OXIDATIVE DESULFURIZATION OF TIRE PYROLYSIS OIL

Article Highlights
- Experimental investigation of oxidative desulfurization of tire pyrolysis oils
- Comparison of various additives is carried out for purification of pyrolysis oils
- Boiling range of fractions is determined for blending with other fuels

Abstract
This paper presents a low cost method for the purification of oils obtained from the pyrolysis of used tires. Oxidative desulfurization is a promising route for purification of tire pyrolysis oils as hydro-desulfurization may not be affordable for small scale industries. Different additives and acids have been employed for the enhancement of properties of pyrolytic oils. The experimental conditions were kept identical throughout, i.e., atmospheric pressure and 50 °C temperature for comparison of performance of various additives. The use of hydrogen peroxide-acetic acid mixture (10 wt.%) was found more economical and effective in desulfurization and improvement of fuel properties of sample oils. The contribution of sulfuric acid in desulfurization and decreasing viscosity was also satisfactory but due to the high price of concentrated sulfuric acid its use may not be economical. Calcium oxide and Fuller’s earth was not found to be effective in desulfurization. The results indicate that oxidative desulfurization could render tire pyrolysis oils suitable for blending as heating fuel.

Keywords: tire pyrolysis oils; pyrolysis fuels, desulfurization; oxidative desulfurization.

With growing population and industrialization, the production of solid waste is increasing daily. In developing countries, the disposal of solid waste is a challenging task. The traditional disposal techniques of dumping and burning used tires pose an environmental threat. The use of recently developed techniques presents a viable solution of scrap tires disposal in terms of energy production and environmental safety [1]. The increase in used tires is observed throughout the world. The annual generation of waste tires in North America has been estimated to be 2.5 million and 2 million t for the European Union [2].

The major part in tire composition is rubber, which is a chemically cross-linked polymer [3]. Apart from rubber, metal and textile components are also present in tire composition. Sulfur is also an important part of tire composition that acts as a cross-linking agent [4]. The cross-linked bonding dedicates mechanical strength to tires. This cross-linking of bonds makes recycling and reuse of used tires difficult. The elemental composition of scrap tires is shown in Table 1 [1,5].

Table 1. Composition (wt.%) of scrap tires [1,5]

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon</td>
<td>C</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>H</td>
</tr>
<tr>
<td>Ash</td>
<td>S</td>
</tr>
<tr>
<td>Moisture</td>
<td>N</td>
</tr>
<tr>
<td>GCV, MJ/kg</td>
<td>Others</td>
</tr>
</tbody>
</table>

Ucar et al. [5] observed that the composition of gaseous products from pyrolysis of different tires, passenger car tires and truck tires, were similar. The
pyrolytic oil obtained as liquid product usually lies between naphtha and diesel fraction. However, aromatic and sulfur content may vary depending on the polymer types in scrap tires.

In the past, use of scrap tires as a fuel was common due to its high calorific value. In heavy industries like cement scrap tires were used as a secondary fuel. Due to strict emission restrictions, burning of sulfur containing fluid in the environment have been limited. Open dumping was also an option of scrap tires disposal and about 65.5% of scrap tires used to be dumped in the open air or landfills [6]. Open dumping not only occupies a huge space but also provides a safe haven form germ growth. Moreover, open dumping also provides an opportunity for accidental fires. Recycling of solid wastes is a better option in the solid waste management system. Pyrolysis is one of the recycling techniques producing energy.

The pyrolysis process is carried out by thermal decomposition of scrap tires in the absence of oxygen in a reactor. During pyrolysis, the volatile component, which is mainly rubber, is decomposed and converted into vapours. The vapours are then condensed and separated into oil and gas. The liquid and gas thus produced can be used as a fuel or a source of chemicals.

This research work is focused on enhancing the poor fuel quality of pyrolytic oils by treatment with different additives and acids. The quality enhancement has been carried out in terms of desulfurization and improving other fuel properties. The available literature shows an enormous number of desulfurization techniques including alkylation to shift boiling point of fractions, adsorption, absorption, extraction, catalytic oxidation, oxidative desulfurization, and hydro-desulfurization [7,8]. Oxidative desulfurization is chosen as a low cost alternative technique to hydro-desulfurization, which is well established for desulfurization of petroleum fractions [7].

In this study, the post pyrolysis desulfurization of pyrolytic oils is investigated. Additives and acids have been tested for purification and desulfurization of pyrolytic oils. The distillation along with other critical fuel properties has been investigated. The distillation reveals the availability of petroleum fraction in the liquid oils.

