

Reduction of Sulphur in Crude Tyre Oil by Gas-liquid Phase Oxidative Adsorption

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Keywords: Fuel, Desulphurisation, Distillation, Emissions, Pyrolysis

Abstract—This study investigates the reduction of sulphur compounds in crude tyre pyrolysis oil through gas-phase adsorption over molecular sieve. Crude tyre pyrolysis oil was distilled at 300° C using a bench scale distillation set-up consisting of an electric heating mantle, glass round bottom flask and water cooled glass condenser. The glass condenser bulb was filled with steel wool and molecular sieve pellets for effective oxidation and adsorption of sulphur compounds in the vapours prior to condensation. It was observed that gas-phase adsorption improves total sulphur capture by 19.6%. Reduction in sharp pungent smell of the condensed distilled light fractions is justified by 21.7% total sulphur removal of low boiling point mercaptans and sulphides during moisture removal stage. High boiling point and large molecular size sulphur compounds in the distilled fractions can be further reduced by 3.6% using liquid phase adsorption over activated carbon black.

INTRODUCTION

Sulphur in crude oils can exist in a variety of chemical and oxidation states (Limbachiya and Roberts, 2004). Previous research has revealed that sulphur in crude oils and asphaltenes exists primarily in the organic forms, thiophene, mercaptans and sulphides (Williams, 2005). Sulphur compounds are undesired in petroleum crude oils due to its negative environmental effects associated with the used of fuels derived from these crude oils. Table 1 show different forms sulphur compounds and their respective molecular weights and boiling points range. Most mercaptans boils below 100°C, this explains why they can be removed from the crude oil via gas-phase desulphurisation distillation over an adsorbent with a pore size large enough to capture all molecular size ranges. Some sulphides and di-sulphides have larger molecular weights, size and higher boiling points compared to mercaptans.

Table 1: Typical sulphur compounds in crude oils (Hester and Harrison, 2013).

Name	Carbon chain	Molecular Weight range	Boiling Point range
Mercaptans	C1-C5	48.11-90.16g/mol	6.2 -98.46 °C
Sulphides	C0-C8	32.8-146.3g/mol	-60.7-185 °C
Disulphides	C1-C6	70.13-122.3/mol	46.3-193.5 °C

The use of tyre derived fuel as an alternative fuel for compression ignition engines has been reported in literature (Murugan et al, (2008), Cunliffe and Williams, (1998)). Murugan et al, (2008) discovered that crude tyre derived fuel cannot be used in any internal combustion engine without further processing for the removal of contaminates. Cunliffe and Williams, (1998) investigated the composition of oils derived from the batch pyrolysis of tyres and discovered common properties to diesel fuel. Murugan et al, (2006) further investigated the use of distilled tyre derived fuel blended with diesel fuel in compression ignition engines. Higher exhaust

emissions were noticed when more than 80% by volume of tyre derived fuel in the blend was used however no engine failure or reduced performance was noticed.

Asphaltenes are formed when some sulphur compounds in crude oil oxidise. Asphaltenes are a dark brown to black solids components of the crude oil oxidative products. They are characterised by hydrogen to carbon ratio of approximately 1.1, the hydrogen atoms are contained in saturated groups whereas the carbon atoms are contained in aromatic structures (Ringer et al., 2006). They provide low cracking yields and are of low economic value, they are relatively high in undesired heteroatoms and other heavy metals.

Heteroatoms, which occur in polar and even charged groups, have a significant impact on solubility. Asphaltenes are defined by their solubility, and hence the importance of understanding the heteroatom chemistry. Sulphur is of particular interest in crude tyre derived oil since that raw tyre products contains cross linked sulphur compounds which are used during tyre vulcanization process primarily as reinforcement. Roy et al, (1990) has presented analytical methods leading to characterisation of tyre vulcanization system of unknown elastomers (sulphur or peroxide cross-linked). It is to be considered, however 70 that sulphur in rubbers may originate not only from vulcanization process but also from additives such as accelerator reaction products, organic plasticizers (alkyl polyether-thioether), organic stabilizers (Dioctadecyl thiodipropionate), organic fillers (ebonite powder), inorganic (Barium sulphate, free elemental sulphur, metallic sulphide and inorganic pigments (Bhandodaya et al., 2001).

