contains hydrocarbons with flashpoints below $65^{o}$C, hence it has enough flammable vapours capable of starting a fire [23]. Further refining of No.6 fuel oil produces No.2 fuel oil. These fuel oils are variously referred to as distillate oils, diesel fuel oils, light fuel oils which are easy flowing at room temperature. No.2 oil does not require preheating to pump or burn as compared to No.6 fuel oils. Distillate fuel oils are complex mixtures of hydrocarbons that also contain small amounts of sulphur, nitrogen and oxygen containing molecules. They contain normal and branched alkanes, cycloalkanes (naphthenes) and partially reduced aromatics. Fuel oil No. 2 has a carbon range of $C_{11}$-$C_{20}$ [24].

No. 2 oil can be used for home heating installations as well as for medium capacity commercial and industrial burners. Liquid fuels, such as petrol, diesel and jet fuel dominate the transport industry. Fig. 8 shows the various South African energy sources for transport in 2000. Petrol and diesel dominate the application in this sector.

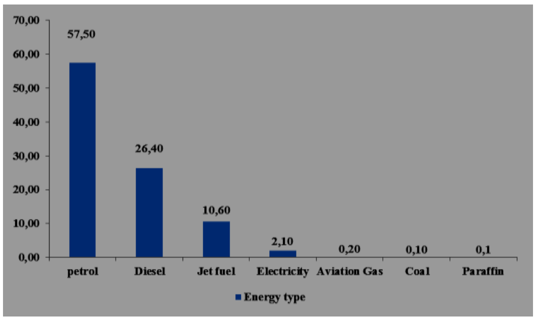

Fig. 8 Transport sector energy distribution (%) in South Africa, 2000 [25].

### *B. Char*

Carbon black, an important industrial carbon, is any of various finely-divided forms of amorphous (non-structured) carbon. Carbon exists in two crystalline forms, and numerous amorphous, less-ordered forms. The crystalline forms are diamond and graphite, and the less-ordered forms are mainly cokes and chars. Carbon blacks differ in particle size; surface area; average aggregate mass; particle and aggregate mass distributions; structure and chemical composition. The application of carbon depends on chemical composition, pigment properties, state of subdivision, adsorption activity, and other colloidal properties [26]. Potential uses include upgrading to commercial carbon black, specialized carbon blacks, printing ink, activated carbon, and fuel. The char from PGL processes with a heating value close to 30.5 MJ/kg is a valuable energy source. Its heating value is higher than that of South African lignite coals (16.7 MJ/kg) and compares well with petroleum coke (34.9 MJ/kg) [16]. Thus, the char from PGL processes can substitute coal.

### *C. Gas*

The pyrolysis gas has high concentrations of methane and ethane, resembling a natural gas. In most pyrolytic processes, this is used as a source of fuel. The large quantities of carbon monoxide and carbon dioxide in the gas hinder its blending with natural gas. One satisfactory advantages of waste tyre pyrolysis is that the gas produced can be used as fuel to sustain the process enhancing its performance. The process can run with 10 – 15% of the gas generated. This significantly reduces operating costs. The rest can be supplied to burners, boilers and internal combustion engines or can be compressed and stored for future use [3].

### *D. Steel*

Clean scrap iron and steel can easily be marketed. In order to increase the market potential of steel from shredded tyres, it needs to be baled.

## V. SUCCESSES AND FAILURES OF WASTE TYRE PYROLYSIS

In 2010, about 3.3 million tonnes of used tyres were managed in an environmental acceptable manner in the European Union (EU), a 2% increase from 2009 [27]. About 2.7 million tons of used tyres were treated; the balance was either recycled or recovered [27]. The potential of waste tyre treatment through processes such as gasification, pyrolysis and liquefaction is undervalued. However with the increase in global awareness in environmental friendly treatment methods, EU countries have considered these processes as future waste tyre treatment methods.

Currently there is a great deal of research on waste tyre pyrolysis. Juniper [28] identified 40 companies worldwide working on tyre pyrolysis. However, there is only one dedicated tyre pyrolysis plant in the United Kingdom (UK) operating on a semi-commercial basis. It is owned by Anglo Unites Environmental (AUE) and handles 1500 tonnes of waste tyres per year. Other semi-commercial plants have been operated in the UK, Germany, South Korea and Taiwan, but with limited success. Most of them have ceased operation, reportedly due to financial difficulty [29]. One of the most recent pyrolysis plant to be commissioned is in Cyprus (May 2010), with a monthly design capacity of 150 tonnes of N660 carbon black, 180 tonnes oil and 70 tonnes of steel [30].

Despite the 30 years of research and development, the pyrolysis of scrap tyres and related waste materials has not achieved commercial success in the United States. With economic viability and product quality being the primary stumbling blocks [27]. Despite all these challenges, pyrolysis is still considered as a potential waste tyre treatment option for developing countries such as South Africa.

Several pyrolysis plants have been shut down in South Africa due to limited and unregulated markets as well as noncompliance with environmental regulations [31]. In South Africa, presently there is one operating pyrolysis plant in Pretoria and another in Durban at the commissioning stage. The Pretoria plant produces pyrolysis oil for industrial applications, the gas is flared and no use for the carbon black has been found [32]. There are 12 other plants in South Africa recycling waste tyres for other applications such as rubber crumb, mats and sandals [33]. Major tyre companies like Goodyear and Firestone have invested in pyrolysis but could not find markets for the by-products and also failed to integrate the venture into their core business [34].

The main barriers for the development of tyre pyrolysis processes on a commercial scale are: Markets for pyrolytic char are presently not sound. Carbon black char is a fine particulate composed of carbon black, ash, and other inorganic materials, such as zinc oxide, carbonates, and silicates. Its application as virgin carbon black is very much restricted since it contains a lot of impurities ±10% [29] and can only be used as low quality grade carbon black. Similarly the use of char as activated carbon requires upgrading techniques to increase the surface area. Reference [2] has shown that tyre pyrolysis oil can be used as a chemical feedstock to recover valuable chemicals such as limonene. However, waste tyre oils have a complex mixture of organics and the separation of these compounds to pure products can be costly.

## VI. CONCLUSION

This work reviewed the process of pyrolysis from ancient Egyptians application. The influence of operating matters and pyrolytic products are discussed. An analysis of the pyrolysis product market is also comprehensively presented. The successes and failures of waste tyre pyrolysis are also highlighted. A further treatment step for primary products needs be integrated into the pyrolysis process to produce valuable quality products. The success of waste tyre pyrolysis also depends on product market availability.

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