Pyrolytic Tyre Derived Fuel: Potential Diesel Additive

Jefrey Pilusa, and Edison Muzenda

***Abstract*—**Characteristics of distilled oil derived from slow pyrolysis of waste rubber were investigated in order to explore its application as diesel additive for application in compression ignition (CI) engines. Light oil fractions were obtained from batch distillation of crude rubber pyrolysis oil at 250°C. Physical properties such as calorific value, density, viscosity, flash point, water content, total contamination and sulphur were measured followed by functional group identification using a Fourier Transform Infra-Red Spectroscopy (FTIR). Distilled tyre oil exhibited near comparable properties to diesel fuel with low viscosity, flash point and high sulphur content. A number of functional groups were identified in distilled oil which were also found in commercial diesel. It was observed that distilled rubber oil that is filtered through 13X molecular sieves may be potentially used as an alternative diesel additive.

***Keywords*—**Alternative Fuel, Compression Ignition, Distillation, Molecular filtration, Pyrolysis Oil, Waste-to-Energy.

I. INTRODUCTION

DISPOSAL of waste rubber products is becoming an environmental challenge in many developing countries due to their non-bio degradability characteristic. Majority of waste rubber products are generated from worn or damaged automotive tyres and industrial conveyor belts. In South Africa alone, over 200,000 tons of tyres were generated annually in 2010; about 11 million used tyres were disposed illegally or burnt to retrieve the steel wire, with this figure estimated to increase by around 9.5 % annually [1]. Yet still the means of degrading or recycling them is a major environmental challenge. Tyres consists of complex mixtures of very different materials which include several rubbers, carbon black, steel cord and other organic and inorganic minor components [2]. They are bulky, designed to be tough and durable and once they are no good as tyres, they are difficult to cut up, hard to store or transport, thus making them very difficult to recycle in an economically viable manner [1].

Crude rubber oil is derived by slow pyrolysis of waste rubber products such as tyres and conveyor belts. In a slow pyrolysis process, the rubber containing material is heated in an oxygen free reactor at temperatures between 300 and 350°C and the resulting gasses are condensed into liquid crude rubber oil. Pyrolysis is the thermal decomposition of rubber at higher temperatures in an inert atmosphere, yielding pyrolytic oil, gas and carbon black [3].

The oil derived from pyrolysis of rubber has been known as a material with excellent and consistent fuel properties with a high calorific value, thus maybe used directly as fuel or blended with other fuels [4]. The gas may also be useful as a source of energy and the solid char maybe used either as smokeless fuel, carbon black [4]. Pyrolysis yield and characteristics of the product obtained are dependent on the operating conditions of the system [5]. A number of studies have been reported in literature relating to the distribution of the hydrocarbon composition of the pyrolytic oil at various operating temperatures. It has been reported that the aromatic hydrocarbons were about 34.7- 75.6w/w% when the pyrolysis temperature was varied from 300°C to 700°C while the aliphatic hydrocarbons were about 19.8 - 59.2w/w% [6]. It was also reported that 30w/w% of the pyrolytic oil boils between 70°C and 210°C which is the boiling point range of commercial petrol, and 75% of the pyrolytic oil has a boiling point under 310°C. The distillation range of the oil was found to be between 150°C and 350°C [7]. However, tyre pyrolysis oils have been shown to contain a wide range of polycyclic aromatic hydrocarbons, including naphthalene, biphenyl, flourene, phenanthrene, acenaphthene, anthracene and pyrene [8]. Some of the polycyclic aromatic hydrocarbons found have been shown in various biological tests to be carcinogenic and or mutagenic, for example chryrene, benzoflouranthene, benzopyrene [8].