Molecular Sieves

Molecular sieves are crystalline alumina-silicates with a three-dimensional porous structure. They can be synthesized with different crystal structures, definitive pore sizes, framework Si/Al ratios and adjustable acid centres to have some important catalytic properties. Aluminium atoms and ions in skeletons and porosity supply the acidic sites (Wang et al., 1980). Zeolites have extremely high internal surface area $\sim 600 \text{ m}^2/\text{s}$ and high thermal-stability 1000°C , and are suitable for application as the most popular solid catalysts (Kulprathipanj, 2010). Internal diffusion resistances are considered to limit reaction rate significantly. Thus, large-pore zeolites are active for the reaction with satisfactory reaction rate. Molecular sieves were used in desulphurization of tyre pyrolysis oil as heterogeneous catalyst/adsorbent.

Activated Carbon Black

High surface area, activated carbon has an affinity for some organic sulphur compounds and can be used as an adsorbent for sulphur in chemical treatment processes (Cunliffe and Williams, 1998). For example two parallel activated carbon beds can be used for adsorption of sulphur impurities in natural gas. One bed can be operated while the other is regenerated; however mercaptans and carbonyl sulphides are not strongly bound to activated carbon and can be displaced by higher molecular hydrocarbons in the gas stream (Pradeep and Sharma, 2005). To improve adsorption efficiency the carbon can be impregnated with iron or copper oxide.

Traditional Crude Oil Desulphurisation

Hydrodesulphurisation is commonly used for removal of sulphur compounds from crude oil fractions by reaction with hydrogen. As the process evolved to include nitrogen and oxygen removal, together with hydrogenation of aromatics and olefins, the group of process became known as hydro treating (Williams, 2005). These processes convert organic sulphur, nitrogen and oxygen compounds into hydrocarbons, hydrogen sulphide, ammonia and water, respectively. At the same time olefins and aromatics may be converted into saturated hydrocarbons without any cracking of the hydrocarbons (Ringer et al., 2006). This study investigates the reduction of sulphur compounds in crude tyre pyrolysis oil through gas phase adsorption over molecular sieve followed by micro filtration and molecular filtration over activated carbon black granules.

EXPERIMENTAL PROCEDURE

A schematic block diagram of the extraction system used in this study is presented in Fig.1. The process consists of two stages: A sample of crude tyre derived oil was characterized as an alternative fuel for compression ignition engines as per test data presented in Table 2. The initial total sulphur in the crude oil was measured as a point of interest for this research. A bench scale distillation set-up consisting of 1000 ml round bottom flask, heating mantle, glass water cooled condenser and a collecting flask as shown in Fig 2.

The glass condenser was fitted with 8g of steel wool in order for the water vapour from the oil to promote oxidation of steel wool into ferric oxide which will act as a catalyst for the removal of sulphur compounds. The temperature of the feed crude oil was monitored and maintained at 100°C to allow for evaporation and recovery of water, low boiling point mercaptans, sulphides and disiphides in the crude oil. The crude oil was slowly cooled down to ambient temperature followed by measuring the total sulphur the crude oil and condensed water removed from the crude oil. The condenser bulb was filled with 13g of 13x molecular sieves supported over oxidized steel wool. This was to ensure oxidation of high boiling point sulphur compound and adsorption over the active layer of micro-porous sieves in a gas phase prior to condensation. 13x molecular sieve pellets to enhance oxidation and adsorption of low boiling points sulphur compounds as well as water removal from the fuel, however large quantities of water may reduce its active surface area and reduced adsorption rates.

The distillation temperature of the crude oil was raised 300° C for extraction of light and heavy fuel fractions from the crude oil while oxidizing and capturing the sulphur compounds over the active layer of molecular sieves in the condenser bulb as shown in Fig 2. The system was properly sealed at each connection point to ensure that all vapours passes through the ferric oxide and molecular sieves before they are condensed into light fraction fuel. The condensed fuel was filtered through a series of micro-molecular filtration system presented in Fig. 2 for the removal of suspended and dissolved contaminants. This fuel was characterized as an alternative fuel for diesel engine compared to commercial diesel as shown in Table 2.

