COMPATIBILITY OF FAST PYROLYSIS BIO-OIL/BIOETHANOL BLENDS WITH PLASTIC POLYMERS

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EXTENDED ABSTRACT

Fast pyrolysis allows the transformation of lignocellulosic biomass into a liquid bio-oil (BO). The combustion behavior of this fuel can be improved by blending with ethanol, methanol, biodiesel and other conventional fuels. This paper provides a comprehensive characterization of the chemical, physical and fuel properties of a fast pyrolysis bio-oil produced from pine wood using a spouted bed reactor. The following parameters were determined using standard procedures: viscosity at 40 °C; acid and base numbers; water content; elemental analysis; carbon residue; corrosiveness to copper; flash, fire and pour points; relative density; higher and lower heat of combustion; and thermogravimetric analysis. Similar analyses were performed on conventional fossil (diesel) and non-fossil (barley bioethanol) fuels for comparative purposes. Static immersion tests (70 °C over 168, 336, 504, 672 hours) were performed according to standard method UNE EN 53510 to evaluate the compatibility of various synthetic polymers (PE, PP, PVC, Viton and SBR) upon exposure to bio-oil/bioethanol (75/25 and 50/50, v/v) blends. Similar compatibility tests were performed on conventional diesel for comparative purposes. The degradation of the polymers under investigation was determined through characterization of their physical properties (breaking strength; elongation; hardness (ASTM D751 and ASTM D2240). The results evidence the unconventional fuel properties of the bio-oil, which has been attributed to its chemical nature (containing high concentration of oxygenated compounds) and high water content. Materials compatibility analyses describe changes in the mechanical properties of all synthetic polymers when submerged in bio-oil/bioethanol mixtures. The results suggest that not all mechanical properties in the polymers are degraded to the same extent upon exposure to the fuels under investigation. The following conclusions were reached: the hardness of synthetic plastics (PP, PVC, PE) was not affected when they were exposed to bio-oil/bioethanol blends and diesel. The hardness of elastomers (mainly SBR but also Viton) was affected after long exposure periods to bio-oil blends. In contrast, exposure of elastomers to bio-oil blends had a limited effect on breaking strength and elongation capacity of the elastomers. The resistance to degradation of breaking strength and elongation properties in the case of plastic polymers followed the following order: PE > PVC > PP.

Keywords: biomass, pyrolysis, bio-oil, compatibility, plastics, polymers.

1. INTRODUCTION

It is widely recognized that the use of biomass derived fuels can significantly reduce our dependence on fossil resources and help reduce environmental pollution. However, the use of raw biomass resources for energy purposes encounters technical, environmental and economic problems associated with the solid nature of the material, its low energy
density and its poor combustion properties (IEA, 2012). There is growing commercial interest in the development of technologies capable of transforming raw biomass feedstocks into liquid products with improved fuel properties. The industrial production of bio-diesel from vegetable oils and animal fats and the generation of bioethanol from carbohydrate containing crops for automotive consumption is a widely established business. Another alternative receiving increasing attention involves fast pyrolysis, which allows the transformation of lignocellulosic biomass into bio-oil (BO) with yields typically ranging between 65-75 wt% (Mohan et al., 2006; Venderbosch and Prins, 2010; Bridgwater, 2012; San Miguel et al., 2012). Fast pyrolysis bio-oil has chemical and fuel properties that are distinct from those of conventional biomass and petroleum derived fuels. This fuel is described in the literature as a micro-emulsion consisting of an aqueous phase containing lighter oxygenated organic compounds and a non-aqueous phase containing heavier water insoluble aromatic compounds (Oasmaa et al., 2010). The yields and specific properties of the bio-oil are defined by the nature of the biomass feedstock, the pyrolysis technology and the processing conditions employed.