Previous work on pyrolysis of scrap tires

The tire composition can be broadly divided into organic material and inorganic material. The organic material of tire is mainly composed of volatile rubber (58.8 wt.%) and non-volatile carbon blacks (27.7 wt.%) while the main inorganic compound is steel (9.6 wt.%) [3]. Natural rubber (NR), styrene butadiene rubber (SBR) and butadiene rubber (BR) are the main components of rubber tires while moisture, plasticizers and additives are minor components. Prior to carrying out pyrolysis, the analysis of used tires in terms of its composition is of utmost importance. Generally, the tire is composed of elastomers (natural or synthetic rubber), reinforcing agent (carbon black), accelerating agents, plasticizers (hydrocarbon oil), vulcanizing agent (sulfur and sulfur compounds). These constituents vary in proportion according to the types and application of tires [9].

The wide range of applications of pyrolysis products has stimulated research on the pyrolysis of scrap tires for the last few decades. Rodriguez et al. [3] carried out pyrolysis of tire pieces (2-3 mm) in nitrogen atmosphere at different temperatures, ranging from 300 to 700 °C in an autoclave reactor. The system was heated at 15 °C/min heating rate and was kept for 30 min at the pyrolysis temperature. It was found that after 30 min of heating, pyrolysis reactions are complete and products formation stops [3]. Pyrolysis of scrap tires with different heating rates indicates that thermal decomposition occurs in the range of 290-550 °C [10-13]. The pyrolysis of scrap tires produces oil, gas and solid residue as pyrolysis products. The high calorific value of gas can be utilized as energy requirement for the pyrolysis process [14,15]. The char obtained as solid residue can be used as activated carbon or carbon black [16]. The oil fraction collected by condensing pyrolysis vapours has a large number of applications because of its ability to be stored and transported anywhere easily [17,18].

Rodriguez et al. [3] found that C/H ratio of TPO is about 1.4, which indicates the presence of aromatic and aliphatic hydrocarbons in pyrolytic oils. The presence of aromatic and aliphatic compounds is due to the styrene butadiene rubber (SBR). The sulfur content was found to be similar to light fuel oil. The most prominent effect on the composition of oil is that of temperature. At lower temperatures the yield of aromatics is higher, while at higher temperatures aromatics are found to be in higher amounts [2]. It may also be observed from previous literature that the yield of gas, liquid, and solid residue by pyrolysis of scrap tires may vary depending on the operating conditions as well as the processing technology. For example, pyrolytic oil yield (wt.%) varies in the range of 43-65% in fluidised bed reactors [19-21], 57-60% in fixed bed reactors [22] and 44-64% in spouted bed reactors [23,24].
Desulfurization and distillation of tire pyrolysis oils

The desulfurization of any sulfur-containing fuel is important for many reasons. Emission of combustion products of sulfur-containing fuel into the atmosphere has been proven as disastrous for the environment. The research in desulfurization has helped in developing different approaches and techniques such as hydro-desulfurization, bio-desulfurization, selective adsorption, and oxidative desulfurization [7,25,26]. These techniques can further be classified on the basis of operating conditions or desulfurizing agents.

In oil refineries, hydro-desulfurization has been adopted for the desulfurization of petroleum products. In the hydro-desulfurization process, in the presence of catalyst, at high temperature (350-450 °C) and pressure, the desulfurization reactions take place. Due to severe operating conditions and utilization of expensive catalysts in hydro-desulfurization, oxidative desulfurization may be preferred now for tire pyrolysis oils [7]. The oxidative desulfurization reactions are carried out at mild operating conditions. In oxidative desulfurization, the sulfur-containing compounds of fuel oils are converted into their respective sulfoxides and then sulfones [7]. These compounds are polar which can be removed by extraction, or adsorption [7,25,27]. To remove the soot, aromatics, and sulfur of fuel oils, sulfuric acid can be employed. Eterigho et al. [28] employed sulfuric acid and sodium hydroxide for quality improvement of fuel oils. The viscosity and total sulfur content was found to be decreasing while an increase of flash point was reported. Oxidative desulfurization has been investigated in various experimental studies employing formic acid and hydrogen peroxide [7,13,29], sulfuric acid [30], acetic acid and hydrogen peroxide [13,31].

Rodriguez et al. [3] performed distillation of pyrolytic oils and observed that 30% of the oils were easily distilled in the boiling point range of 70 to 210 °C, which is the boiling point range specified for commercial gasoline. 60% of the oils were distillable in the boiling point range of 150 to 370 °C [3]. Arpa et al. [32] performed pyrolytic distillation experiments to convert waste lubricating engine oil into diesel like fuel. Al-Lal et al. [7] demonstrated experimentally that the sulfur content of light, intermediate, and heavy fractions of pyrolytic oils varies increasing with the density of oil fraction.