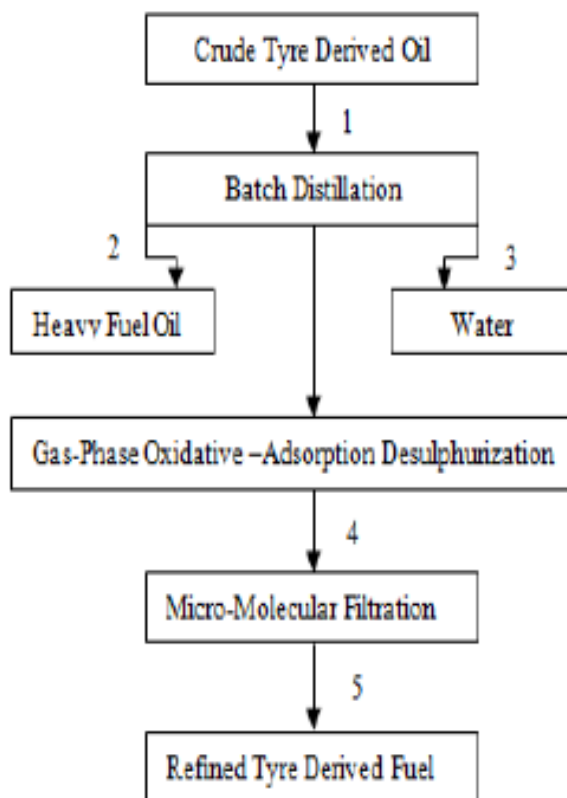


Fig. 1 Process flow diagram for experimental set-up

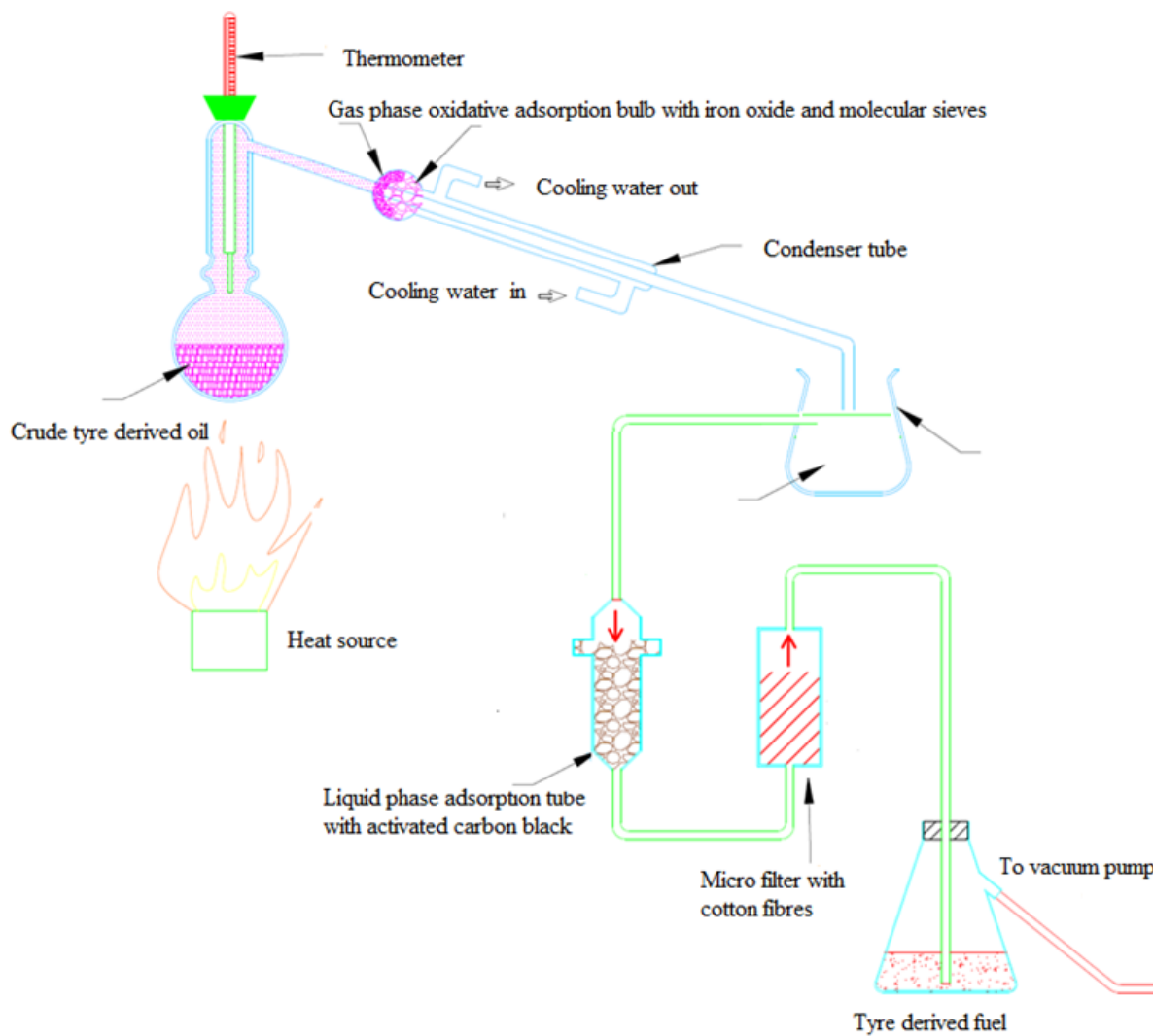


Fig. 2 Bench scale experimental setup

RESULTS AND DISCUSSIONS

The characteristics of crude tyre derived oil and diesel fuels are presented in Table 2. Crude tyre derived oil contains significantly large amount of contaminants, water and total sulphur which makes it unsuitable for use as a combustion fuel without refining. Tyre derived fuel is distillable at temperature range of 115 to 327 °C, up to 50 and 83 vol.% of this fuel can be recovered at distillation temperatures of 225 and 300°C respectively as shown in Fig. 3. 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, sulphides, di-sulphides or lower member ring compounds which are relatively easier to de-sulphurise (Williams, 2005). Table I show that typical sulphur compounds such as mercaptans, sulphides and disulphides boils below 193°C and can be easily evaporated for effective gas phase desulphurization over an active surface layer of adsorbent such as molecular sieves or activated carbon.