Murugan *et al.* (2008) [9] studied the modification of the crude tyre pyrolysis oil and found that it could be modified in three stages (i) Moisture removal, (ii) De-sulphurisation, (iii) Vacuum distillation. It was found that the distilled pyrolysis oil had a 7% high heating value than the crude pyrolysis oil, and this was due to the elimination of the impurities, moisture, carbon particles, sulphur and sediments. Majority of liquids mercaptans in crude oils such as ethyl, n-propyl, n-butyl and carbon disulphide mercaptans are less reactive and have boiling points below 98°C [10]. The most common mercaptans boils below 100 °C, which explains why they can be removed from the crude oil via gas-phase desuplirasation distillation

---

Jefrey Pilusa is with the Department of Mechanical Engineering Science at the University of Johannesburg, Auckland Park, South Africa (corresponding author: e-mail: pilusat@webmail.co.za

Edison Muzenda is a Full Professor in the Department of Chemical Engineering Technology at the University of Johannesburg, Doornfontein, South Africa e-mail: emuzenda@uj.ac.za

http://dx.doi.org/10.15242/IIE.E1213078

over an adsobent with a pore size large enough to capture all molucular size ranges.

Asphaltes are formed when some sumphur componds in crude oil oxidises. Asphaltemnes are a dark brown to balck solids components of the crude oil oxidative products. They are charectarised by a hyrogen to carbon ratio of approximately 1.1, the hydrogen atoms are contained in saturated groups whereas the carbon atoms are contained in aromatic structures. They provide a low cracking yields and are of low economic value, they are relatively high in undersired heteroatoms and other heavy metalsThese compounds can be removed along with the moisture during distillation process.

The quality and characteristics of the rubber derived pyrolytic oil mainly depend on the type of compounds in the mixture, which are influenced by the pyrolysis process characteristics, process temperature and the nature of the rubber used [10,11]. Knowledge of the composition of these mixtures is important in the evaluation of the quality of the pyrolytic oil.

Molecular sieves are commercially available for the removal of mercaptans and de-waxing in oil refining applications. Recent experimental work in a Laboratory of Transport Phenomena and Applied Thermodynamics, at the Technical University of Crete, has shown a potential complex removal from solutions [12]. The aim of this study was to investigate the potential of using distilled rubber oil as diesel fuel additive for application in compression ignition engines.

II. METHOD

A. Recovery of Light Fraction Oils

A representative sample of crude rubber oil derived through a slow pyrolysis process was obtained from Pace oils (Pty) Ltd in South Africa. Physical properties of the crude oil were measured with reference to diesel fuel and presented in Table I. The crude oil was heated at 100°C using the apparatus shown in Fig.1. The temperature was maintained at 100°C while condensing the vapours to remove moisture and distillable liquid mercaptans. The temperature was raised to the desired range to distil and condense the light fractions from the crude rubber oil at 150, 200 and 250°C. The properties of the three light fractions obtained are presented in table II.

TABLE I
PHYSICAL PROPERTIES OF CRUDE RUBBER OIL AND DIESEL FUEL

Property	Crude Rubber Oil	Diesel Fuel	SANS 342 Specification
Density @ 20°C (kg/m^3)	926	831	800-950
Viscosity @ 40°C (cSt)	9	2.6	2.2-5.3
Flash Point (°C)	94	54	>55
Total Contamination (mg/kg)	143	29	<24
Total Sulphur (ppm)	9106	498	<500
Water Content (vol. %)	3.54	0.05	<0.04
Gross Calorific Value (MJ/kg)	43	46	-