MATERIALS AND METHOD

The chemicals used in experimentation were concentrated sulfuric acid (98%), acetic acid, hydrogen peroxide, and calcium oxide purchased from Merck, and Fuller’s earth. Samples of pyrolytic oils were collected from tire pyrolysis plant. The plant is operational at Hayatabad Industrial Estate, Peshawar, Pakistan. Table 2 presents properties of the pyrolytic oil sample in comparison with petroleum fractions.

Additives, H₂SO₄, H₂O₂-CH₃COOH (mole ratio 1:2), Fuller’s earth and CaOH, were added in amounts 5, 10 and 15 wt.% to react with sulfur containing compounds in a beaker with magnetic stirring at 50 °C and atmospheric pressure for one hour. The reaction products were allowed to settle for 8 h and the residue was separated from the upper light clean pyrolytic oil.

The clean pyrolytic oils were tested for sulfur content and other fuel properties for comparison with diesel and gasoline specifications. The determination of sulfur content was carried out in equipment based on ASTM 1552. The testing was performed at Attock Refinery Limited, Pakistan. In order to find the amounts of diesel and gasoline like fractions, distillation of pyrolytic oils was carried out according to ASTM D-93.

RESULTS AND DISCUSSION

Pyrolytic oils obtained from the pyrolysis of scrap tires contain high amounts of sulfur due to the fact that sulfur is used for strengthening in tire manufacturing process. The removal of sulfur was tested with different additives and acids at the same mild operating conditions via oxidative desulfurization. The impact of sulfuric acid, combination of hydrogen peroxide and acetic acid, Fuller’s earth and CaO as

Table 2. Properties of pyrolytic oil sample in comparison with petroleum fractions; HSD: high speed diesel, LDO: light diesel oil, FFO: furnace fuel oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Specific gr@ 15.6/15.6 °C</th>
<th>Sulfur, total, mass%</th>
<th>Pour point, °C</th>
<th>Flash point, PMCC, °C</th>
<th>Kin. viscosity at 37.8 °C, cSt</th>
<th>Gross calorific value, Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
<td>ASTM-D1298</td>
<td>ASTM-D4294</td>
<td>ASTM-D97</td>
<td>ASTM-D93</td>
<td>ASTM-D445</td>
<td>ASTM-D4868</td>
</tr>
<tr>
<td>Sample</td>
<td>0.94</td>
<td>0.96</td>
<td>&lt;18</td>
<td>24</td>
<td>1.56</td>
<td>19359</td>
</tr>
<tr>
<td>HSD</td>
<td>0.84-0.850</td>
<td>1.0 max.</td>
<td>0.20-0.35</td>
<td>9 max.</td>
<td>0-6</td>
<td>54 min.</td>
</tr>
<tr>
<td>LDO</td>
<td>0.920 max.</td>
<td>0.875-0.890</td>
<td>1.80 max.</td>
<td>-</td>
<td>14 max.</td>
<td>0-6</td>
</tr>
<tr>
<td>FFO</td>
<td>0.970 max.</td>
<td>0.936-0.945</td>
<td>3.5 max.</td>
<td>0.90-1.2</td>
<td>24 max.</td>
<td>21-24</td>
</tr>
</tbody>
</table>
The effect of additives on sulfur content is shown in Figure 1. It may be observed from Figure 1 that the sulfur content of pyrolytic oils decreased with increasing amount of sulfuric acid. The maximum desulfurization achieved by treatment with 15 wt.% sulfuric acid was 35% corresponding to 0.63 wt.% sulfur in treated oil. Sulfur content also decreased with increasing H$_2$O$_2$-CH$_3$COOH, with maximum desulfurization 50% corresponding to 0.5 wt.% sulfur in treated oil. The desulfurization ability of H$_2$O$_2$-CH$_3$COOH, reported by [13,29] is in agreement with these findings. Fuller’s earth is a clay-like material made from aluminum silicate. It can be used as deodorizing agent, decolorizing agent and absorbent in purification of waste oils. In this research work Fuller’s earth was also tested for purification and desulfurization of pyrolytic oils. It may be observed that Fuller’s earth did not contribute towards desulfurization of pyrolytic oils, as shown in Figure 1. The efficacy of CaO on quality improvement of pyrolytic oils is also shown in Figure 1, resulting in a maximum of 20% desulfurization corresponding to 0.77 wt.% sulfur in treated oil. The marginal desulfurization ability of CaO is mainly attributed to the mild operating conditions, and may be enhanced by using it at high temperatures during pyrolysis, as reported in the literature [13]. It may be worthwhile to mention that oxidative desulfurization can be improved by subsequent treatment of reactor effluent either by extraction with a polar solvent such as methanol or through adsorption by a polar adsorbent such as silica gel or alumina as demonstrated by Al-Lat et al. [7]. Such post-treatment has been shown to increase desulfurization up to 75% [7].