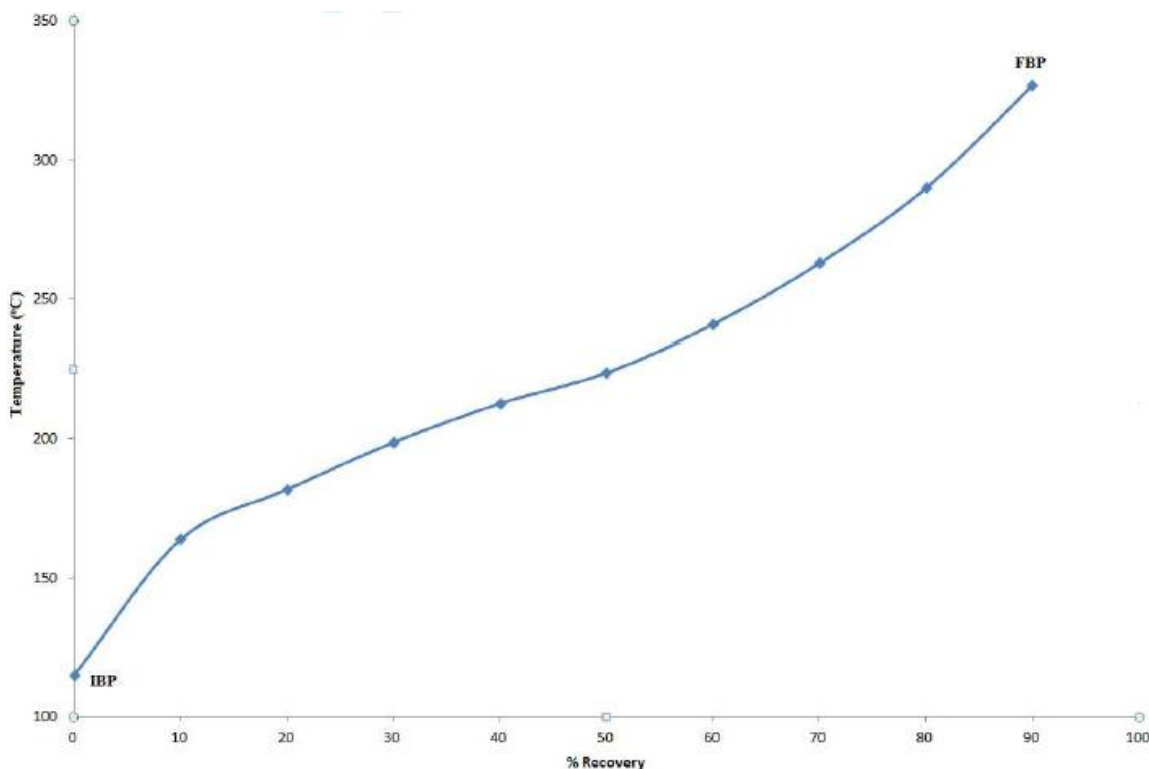


Fig. 3 Distillation profile of tyre derived fuel

Analysis of the crude tyre derived oil, diesel and selected distilled rubber oil chemical composition were conducted using a Fourier Transform Infra-Red Spectroscopy (FT-IR) to identify the functional groups present, Fig. 4 shows specific functional groups present in both diesel fuel and tyre fuel oil distillates obtained at 300°C.

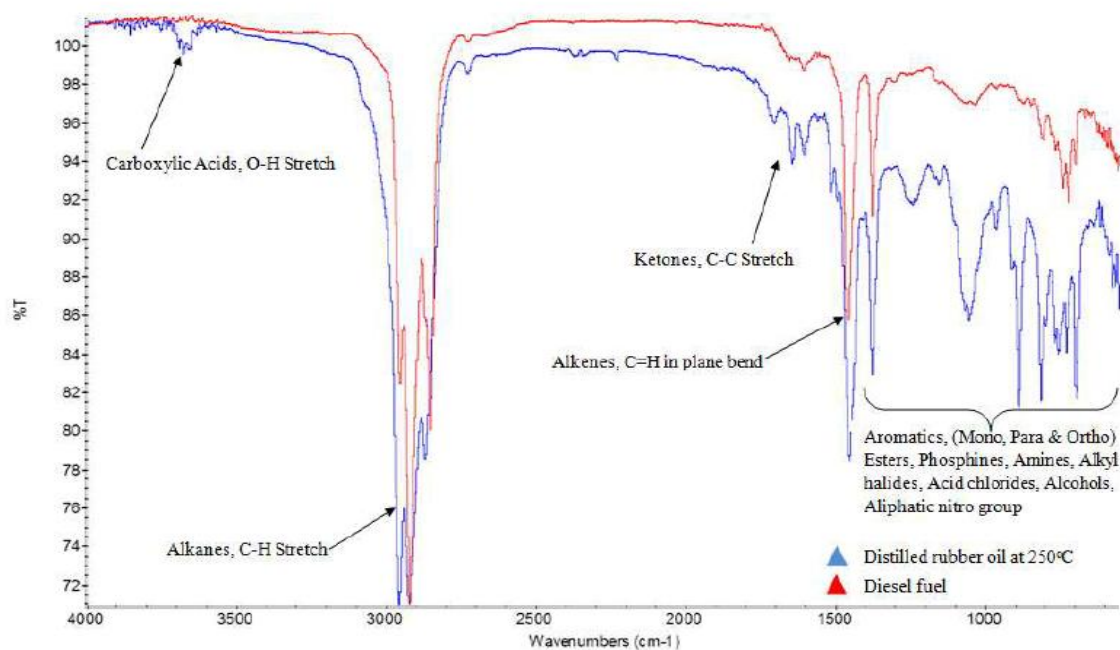


Fig. 4 Functional groups in tyre derived fuel and diesel fuel

Distilled tyre derived fuel 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 (Murugan et al., 2008). 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 emissions (Pradeep and Sharma, 2005), this will not be the case for distilled tyre derived fuel since the intensity of aromatic compounds present in the oils is lower compared to diesel fuel as presented in Fig. 4. Other functional groups were identified in distilled tyre derived fuel which was not present in the commercial diesel. These include carboxylic acids (O H stretch) and ketones (C-C stretch).