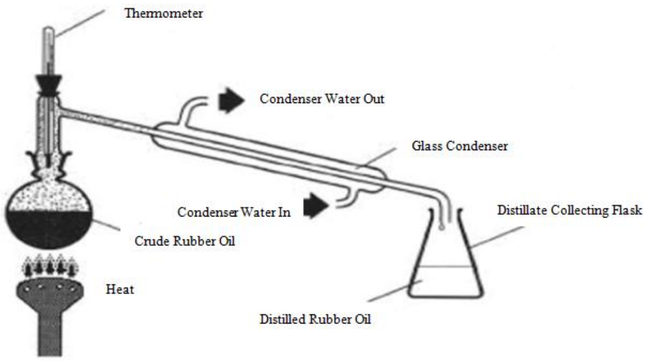

Fig. 1 Set-up for batch distillation of crude rubber oil

TABLE II
PHYSICAL PROPERTIES OF DISTILLATES AT VARIOUS TEMPERATURES

Property	150°C	200°C	250°C
Density @ 20°C (kg/m^3)	743	789	807
Viscosity @ 40°C (cSt)	0.8	0.9	1.5
Flash Point (°C)	26	35	43
Total Contamination (mg/kg)	3.5	5.5	6.5
Total Sulphur (ppm)	6923	6984	7030
Water Content (%)	0.04	0.05	0.05
Gross Calorific Value (MJ/kg)	38.6	39.5	43.7

Fig. 2 Distilled rubber oil at 150, 200 and 250°C from left to right

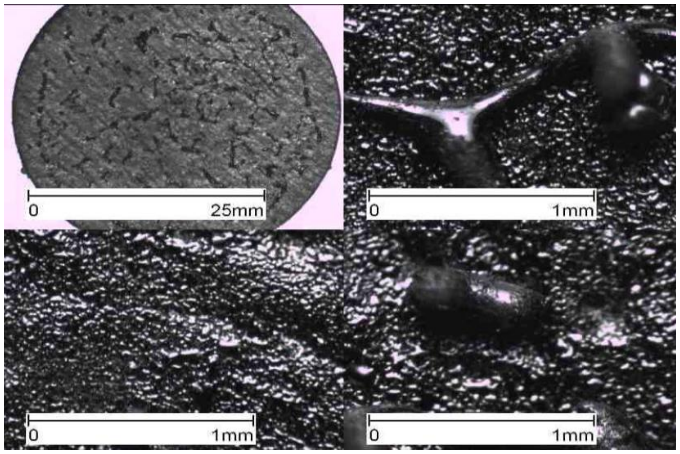

Fig. 3 Debris image of crude rubber oil

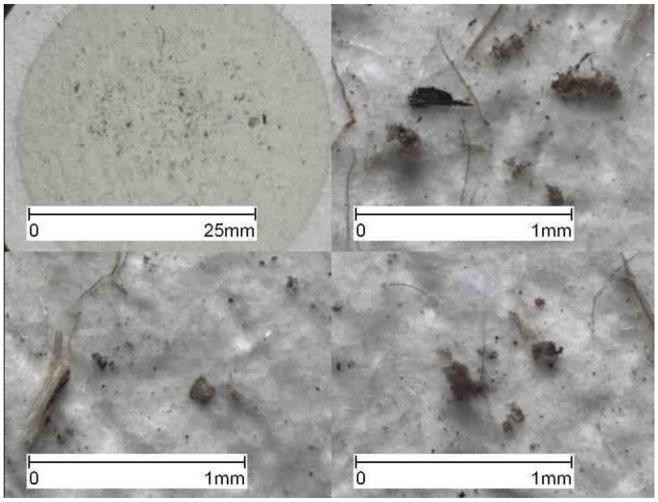

Fig. 4 Debris image of distilled rubber oil

B. *Molecular Filtration*

The distillates obtained at 250°C being the fractions that resemble diesel fuel underwent further treatment to reduce the residual sulphur compounds. Since a fraction of mercaptans were removed from the oil, the free sulphur remaining in the oil was reduced through adsorption using 13X molecular sieves. Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of alumina silicates. The pore opening of the sodium form of zeolite X (13X) is approximately 8 Angstrom. The ability to adjust the pores to precisely determined uniform openings allows for molecules smaller than its pore diameter to be adsorbed whilst excluding larger molecules, hence the name molecular sieve. The different pore sizes of synthetic zeolites open up a wide range of possibilities in terms of sieving molecules of different size or shape from gases and liquids.

Fig. 5 Distilled rubber oil undergoing molecular filtration

C. *Identification of Functional Groups*

Analysis of the crude rubber oil, diesel and selected distilled rubber oil chemical composition were conducted using a Fourier Transform Infra-Red Spectroscopy (FTIR) to identify the functional groups present, Table III shows the functional groups identified in crude rubber oil, while Fig. 2 shows specific functional groups present in both diesel fuel and rubber oil distillates obtained at 250°C.

