

Pyrolytic Tyre Derived Fuel: A Review

T.J Pilusa, M. Shukla, and E. Muzenda

Abstract—This paper reviews the potential of using waste tyre pyrolytic fuel as an alternative energy taking into account its environmental impact and national regulations. The properties of tyre derived oil and its derivatives were evaluated as a potential alternative low cost fuel for various industrial applications. The benefit of pyrolysis versus landfill disposal of waste tyres while producing low cost fuel and other value add products remains a driving force for this initiative. The downstream challenges associated with combustion of high sulphur bearing fuels such as tyre pyrolytic fuels calls for more research into purification and refining of these fuels. Environmental Legislations on permitting the fuel production facilities, blending of the fuel derivatives with existing commercial diesel need to be clearly defined and facilitated accordingly.

Keywords—Alternative Fuel, Crude Oil, Diesel, Emissions Waste Tyres.

I. INTRODUCTION

THERE are global initiatives to find alternatives for petrol and diesel fuel due to the impact of fossil fuel crisis, hike in oil price and stringent emission norms. Waste to energy is the recent trend in the selection of alternate fuels. Fuels like alcohol, biodiesel, liquid fuel from plastics etc. are some of the alternative fuels for use in internal combustion engines. Tyre derived oil has also been tested as an alternative fuel for CI engines [1].

The liquids are a very complex mixture, containing many aliphatic and aromatic compounds with their total concentration of 49.54% and 16.65%, respectively. The aliphatic compounds mainly consist of alkane and alkene groups but the alkenes are predominant (43.23%). The aromatic compounds are only single ring alkyl aromatics [2]. The aromatic nature of the tyre oils is due to the source of

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polymeric materials, which already contains aromatic rings and hence chain splitting may easily lead to the formation of aryl chain fragments of olefin structures through dehydrogenation reaction, which happen during pyrolysis process [3].

The oxygenated compounds originate from the thermal degradation of oxygenated components of the tyre, such as stearic acid, extender oils, etc. The presence of nitrogen and nitro-sulphureted compounds transpire from the thermal degradation of the accelerators used in tyre compounding, which are frequently sulphur and nitrogen based organic compounds [4].

II. CHARACTERISTICS OF TYRE DERIVED OIL

Tyre Derived Oil (TDO) is a thick, syrupy, black, tar-like liquid. It smells like tar, and may even become semi-solid in cooler temperatures. TDO, also known as bunker oil or black liquor, is a petroleum product consisting of a complicated mixture of hydrocarbons with varying boiling points. It can be classified as fuel after more valuable hydrocarbons have been removed. Manufacturing companies use it 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. Since TDO is thick and viscous, users heat the oil up before they burn it. Heating makes the oil flow more easily; reducing pump demands and allows spray nozzles in the burner to turn the oil into a mist for maximum burning efficiency.

TABLE I
PROPERTIES OF TDO AND DF,[5]

| Parameter | TDO | DF | Petrol |
|-------------------------------------|------|------|--------|
| Carbon (wt. %) | 83.0 | | |
| Hydrogen (wt. %) | 6.6 | | |
| Oxygen (wt. %) | 8.6 | | |
| Nitrogen (wt. %) | 0.3 | | |
| Total Sulphur (wt. %) | 1.5 | 0.05 | - |
| Gross Calorific Value(MJ/kg) | 38.0 | 43.8 | 46.0 |
| Viscosity @ 40°C (cSt) | 10 | 2.58 | - |
| Flash point °C | 65 | 55 | 40 |
| Water content(mg/kg) | 1.6 | 0.05 | |
| Total contamination(mg/kg) | 143 | 24 | |
| Density (kg/m ³) @ 15°C | 920 | 822 | 740 |

The oils exhibit a high content of carbon, leading to the production of high value carbon materials that are used in

various industries (i.e. production of calcium carbide, steelworks, etc.) as shown Table I. The oils contain higher total sulphur, contamination level and viscosity. There is little contamination of these oils with metal and metalloid impurities as shown in Table II. The chemical composition of the tyre pyrolysis oil in terms of olefins is similar to that of the condensates obtained by coking of different petroleum residues, by thermal cracking of gas oil fractions and steam cracking of gasoline [6]. Therefore, the pyrolytic oil may be blended with these condensates and subjected to the same thermal treatments.