The effect of treatment with additives, on kinematic viscosity of tire pyrolysis oils is shown in Figure 2. The viscosity was found decreasing with increasing amount of H$_2$SO$_4$. The optimum percentage of viscosity decrease was found with 10 wt.% use of H$_2$SO$_4$ corresponding to 1.08 cSt of product oil. The decrease in viscosity is due to the removal of aromatic compounds. This tendency of decreasing viscosity with H$_2$SO$_4$ is endorsed by the research work carried out by [28,33]. The impact of H$_2$O$_2$-CH$_3$COOH was also observed in altering the viscosity of the pyrolytic oils as shown in Figure 2. The decrease in viscosity, i.e., from 1.56 to 1.12 cSt, was noted with increasing amount of H$_2$O$_2$-CH$_3$COOH mixture. This impact of H$_2$O$_2$-CH$_3$COOH mixture on viscosity is in agreement with literature [28,33]. The main concern about using the Fuller’s earth in treatment of pyrolytic oils was its negative impact on viscosity. The addition of Fuller’s earth caused an increase in viscosity from 1.56 cSt of sample oil to 1.87 cSt of product oil. The reason for this increase in viscosity is attributed to the poor settling of effluent not resulting in separation of light hydrocarbon oil from sludge. A similar trend may also be observed for treatment with calcium oxide, as shown in Figure 2. To assure efficient mixing of fuel/air in engines, oils of lower viscosity are preferred.

To measure the quality and quantity of diesel and gasoline fractions of pyrolytic oils, distillation was carried out. Table 3 shows the temperature profile...
against volume fraction for pyrolytic oil sample and product oil after treatment with hydrogen peroxide and acetic acid.

Comparing the gasoline boiling temperature range 70-210 °C with distillation temperatures of pyrolytic oils shows that about 30% of pyrolytic oil is composed of fraction similar to commercial gasoline. This finding is in agreement with the literature [3]. Comparing the distillation temperatures of pyrolytic oil and oxidized pyrolytic oil (treated with hydrogen peroxide and acetic acid), it may be noted that there is little difference in distillation behavior of the two. This unique behavior of pyrolytic oils is endorsed by a previous study [33].

CONCLUSIONS

This paper presents an experimental investigation of treatment of tire pyrolysis oils with various additives employing oxidative desulfurization. All desulfurization experiments were carried out at mild operating conditions (atmospheric pressure, 50 °C temperature), with a reaction time of one hour, and settling time of 8 h. For oxidative desulfurization, the use of 15 wt.% H₂O₂-CH₃COOH mixture (mole ratio 1:2) was found to be suitable on the basis of low cost and higher desulfurization, i.e., 50% corresponding to 0.5 wt.% sulfur in treated oil compared to sulfuric acid, Fuller’s earth and calcium hydroxide at mild operating conditions. The proposed desulfurization technique may render tire pyrolysis oil suitable for blending in heating fuels. For further desulfurization post-treatment in the form of extraction or adsorption may be carried out. In addition to desulfurization, H₂O₂-CH₃COOH combination was also found to be helpful in decreasing the viscosity, which is desirable for smooth fluidity and better atomization of pyrolytic oils. The use of CaO as a desulfurizing agent was not found to be satisfactory in treatment of pyrolytic oil samples. Although CaO has been reported frequently, for desulfurization, however its inability in the present research work is attributed to mild operating conditions.

Acknowledgements

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REFERENCES

Ovdje je jeftina metoda za prečišćavanje ulja dobijenih pirolizom korišćenih pneumatika. Oksidaciono odsumporavanje je obećavajući način za prečišćavanje pirolitičkog ulja otpadnih pneumatika pošto hidro-odsumporavanje nije pogodno za mali kapacitet. Različiti aditivi i kiseline se koriste za poboljšanje svojstava pirolitičkog ulja. U cilju poređenja efekata različitih aditiva svi eksperimenti su izvedeni na atmosferskom pritisku i 50 °C. Utvrđeno je da je korišćenje smešte vodonik peroksida i sirćetne kiseline (10%) za odsumporavanje i poboljšanje gorivih svojstava uzorka ulja pekonomičnije i efikasnije. Doprinos sumporne kiseline odsumporavanju i smanjenju viskoznosti je takođe zadovoljavajući, ali zbog visoke cene koncentrovanih sumporne kiseline njegov upotreba ne može biti ekonomičan. Utvrđeno je da kalcijum oksid i Fulerova zemlja nisu efikasni u odsumporavanju. Rezultati pokazuju da oksidaciono odsumporavanje može učiniti pirolitičko ulje otpadnih pneumatika pogodnim za mešanje kao gorivo za grejanje.

Ključne reči: pirolitičko ulje otpadnih pneumatika, pirolitička goriva, odsumporavanje, oksidaciono odsumporavanje.