TABLE III

FUNCTIONAL GROUPS IDENTIFIED IN CRUDE RUBBER OIL

Functional Group	**Molecular Motion**	**Wavenumber (cm^{-1})**
Alkyl halides	C-I stretch	600-485
Alkenes	C=C stretch	1690-1630
Alcohols	C-O stretch	1260-1000
Acid chlorides	C-Cl stretch	730-550
Alkyl halides	C-F stretch	1400-1000
Alkyl halides	C-Cl stretch	785-540
Amines	C-N Stretch (alkyl)	1200-1025
Amides	N-H stretch	3500-3180
Aromatics	C-H bend (mono)	715-685
Carboxylic acids	O-H stretch	3400-2400
Ethers	C-O-C stretch (dialkyl)	1300-1000
Amines	-R_2C=N-R stretch	1690-1640
Phosphine oxides	P=O	1210-1140
Ketones	C-C stretch	1300-1100

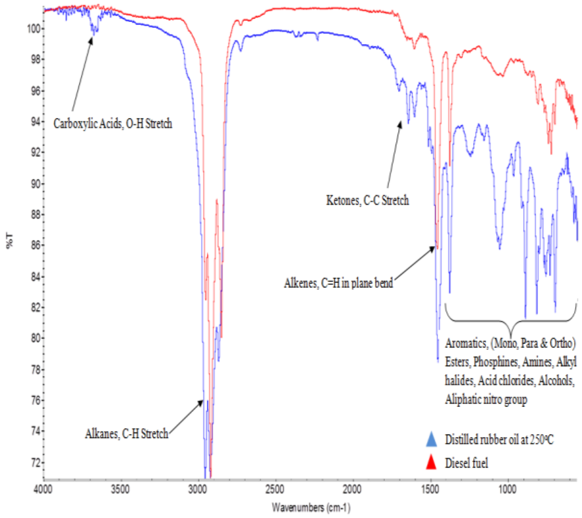

Fig. 6 Common functional groups identified in distilled rubber oil and diesel fuel

III. RESULTS AND DISCUSSIONS

The compounds that are distillable at temperature range of 150 to 250°C are napthas, at this temperature range sulphur is more easily removed because, lower boiling oil fraction primarily contain sulphurous compounds that are in the form of mercaptans or lower member ring compounds which are relatively easier to de-sulphurise [13]. This is noticed by reduction in sulphur content from 9106ppm to 7030ppm when crude rubber oil is distilled at 250°C. Majority of liquids mercaptans in crude rubber oil were mostly removed along with the moisture during the pre distillation stage.

The crude rubber oil is a dark brown to almost black liquid which is highly viscous with a sharp and irritating smell, and contain high concentration of sulphur due to the nature of rubber production [14]. Due to its high viscosity, contamination and high sulphur content as shown in Table I, its application as a fuel in diesel engines is not recommended without refining. Fig. 2 shows images of rubber oil distillated obtained at 150, 200 and 250°C. The results presented in Table II reveals that the light fractions obtained at 250°C are near the properties of diesel fuel as per South African National Standards (SANS-342) presented in Table I. Total contamination of fuel is capped at 24mg/kg according to SANS 342, crude rubber oil has a total contamination value of 6 times the acceptable contamination limit. In contrast, distilling the oil does not only increase the calorific value of the fuel but it also reduces total contamination by 95%. The effect of this is consolidated by the microscopic debris images of the crude and distilled oil as presented in Figs. 3 and 4 respectively.

High sulphur contents in fuels result in significant generation of sulphur oxides emissions which is a major environmental pollutant. Sulphur reduces catalyst efficiency in modern vehicles, and vehicles operating with higher sulphur fuels have higher emissions [7]. On the other hand there are some side effects from using low sulphur diesel fuel. The reduction in sulphur contents can reduce the natural lubricating properties of diesel fuel, which is essential for the lubrication and operation of fuel system components such as the fuel pumps and injectors [10].The use of molecular sieves reduced the concentration of residual sulphur in the oil by 44.4% from 7030ppm to 3010ppm.