TABLE II
IMPURITIES PRESENT IN TYRE DERIVED OIL IN PPB [6]

| Na | Ba | Ti | Fe | Cu | Al | Zn | Pb | Ca | Cr |
|------|-----|------|------|-----|------|------|-----|-----|----|
| 1280 | 198 | 5585 | 4030 | 104 | 4030 | 2044 | 918 | 458 | 93 |

The flashpoint of TDO is approximately 65°C [5]. If the vapours mix in the correct proportion to air, an ignition source as small as a stray welding spark can cause a violent explosion. This fuel oil is a perplexed mixture, and it sometimes contains hydrocarbons with flashpoints significantly lower than 65°C. For this reason, TDO will sometimes give enough flammable or combustible vapours to start a fire when the oil is stored at ambient temperatures. When these vapours burn inside the tank, they produce enormous pressure. Such explosions have been known to tear storage tanks off their foundations, causing oil-spills and destructive fires [4].

Cunliffe *et al.*, (1998) [7], studied the composition of oils derived from the batch pyrolysis of tyres in a nitrogen purged static-bed batch reactor. It was reported that pyrolysis of scrap tyres produced oil similar in properties to a light fuel oil, with similar calorific value, sulphur and nitrogen contents.

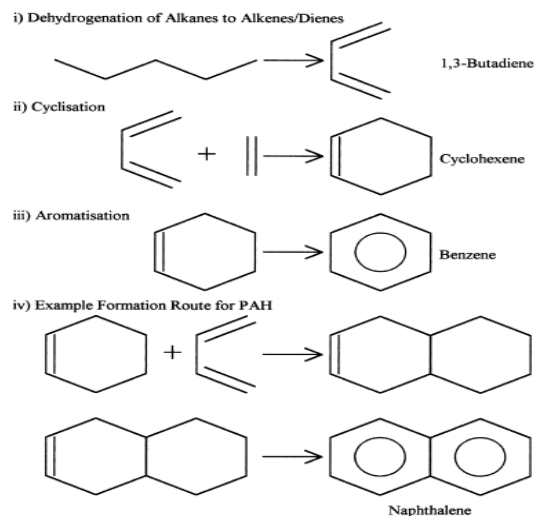


Fig. 1 Diels–Alder reaction for the formation of polycyclic aromatic hydrocarbons in scrap tyre [8].

Diels–Alder type mechanism involving cyclisation of alkenes and dehydrogenation to form aromatic hydrocarbons is shown in Fig.1. A range of potentially high value volatile

hydrocarbons was identified in significant concentrations in the oils. Optimum pyrolysis of tyres was found to take place at 570 °C. de Marco *et al.*, (2001) [3] studied the behavior and chemical analysis of tyre pyrolysis oil. In this work it is reported that tyre oils are a complex mixture of organic compounds of 5-20 carbons with a higher proportion of aromatics. It was observed that more than 30 % of the tyre pyrolysis oil was easily distillable fraction with boiling points between 70°C and 210°C, which is the boiling point range specified for commercial petrol. On the other hand, 75 % of the pyrolytic oil has a boiling point under 370°C, which is the upper limit specified for 95 % of distilled product of diesel oil. It was reported that distillation carried out between 150°C and 370 °C has a higher proportion of the lighter and heavier products and a lower proportion of the middle range of products than commercial diesel oil. The chemical compositions of tyre pyrolysis oil derived at 570°C are: Carbon (85.6 %), Hydrogen (10 %), Nitrogen (0.4 %), Sulphur (1.4 %), Ash (not available) and Oxygen by difference (2.5 %).

III. INDUSTRIAL APPLICATION OF TDO

Oil derived from the tyre pyrolysis process is similar to grade 6 fuel oil. It may also be regarded as residual oil implying that it may contain various undesirable impurities including 2 percent water and one-half percent mineral soil [4].

A. Use as fuel

TDO can be fired in burners with pre-heaters which accept high viscosity fuels, the liquids may also be directly used as fuels for industrial furnaces, power plants and boilers. The heating value of oil determines its value as a fuel. Nevertheless, with preliminary treatments such as decanting, centrifugation, filtration, desulphurization and hydro-treating they can be used as fuel [2].

The use of tyre pyrolysis oil as a substitution to diesel fuel is an opportunity in minimizing the utilization of the natural resources. Several studies have been carried out on the pyrolysis of waste automobile tyres. Pyrolysis is the process of thermally degrading a substance into smaller, less complex molecules [9]. Pyrolysis produces three principal products: such as pyrolytic oil, gas and char. The quality and quantity of these products depend on the reactor temperature and design. In the Pyrolysis process, larger hydrocarbon chains break down at certain temperatures in the absence of oxygen that gives end products usually containing solids, liquids and gases. If the temperature is maintained at 570 °C, the main product is a liquid, which could be a mixture of various hydrocarbons depending on the initial composition of the waste material [10].

