Molecular Filtration of Rubber Derived Fuel

Jefrey Pilusa, Edison Muzenda, and Mukul Shukla

Abstract—The work presented in this article reviews the possible methods for removal of mercaptans from distilled rubber derived fuel. Distilled rubber derived fuel is a potential additive for diesel fuel; therefore reduction of sulphur compounds in this fuel is essential for application in compression ignition engines. Membrane filtration of distilled rubber fuel using 13-X molecular sieves has shown a significant reduction in sulphur content. It was observed that distilled rubber fuel can be effectively filtered via single pass to remove up to 53.67% of the fuel’s initial sulphur.

Keywords—Diesel additive, Compression ignition, Fuel, Membrane filtration, Pyrolysis fuel, Waste-to-energy

I. INTRODUCTION

Rubber fuel is derived by the slow pyrolysis of rubber containing waste products such as tyres. Crude fuel is further distilled to recover high aromatic fuel resembling the characteristics of diesel fuel. Previous research has shown that this fuel can be used directly in compression ignition engines without any engine modification. However high toxic exhaust emissions were realised due to the use of this fuel [1].

This fuel has also been reported to contain sulphur content of approximately 9,000–12,000 ppm [2]. This high sulphur content is as result of natural rubber vulcanisation in tyre manufacturing process [2]. 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 containing a filter can retain at a rated flow and given end-point. The type of media (i.e. glass, cellulose, synthetic, membranes etc.) and the active filtration area of media define capacity. Coppo et al. (2006) [8] explained the filter restriction in terms of the pressure drop across the element at a given flow, temperature, and fluid viscosity.

Molecular Sieves are crystalline, three-dimensional molecules made up of silicon and aluminum atoms. The extensive networks that make up molecular sieves contain surface pores and channels which selectively absorb only molecules of a certain size and shape [9]. Positive ions, most commonly sodium, calcium, or potassium are added in order to balance the molecule [10].

The specific cation chosen influences the pore diameter and therefore the adsorptive properties of the molecular sieve. The sodium modified molecular sieve, with a pore diameter of ten angstroms will absorb those molecules with a critical diameter of less than 10 angstroms [11]. Eq. 1 show the chemical formula of the porous membranes selected as a filter media for the application described in this article.

\[
Na_xO.A1_2O_3.0.254SiO_2.xH_2O
\] (1)

Molecular sieves are suitable for drying, purifying, and separating a wide variety of compounds, such as inorganic gases, hydrocarbons, halogenated hydrocarbons, and sulphurous compounds. They are being used to adsorb, and temporarily isolate molecules. When loaded on a molecular sieve [12]. A saturated molecular sieve can be restored to its original capacity by regeneration, the principle of which involves changing the conditions surrounding the adsorbent to correspond to a very low equilibrium capacity. In general, the greater the difference between the equilibrium capacities of adsorption and regeneration, the more rapid and complete
the regeneration. The maximum regeneration temperature for Silica is approximately 300°C [12].

The type of media and general filter construction defines restriction and fuel flow through the active area of the filter media. The flow rate of diesel fuel system can be estimated by the following equation as described by Ensfield, (2002) [13].

\[
m_f = \frac{P_b \cdot 3600}{cV_l \cdot \eta_{en}}
\]

where

- \(P_b\) is brake power in kW
- \(m_f\) is fuel mass flow rate in kg/h.
- \(\eta_{en}\) is engine efficiency
- \(cV_l\) is the lower calorific value of the fuel in kg/kJ

This work investigates the possibility of using porous membranes for the removal of mercaptans in distilled rubber derived fuel.

II. METHOD

A. The Sample Characterisation

A representative sample of crude rubber fuel derived through a slow pyrolysis process was obtained from Pace fuels (Pty) Ltd in South Africa. Physical properties of the crude fuel were measured with reference to diesel fuel and presented in Table I. The crude fuel 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.

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

The temperature was raised to the desired range to distil and condense the light fractions from the crude rubber fuel at 150, 200 and 250°C. The properties of the three light fractions obtained are presented in table II.

B. Screening Tests

Samples of distilled rubber derived fuel were added into porous membranes in closed sample containers for 24 hours as shown in Fig. 3. A discoloration in both porous membranes and fuel were observed. A continuous fuel filtration system was developed to explore the effectiveness of single pass adsorption at various flow rates.

Fig. 3 Distilled rubber fuel undergoing molecular filtration

C. Continuous single pass filtration

An experimental set-up consisting of stainless steel filter housing tube packed with porous membranes connected to a vacuum system is shown in Fig. 4. Fuel samples of known initial sulphur content were passed through a layer of porous membranes at various flow rates. Diesel fuel, distilled rubber fuel and 50% vol. diesel-rubber fuel blends were passed over a porous layer of molecular sieves with a packing density of 853.41 kg/m³ and active filtration area of 0.13 m².