This is noticed by reduction in sulphur content from 13732 ppm to 2300 ppm when crude tyre derived oil is distilled at 300°C. Majority of low boiling points mercaptans in crude oil were mostly removed along with the moisture during the pre distillation stage where by 15wt.% water was recovered from the crude oil. The water was found to contain about 3234 ppm total sulphur, this sulphur is mainly attributed by distillable sulphur compounds below 100° C. The water removal stage was performed with only steel wool in the condenser bulb to enhance oxidation of steel into iron oxide. Dry molecular sieve pellets were added into the condenser bulb over oxidized steel wool to act as a media for catalyzed desulphurisation of moisture free fuel vapours for efficient adsorption on to the active surface of molecular sieves. This process further reduced total sulphur in the condensate to 2300 ppm as a result of gas-phase adsorption. The condensed fuel fraction contained some fibrous contaminants and colour fading from light yellow to dark brown when it is cooled down. This was further processed through micro-molecular filtration using micro cotton fibers and activated carbon black. There was a 21.7 % sulphur reduction from the gas-phase de sulphurisation due to liquid adsorption over activated carbon black surface.

Table 2: Physical properties of tyre derived fuel as an alternative CI engine fuel

Property	Crude Tyre derived Oil	Distilled Tyre derived Fuel	Low sulphur Diesel Fuel	SANS 342 Specification for CI engine fuel
Density at 20°C (kg/m ³)	926	824	898	800-950
Viscosity at 40°C (cSt)	10.8	1.6	3.5	2.2-5.3
Flash Point (°C)	93	26	56	>55
Total Contamination (mg/kg)	589	29	18	<24
Total Sulphur (ppm)	137222	1800	48	<500
Water Content (vol. %)	15.24	0.03	0.05	<0.04
Gross Calorific Value (MJ/kg)	39.54	43	46	-

The crude tyre derived 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 vulcanisation process and addition of sulphur containing stabilizers during tyre manufacturing process (William and Bottril, 1995). Due to its high viscosity, contamination and high sulphur content as shown in Table 2, its application as a fuel in diesel engines is not recommended without refining. Fig. 5 shows images of tyre derived fuel obtained 300°C. The results presented in Table 2 reveals that the light fractions obtained at 300°C are similar properties to diesel fuel as per South African National Standards (SANS-342). Total contamination of fuel is capped at 24 mg/kg according to SANS 342, crude tyre derived oil has a total contamination value of 25 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, distilled tyre derived fuel compared to diesel fuel oil as presented in Fig.5.