Viscosity is an important characteristic because it affects the performance of the engine's fuel injection equipment. Correct fuel atomisation depends on the fuel's viscosity, the injection pressure and injector hole size. Thus to burn most cleanly, fuel must be injected such that the atomised fuel is dispersed evenly throughout a combustion chamber [12]. According to Murugan *et.al*, [10] high viscosity fuels atomise into larger droplets with higher momentum and are more likely to collide with the relatively cooler liner wall, thus extinguishing the flame and increase the soot deposits and emission.

Distilled rubber oil exhibits significantly low viscosity and flash point. Islam *et al*., (2003)[14] also reported low flash point with a similar temperature difference of 43°C. The flash point is important for safe handling of the fuel, and a low flash point makes the fuel highly flammable and fire hazardous [14]. It is suggested that diesel with a very low flash point might be contaminated with a more volatile and explosive fuel such as petrol [13], thus during distillation of crude rubber oil the lighter fractions of the oil might have been distilled closely to the heavier diesel like fraction. Trongkaew *et al.*(2011) [11] reported that the flash point has no effect on the engine performance, it does not influence the auto-ignition temperature of the fuel. The low viscosity of distilled rubber oil will affect the combustion of the fuel, thus reducing the fuel economy and power output. Fuel additives like lubricity enhancers might assist in improving the viscosity.

The distilled oil fractions exhibit higher heating values than that of bituminous coal (28MJ/kg) and wood charcoal (30MJ/kg) [9]. Roy *et al*. (1999) [8] studied several fractions of the pyrolytic oil and found that when the light fraction of the oil (204°C) was compared to typical petroleum naphtha (160°C), it was rich in aromatics including Toluene, Xylene, and Benzene and Alkyl benzene. It was also suggested that this oil could also be used for industrial furnaces, power plants and boilers due to the high heating value.

The low flash point of the oils makes them fire hazardous. Mixing the oils with other commercial oils prior to their use as fuel oils might improve the viscosity [6]. The lighter fraction exhibit petroleum properties, thus it can be blended with petroleum fuels before it can be used as a fuel. Due to their higher octane number, aromatic hydrocarbons are desirable in the composition of diesel fuel [9].

Table III shows the presence of aromatics among other functional groups in crude rubber oil. Refineries incorporate a reforming process which consists of enhancing the fuel's octane number by n-paraffins conversion into iso-paraffins and aromatics [9]. However, it has been found that under regular engine operating conditions, aromatic hydrocarbons condense, leading to the formation of polycyclic aromatic hydrocarbons which have been reported to be hazardous [5]. Thus there are regulations governing quantity of aromatics in diesel fuel.

The distilled rubber oil has noticeable fractions of aromatic compounds which are said to increase the density of a fuel and the heating value of the fuel resulting in improved cold flow properties [16]. On the other hand aromatics are restricted in diesel fuels because they reduce the centane number of the fuel and have been identified as contributors of nitrogen oxides (NO_x) emissions [16], this will not be the case for distilled rubber oil since the intensity of aromatic compounds present in the oils is lower compared to diesel fuel as presented in Fig. 6. Other functional groups were identified in distilled rubber oil which was not identified in the commercial diesel. These include carboxylic acids (O-H stretch) and ketones (C-C stretch) as shown in Fig 6 (N-H bend).

IV. CONCLUSIONS

The findings of this study revealed that the fuel properties of distilled oil obtained at 250°C are nearly comparable to commercial diesel with high heating value as well as low water content and total contamination. It was also discovered that the oil cannot be used directly into compression ignition engines in its pure form due to its higher sulphur content, low viscosity and low flash point. A blend of this oil with diesel fuel may be considered to an extent whereby the overall viscosity and flash point of the blend fuel is at least 2.2cSt and 55°C respectively. The sulphur content in the oil was reduced by 22.5% via distillation process and further 44.4% by molecular filtration using 13X molecular sieves.