Each fuel sample was added into a sample container with a porous layer. Samples were collected every 30 seconds for 120 seconds. The same porous layer was re-used for filtration of diesel-rubber fuel blend and pure rubber fuel over the same time interval. It was observed that the majority of the sulphurous compounds in the fuels are removed during the first 30 seconds of contacting the fuel with the micro porous layer. The residence time for fuel contacting with the porous filter media and the final sulphur content were recorded. The results for these tests are presented in table IV.

Fig. 4 Experimental set-up for single pass filtration
III. RESULTS AND DISCUSSIONS

A. Fuel Characterisation

The distillates obtained at 250°C being the fractions that resemble diesel fuel underwent further treatment to reduce the residual sulphur compounds. The compounds that are distillable at 150 to 250°C are naphthas, at this temperature range sulphur is more easily removed because, lower boiling fuel fraction primarily contain sulphurous compounds that are in the form of mercaptans or lower member ring compounds which are relatively easier to de-sulphurise [14]. This is noticed by reduction in sulphur content from 9106 ppm to 7030 ppm when crude rubber fuel is distilled at 250°C. 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.

TABLE I

<table>
<thead>
<tr>
<th>Property</th>
<th>Crude Rubber Fuel</th>
<th>Diesel Fuel</th>
<th>SANS 342 Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gross Calorific Value (MJ/kg)</td>
<td>38.6</td>
<td>39.5</td>
<td>43.7</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>94</td>
<td>94</td>
<td>&gt;55</td>
</tr>
<tr>
<td>Viscosity @ 40°C (cSt)</td>
<td>9.4</td>
<td>2.6</td>
<td>2.2-5.3</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>3.54</td>
<td>0.05</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>Density @ 20°C (kg/m³)</td>
<td>926</td>
<td>831</td>
<td>800-950</td>
</tr>
<tr>
<td>Total Sulphur (ppm)</td>
<td>9106</td>
<td>498</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Total Contamination (mg/kg)</td>
<td>143</td>
<td>29</td>
<td>&lt;24</td>
</tr>
</tbody>
</table>

Fig. 2 shows images of rubber fuel distillates 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 24 mg/kg according to SANS 342, crude rubber fuel has a total contamination value of 6 times the acceptable contamination limit. In contrast, distilling the fuel does not only increase the calorific value of the fuel but it also reduces total contamination by 95%. Majority of liquids mercaptans in crude rubber fuel were mostly removed along with the moisture during the pre distillation stage.

TABLE II

<table>
<thead>
<tr>
<th>Property</th>
<th>150°C</th>
<th>200°C</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 20°C (kg/m³)</td>
<td>743</td>
<td>789</td>
<td>807</td>
</tr>
<tr>
<td>Viscosity @ 40°C (cSt)</td>
<td>0.8</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>26</td>
<td>35</td>
<td>43</td>
</tr>
<tr>
<td>Total Sulphur (ppm)</td>
<td>3.5</td>
<td>5.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Total Contamination (mg/kg)</td>
<td>6923</td>
<td>6984</td>
<td>7030</td>
</tr>
<tr>
<td>Water Content (%)</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Gross Calorific Value (MJ/kg)</td>
<td>38.6</td>
<td>39.5</td>
<td>43.7</td>
</tr>
</tbody>
</table>

B. Identification of Functional Groups

Analysis of the crude rubber fuel, diesel and selected distilled rubber fuel chemical composition were conducted using a Fourier Transform Infra-Red Spectroscopy (FTIR) to identify the functional groups present. Fig 5 shows specific functional groups present in both diesel fuel and rubber fuel distillates obtained at 250°C. The distilled rubber 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 [15]. 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 (NOx) emissions [16]. This will not be the case for distilled rubber fuel since the intensity of aromatic compounds present in the fuels is lower compared to diesel fuel as shown in Fig. 6. Other functional groups were identified in distilled rubber fuel which are not present in commercial diesel. These include carboxylic acids (O-H stretch) and ketones (C-C stretch).

Fig. 5 Common Functional Groups Identified in Distilled Rubber Fuel and Diesel Fuel

C. Continuous single pass filtration

Barth et al., 2004 [17] indicated that the average engine efficiency for heavy duty diesel trucks is about 47-49%. The maximum fuel flow through the ADE 407T truck engine to be used as a test model with technical specifications presented in Table III was estimated using Eq.2. The maximum fuel flow rate through this engine under extreme operating conditions is approximately 700ml/min. The packing density of the porous membranes is defined as a function of membrane pellet mass and its diameter, this relationship is represented by Eq. 3.