B. Use as a Lubricant

Refineries process used oil into a variety of products, including heating oil, gasoline, jet fuel, chemical feedstock, and plastic feedstock. Pyrolytic oils contain approximately 1-

1.2 parts hydrogen to every one part carbon. Lubrication oil contains at least two parts hydrogen for every one part carbon. Upgrading used oil to meet lubricating oil specifications entails adding hydrogen to the hydrocarbon molecule, which requires the use of a catalyst. This upgrading procedure is uneconomical and chemically unfeasible for a crude chemical feedstock such as tyre-derived oil. Furthermore, most refiners do not have the technology necessary to process the oil derived from tyre pyrolysis.

IV. MARKET ASSESSMENT

Tyre-derived pyrolytic oil has four potential uses, some of which appear to be economically feasible, except perhaps in limited, special circumstances. Blending the distilled fractions of oil with other fuels to produce a useable fuel is in the research stage. The possibility of upgrading the oil to a higher quality product (e.g., a No. 4 grade), using distillation, is being explored, but the economics are unknown for a commercial-scale operation. Marketing the oil as a fuel is not currently feasible as cleaner fuels exist.

A. Petroleum Product Standards

According to the International Energy Agency (IEA), electricity generation and heating processes contributed about 64% of South Africa's total carbon dioxide emissions in 2007[11]. The transport sector is also a significant contributor to greenhouse gas emissions due to the high concentration of vehicles in the cities. This poses a risk both to human health and the environment. Consequently, stringent fuel specifications and standards should be in place to reinforce measures that are aimed at achieving the reduction of emissions from vehicles as well as improved air quality.

The Petroleum Products Amendment Act, 2003 (Act No. 58 of 2003) was crafted to empower the Minister of Energy to regulate the specifications and standards of petroleum products. Accordingly, in 2006, Government promulgated Regulations regarding Petroleum Products Specifications and Standards (hereafter referred to as the 2006 Regulations) in Notice R. 627 of Government Gazette No. 28958.

These regulations included, amongst others: the banning of the addition of lead (for octane enhancement) in all grades of petrol; the reduction of the permitted sulphur concentration in diesel from 3,000 parts per million (ppm) to 500 ppm; the creation of a niche diesel grade with a maximum sulphur concentration of 50 ppm; as well as permitting various blends of bio-diesel up to a level of 100% bio-diesel. The latter highlights one important aspect of the specifications and standards, being that of enabling the blending of bio-fuels (both bio-diesel and bio-ethanol) into the mineral fuel pool.

Prior to the 2006 Regulations, the oil industry had been subjected to self-regulation which was based on the relevant voluntary specifications and standards that were stipulated by the South African National Standards under the auspices of the South African Bureau of Standards (SABS). Self-regulation was possible largely because of product swaps among industry players. However, the successful implementation of the self-

regulation of fuel quality now referred to as Cleaner Fuels One (CF1) was not viewed as an end in itself, but rather as an enabling step towards further improvements of fuel quality.

The current South African fuel specifications and standards are perfectly suited to meeting Euro 2 emissions standards. The originally envisaged path towards cleaner fuels was to attain Euro 2 standards as from 2006; Euro 3 from 2008 and Euro 4 from 2010. In view of the fact the full implementation of the tighter fuel specifications and standards will only come into effect in 2017, it is proposed that CF2 specifications and standards should largely be compliant with the Euro 5 emissions standard on the targeted key parameters as outlined in Table III [11].

TABLE III
FUEL SPECIFICATIONS IN TERMS OF PROPOSED SOUTH AFRICAN SPECIFICATIONS

| Parameter | Unit | RSA (CF1) Spec | RSA (CF2) Spec |
|---------------------|--------|---------------------|----------------|
| Petrol | | | |
| Sulphur | mg/kg | 500 | 10 |
| Aromatics | Vol. % | 50 | 35 |
| Benzene | Vol. % | 5 | 1 |
| Reid vapor pressure | kPa | 45-75 | 45-60 |
| Olefins | Vol % | No-max | 18 |
| Diesel | | | |
| Sulphur | mg/kg | 500/50 ³ | 10 |
| PAH | % min | No max | 11 |
| Cetane number | none | 45 | |
| Distillation | | | |
| - T90 Max | °C | 362 | N/A |
| - T95 Max | °C | N/A | 360 |