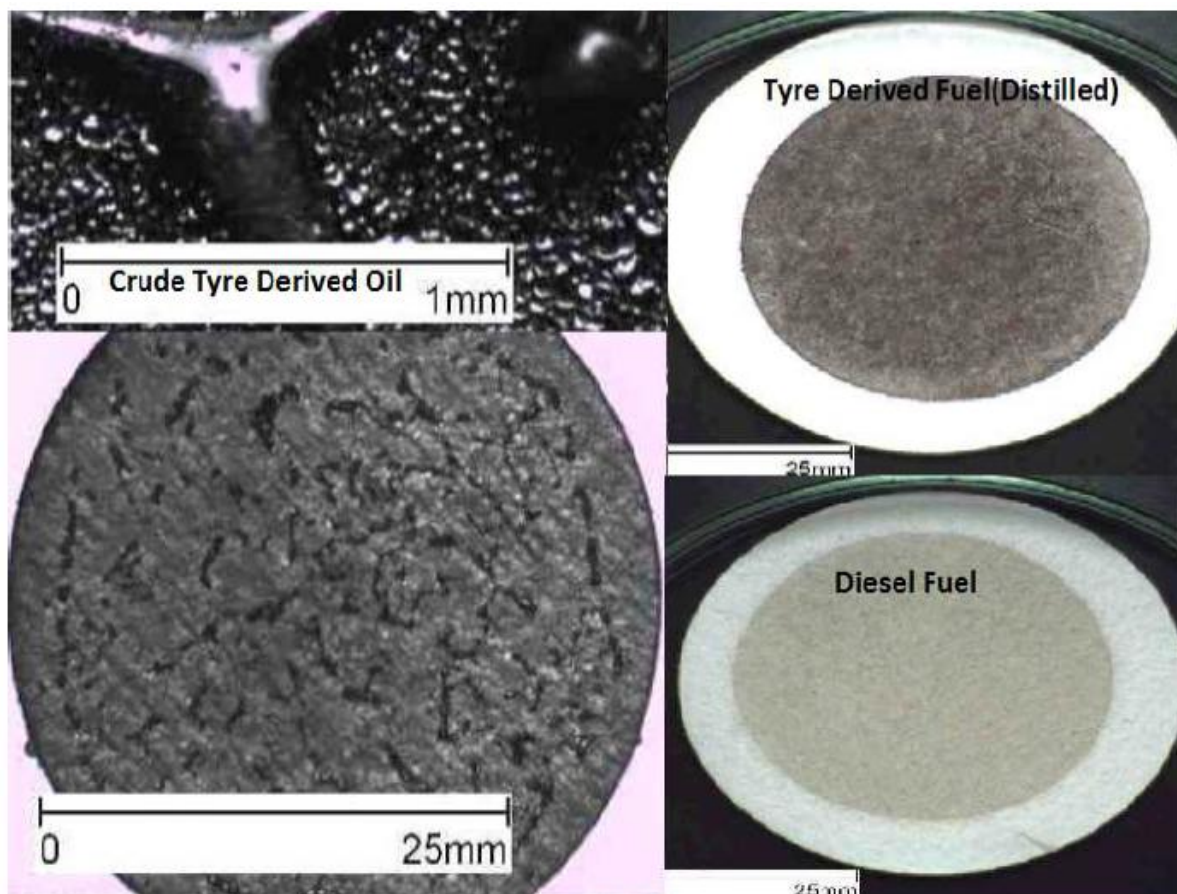


Fig. 5 Debris images of crude and distilled tyre derived fuel compared to diesel fuel

Table 3: Mass and sulphur balance

Stream Number	1	2	3	4	5
Mass(g)	926	234	138.9	553	553
Density(g/ml)	0.926	1.180	1.008	0.824	0.824
Total Sulphur(ppm)	13.732	7.800	3.234	2.300	1.800

Distilled tyre derived fuel exhibits significantly low viscosity and flash point. Islam et al., (2003) 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 (Lin and Tavlarides, 2010). Trongkaew et al. (2011) 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 tyre derived fuel is likely to 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 initial working packing density for the cotton fibers was calculated as a ratio of dry mass of the packed cotton fibers and the active volume of the glass tube. The packing density and active filtration area of granular activated carbon black as a function of the media housing geometry and voids between the granules. The results show 3.6% reduction in total sulphur via liquid phase molecular filtration over activated carbon black granules.

The size fraction in the fuel was analyzed using laser particle analyzer. The largest particle size in the distilled tyre derived fuel was detected at 38 Im before filtration. The micro filter media used was capable of capturing

up to 10.5 μm in size. The total suspended solids test in the distilled tyre derived fuel was reduced to a final value of 29 mg/kg as presented in Table 2 compared to 18 mg/kg in commercial diesel fuel. This suggests that tyre derived fuel contains more particle contaminants due to formation of asphaltenes. The particle size analysis results shows 99.8% of ultra-fine particle contaminants present in the filtered fuel blend with 50% below 2 μm . Although the total suspended solids are within the allowable limits as per SANS 342, these fines carry a potential threat to the fuel injection system as they are likely to be bound together by asphaltenes and subsequently block the injector nozzles

CONCLUSIONS

The findings of this study revealed that the fuel properties of distilled oil obtained at 300°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 crude tyre derived oil cannot be used directly into compression ignition engines in its pure form due to its total contamination, higher sulphur content, high viscosity and high water content. The distilled tyre derived fuel has a potential of being used as a diesel additive. Gas phase oxidative desulphurisation is effective for removing up to 19.6% of the total sulphur and further 3.6% via liquid phase adsorption over activated carbon black granules. Formation of fiber-like structure in the condensed light fuel fraction is as a result of fuel oxidation to form asphaltenes with rosary type grain structure when the fuel cools down. The ultra-fine particles are bound together by these fibers, resulting in soft visible grains easily removable by microfiltration. 23.6% of the total sulphur was removed as distillable low boiling point mercaptans, sulphides and disulphides during water removal stage. The balance of the sulphur compounds remains with the low volume un-distilled heavy fraction as cross linked molecules. A more in-depth investigation on the chemical analysis of sulphur compounds in the heavy fractions is recommended.

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