TABLE III

<table>
<thead>
<tr>
<th>Engine Technical Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine Owner:</td>
</tr>
<tr>
<td>Engine Type:</td>
</tr>
<tr>
<td>Aspiration</td>
</tr>
<tr>
<td>Operation</td>
</tr>
<tr>
<td>Dynamometer</td>
</tr>
<tr>
<td>Max Torque &amp; Power (kW):</td>
</tr>
<tr>
<td>Wet Mass(kg):</td>
</tr>
<tr>
<td>Bore/stroke(mm):</td>
</tr>
</tbody>
</table>


$$\partial \rho = \left( \frac{2.526\ m_i}{d_i^3 \cdot \pi} \right)$$  \hspace{1cm} (3)

$$\nu = \frac{0.14475 \cdot \pi \cdot l \cdot D_t^2}{n}$$  \hspace{1cm} (4)

$$n = \frac{0.6315 \cdot D_t^3 \cdot l}{d_i^3}$$  \hspace{1cm} (5)

$$\kappa = \frac{2.526 \cdot \pi \cdot l \cdot D_t^2}{d_i}$$  \hspace{1cm} (6)

$$t = \frac{1.00525 \cdot \pi \cdot l \cdot D_t^3}{\Phi}$$  \hspace{1cm} (7)

- **$\partial \rho$**: Packing density in (kg/m³)
- **$m_i$**: Average mass of porous membrane bead (kg)
- **$d_i$**: Average diameter of porous membrane bead (m)
- **$\nu$**: Voids volume between porous membranes (m³)
- **$n$**: Number of porous membrane beads
- **$l$**: Active length of filter media housing tube (m)
- **$\kappa$**: Active filtration area of filter media (m²)
- **$t$**: Fuel residence time (s)
- **$\Phi$**: Fuel flow rate (m³/s)
- **$D_t$**: Inside diameter of filter media housing tube (m)

The porous membranes with nominal pore sizes of 10 Åmstrong were obtained from Sigma Aldrich, South Africa. These spherical membranes were 3.2 mm diameter and 34.7 mg per pellet. The packing density of porous membranes in this study as shown in Table IV was calculated to be 853.41 kg/m³ using Eq. 3 for a given average membrane bead mass and diameters of 34.8 mg and 3.2 mm respectively. The voids volume and active surface area were 24.22 ml and 0.13 m² respectively. This was calculated using Eqs. 4 and 6 for a given tube length of 110 mm and inside diameter of 22 mm.

**TABLE IV**

<table>
<thead>
<tr>
<th>Fuel flow (m³/s)</th>
<th>Residence time (ms)</th>
<th>Sulphur removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0025</td>
<td>7.042</td>
<td>58.34%</td>
</tr>
<tr>
<td>0.0050</td>
<td>3.531</td>
<td>56.32%</td>
</tr>
<tr>
<td>0.0075</td>
<td>2.347</td>
<td>52.36%</td>
</tr>
<tr>
<td>0.0117</td>
<td>1.509</td>
<td>47.67%</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>3.6046</strong></td>
<td><strong>53.67%</strong></td>
</tr>
</tbody>
</table>

- **Filter media area(m²)**: 0.13
- **Flux(L/m².s)**: 50.494
- **Tube Volume (ml)**: 41.81
- **Void Volume (ml)**: 24.22
- **Number of membranes sieves**: 1025
- **Volume micro porous layer(ml)**: 17.6
- **Mass of porous layer(g)**: 35.685
- **Filter Media Packing Density(kg/m³)**: 853.41

**D. De-sulphurisation over porous membranes**

Since a fraction of mercaptans were removed from the fuel, the free sulphur remained in the fuel was reduced through adsorption over the porous membrane layer. Sulphur analysis on the fuel samples before and after molecular filtration indicated a 23.6% reduction in total sulphur. The porous membranes beads of 0.1 mm were used for adsorbing mercaptans and other sulphur compounds below 0.1 mm. Active surface area of each spherical porous bead is an important parameter ensuring that selected molecules such as mercaptans are adsorbed effectively. This is seen in Fig. 6 whereby 9.3%, 63% and 44.9% reduction is sulphur content was observed in diesel, diesel-rubber fuel blend and rubber fuel respectively. Further adsorption time does not seem to have any further effect on fuel de-sulphurisation. The selected membrane sieves have shown effective removal of specific molecular range of sulphur compounds. A 9.3% sulphur removal in diesel fuel was observed compared to higher sulphur reduction in high sulphur concentration fuels. Accumulations of the porous media have not been identified in these tests. All the fuels were passed through the same porous media without regeneration and the adsorption efficiencies during the first 30 seconds were consistent for pure distilled rubber fuel as shown in Fig.6.

**E. Filtration fluxes**

Eq. 5 was developed to estimate the number of beads required as a function of filter housing diameter, length and bead diameter. Eq. 7 describes the relationship between the filter media packing and fuel residence time. The filtration flux was computed as the fuel flow rate through a packed porous layer per unit active area. The experimental set-up presented in Fig. 4 has an average filtration flux of 50.495 l/m².s.

**IV. CONCLUSION**

The sulphur content in the fuel was reduced by 53.67% via a single pass molecular filtration using 13X molecular sieves. Adsorption of mercaptans and sulphur compounds occurs very rapidly over an active porous membrane layer. A significant amount of sulphur can be removed from the fuel stream at a rate of 50.49 l/m².h. The fuel properties of distilled fuel obtained at 250°C are nearly comparable to commercial diesel with high heating value of and low water content and total contamination. This work has also shown that the fuel 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 fuel 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 effect of packing density and voids between the membranes on the adsorption rate need to be investigated. Thermal reactivation of the membrane sieves for reuse and life span determination should be evaluated.

ACKNOWLEDGMENT

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REFERENCES