V. HEALTH AND ENVIRONMENTAL IMPACTS

A. Sulphur content of petrol and diesel

Sulphur is inherent in the production process of petrol and diesel as it occurs naturally in crude oil from which these fuels are derived. Sulphur is toxic and harmful to the environment as it causes acid rain. The sulphur content of fuel is directly linked to the emissions that emanate from the combustion of that fuel in a vehicles engines. Generally the higher the sulphur content of fuel, the more will be the particulate matter that is produced during its combustion. With respect to health impact, particulate matter is known to contribute to respiratory related diseases. People with lung disease may not be able breathe as deeply or as vigorously as other people, and they may experience symptoms such as coughing, chest discomfort, wheezing and shortness of breath. Particulates can also cause nose and throat ion, lung damage as well as bronchitis.

B. Polycyclic Aromatic Hydrocarbons (PAH)

PAH are natural components in crude and therefore occur in diesel. They have high energy content but poor combustion characteristics leading to poor auto-ignition quality (cetane) increased thermal cracking, peak flame temperature and delayed combustion process. They lead to increased exhaust emissions of particulates. From a health perspective, particles

smaller than 10 microns diameter are of greatest concern as they are prone to entering the lungs and consequently causing respiratory problems. Furthermore, particulates from diesel vehicles are a significant source of brown haze which contributes to environmental pollution.

C. The impact of greenhouse gas emissions on health

Even though most of emissions are emanating from a variety of sources, research has shown that the emissions that are generated from transport are more dominant and comprise the majority of air pollutants such as CO₂, NO_x and others. One of the obvious factors driving governments across the world to implement new environmentally friendly fuels is the desire to have cleaner air. This is especially important in the case of major cities in South Africa. High levels of pollution through vehicle emissions may pose a serious health risk to the country's citizens; it may lead to significant productivity losses through personnel's frequent visits to hospital which often lead to admissions, as well as asthma and other respiratory related diseases.

TABLE IV
NATIONAL AMBIENT AIR QUALITY STANDARDS

| Averaging period | Concentration | limit |
|--|---------------------------------|-------|
| Sulphur Dioxide (SO₂) , reference method for analysis shall be ISO 6767 | | |
| 10 minutes | 500 mg/m ³ (191 ppb) | 526 |
| 1 Hour | 350mg/m ³ (134 ppb) | 88 |
| 24 Hours | 125 mg/m ³ (48 ppb) | 4 |
| 1 year | 50 mg/m ³ (19 ppb) | 0 |
| Nitrogen Dioxide (NO₂) , reference method for analysis shall be ISO 7996 | | |
| 1 Hour | 200 mg/m ³ (21 ppb) | 88 |
| 1 year | 40 mg/m ³ (106 ppb) | 0 |
| Particulate Matter (PM₁₀) , reference method for analysis shall be EN 12341) | | |
| 24 Hours | 120 mg/m ³ | 4 |
| 24 Hours | 75mg/m ³ | 0 |
| 1 year | 50 mg/m ³ | 0 |
| 1 year | 40mg/m ³ | 0 |
| Ozone (O₃) , reference method for analysis, UV photometric, shall be SANS 13964 | | |
| 8 Hours (running) | 120 mg/m ³ (61 ppb) | 11 |
| Benzene (C₆H₆) , reference method for analysis, EPA compendium method TO-14 A or Method TO-17 | | |
| 1 year | 10 mg/m ³ (3.2 ppb) | 0 |
| 1 year | 5 mg/m ³ (1.6 ppb) | 0 |
| 1 year | 0.5mg/m ³ | 0 |
| Carbon Monoxide (CO) , reference method for analysis shall be ISO 4224 | | |
| 1 Hour | 30 mg/m ³ (26 ppb) | 88 |
| 8 Hour | 10 mg/m ³ (8.7ppb) | 11 |

VI. CONCLUSION

TDO is a petroleum product consisting of a complex mix of hydrocarbons with varying boiling points which can be fractionated into various cleaner fuels. The chemical compositions of TDO derived at 570°C are: Carbon (85.6 %), Hydrogen (10 %), Nitrogen (0.4 %), Sulphur (1.4 %), Ash (not available) and Oxygen (2.5%). Reducing sulphur in this fuel is critical as combustion will further release the toxic sulphur compounds emissions in to the atmosphere. Modifications of TDO as an alternative fuel should take into account the

minimum requirements of air quality standards as prescribed by the South African National Environmental Affairs.

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