ACKNOWLEDGMENT

The authors are grateful the National Research Foundation of South Africa (NRF), Department of Mechanical and Chemical Engineering are acknowledged for supporting the research. The authors are also indebted to the Faculty of Engineering and the Built Environment of the University of Johannesburg for conference support.

REFERENCES

[1] B.E.E. Molewa, "Notice of Approval of an Integrated Industry Waste Tyre Management Plan of the Recycling and Economic Development Initiative of South Africa," *South African National Department of Environmetal Affairs*, vol. 569 No.35927, 2012.

[2] M. P. Hirenkumar, and M.P. Tushar, "Emission Analysis of a Single Cylinder Fuelled with Pyrolysis Oil Diesel and its Blend with Ethanol," *IJEST*, vol. 4, pp. 2834-2838, 2012.

[3] J. Shah, M.R. Jau, and F. Mabood, "Recovery of value-added products from the catalytic pyrolysis of waste tyre," *Energy Conversion and Management*, vol. 50, pp. 991-994, 2009.

[4] A.M Cunliffe, and P.T Williams, "Composition of oils derived from the batch pyrolysis of tyres," *Journal of Analytical and Applied Pyrolysis*, vol. 44, pp. 131-152, 1998.

[5] M.F. Laresgoiti, B.M. Caballero, I. de Marco, A. Torres, M.A Cabrerro, and M.J. Chomon, "Characterization of the liquid products obtained in tyre pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 71, pp. 917-934, 2004.

[6] D. Prandhan, and R.K. Singh "Thermal Pyrolysis of Bicycle Waste Tyre Using Batch Reactor", *International Journal of Chemical Engineering Applications*, vol. 2, pp. 322-336, 2011.

[7] P.T William, and R.P Bottril, "Sulphur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil," *The University of Leeds: Department of Fuel and Energy*, Leeds United Kingdom, 1995.

[8] C. Roy, A. Chaala, and H. Darmstadt, "The vacuum pyrolysis of used tyres-end-uses for oil and carbon black products," *Journal of Analytical and Applied Pyrolysis*, vol. 51, pp. 201-221, 1999.

[9] S. Murugan, M.C Ramaswamy, and G. Nagarayan, "A comparative study on the performance, emissions and combustion studies of DI engine using distilled tyre pyrolysis oil-diesel fuel blends," *Fuel*, vol. 87, pp. 2111-2121, 2008.

[10] L. Kramer, and W. Cappel, "Presentation on Mercaptans in Crude Oil-Baker Hughes Incorporated 2011", unpublished

[11] P. Trongkaew, T. Utisthan, P. Ruebroycharen, and N. Hinchirama, "Photocatalytic desulphurisation of waste tyre pyrolysis oil," *Energies*, vol. 4, pp. 1880-1896, 2011.

[12] D. Giagou, G. Foudoilis, V. Gekas, "Nano filtration: towards a breakthrough", unpublished.

[13] K. Unapumnuk, T.C. Keener, M. Lu, and F. Liang, "Investigation into the removal of sulphur from tyre derived fuel by pyrolysis," *Fuel*, vol. 87, pp. 951-956, 2008.

[14] M.N Islam, M.F.R Khan, and M.Z Alam, "Production and Characterisation of Scrap Tyre Pyrolysis Oil and its blend," *ICME*, 2003.

[15] H.R. Perry, D.W. Green, and J.O. Maloney, *Perry's Chemical Engineers' Handbook*, 7th edition, New York: McGraw-Hill, 1993, pp. 2653-2667.

[16] M.R. Islam, M. Parveen, H. Haniu, and M.R. Islam Sarker, "Innovation in pyrolysis technology for the management of scrap tyres: A solution of energy and environment," *IJESD*, vol. 1, pp. 89-98, 2010.