The commercial utilization of alternative liquid fuels requires a profound understanding of their compatibility with materials that come into contact with them during storage, transportation and energy conversion. These materials usually include ferrous (steel, cast irons) and non-ferrous (aluminum, copper) alloys and also synthetic and natural polymers employed in the construction of tanks, pumps, pressure vessels, injectors, burners, valves, filters, combustion chambers, hoses and gaskets (Haseeb et al., 2011). Metallic elements may undergo corrosion (chemical/ electrochemical attack) and wear upon exposure to the fuels. Polymeric materials like plastics and elastomers can undergo chemical degradation, which results in deterioration of their mechanical properties. It has been described that, due to their chemical composition, this deleterious effect is more intense in the case of biological fuels. A number of papers have been dedicated to investigate the compatibility of bio-diesel, bioethanol (and also their blends with fossil fuels) with metals (Fazal et al., 2010 and 2011; Maru et al., 2010) and elastomers (Frame and McCormick, 2005; Flitney, 2007; Trakarnpruk and Porrntangjitlikit, 2008; Haseeb et al., 2010; Berlanga-Labari et al., 2011). The tests typically involve submersion in the fuels of the materials under controlled experimental conditions, followed by investigation of their mechanical properties (hardness; tensile strength; elongation; swelling, etc). In general, the experimental results suggest that some common elastomers (NBR, SBR, neoprene, nylon 6/6) undergo rapid degradation upon exposure to biomass derived fuels while others (PTFE, Viton® 401-C, Viton® GFLT) show better resistance. The compatibility of conventional biofuels with plastic and natural polymers has been studied less extensively, although results appear to show that polyethylene (PE), polypropylene (PP) and corrugated fiberboard are not compatible with biodiesel (Maru et al., 2009; USDOE, 2006).

Despite the fact that it may represent one of the key obstacles to the commercial production and utilization of pyrolysis bio-oil, very few publications include information about the materials compatibility of this alternative fuel (Oasmaa and Peacocke, 2010). The information analyzed in some papers is based on rather old and hard to access publications that describe experimental work not based on standardized procedures (Kirk et al. 2001, Oasmaa et al. 1997, Jay et al., 1995; Czernik 1994). Some of the conclusions exposed in these publications are contradictory, which may be due to differences in the type of bio-oil investigated and/or the experimental methodology employed. The information suggests that fluorinated polymers (PTFE) are more resistant to bio-oil than conventional PE, while the mechanical properties of PP are highly affected upon exposure to this fuel. Opposing conclusions have been published regarding the degradation of standard (NBR, EPDM) and fluorinated (Viton) elastomers upon exposure to fast pyrolysis bio-oil (Jay et al. 1995; Kirk et al., 2001; Oasmaa and Peacocke, 2010).
The commercial use of fast pyrolysis bio-oil in standard energy systems is negatively affected by its chemical and thermal instability, and also by its poor combustion properties compared to conventional liquid fuels (Lopez and Salva, 2000; Bridgewater, 2012). Blending the bio-oil with alcohols has been proven to improve the fuel properties in terms of acidity, corrosiveness, volatility, ignition temperature, heating value and energy density (Diebold, 2000; Chiaramonti et al., 2007; Boucher et al., 2000; Garcia-Perez et al., 2010). Hence, utilization of bio-oil blended with conventional liquid fuels is likely to have an easier penetration into the energy market than in its pure form.

The aim of this paper is to investigate the compatibility of fast pyrolysis bio-oil blended with bioethanol with common plastics and elastomers widely used in energy systems. For this purpose, bio-oil, bioethanol and petrodiesel were characterized for their chemical, physical and fuel properties. Standard compatibility tests were performed to evaluate the degradation of physical properties in various synthetic polymers upon exposure to bio-oil blended with different proportions (25 and 50 wt%) of bioethanol. Similar compatibility tests were performed on conventional petrodiesel for comparative purposes. The materials investigated include the following synthetic plastics and elastomers: High Density Polyethylene (HDPE), Polypropylene (PP), Polyvinyl chloride (PVC), Styrene Butadiene Rubber (SBR) and Viton® elastomer.

2. MATERIALS AND METHODS

2.1. Fuel characterisation
The bio-oil investigated was produced from pine wood using a 25 kg/hour demonstration scale reactor based on spouted bed technology (Fernandez-Akarregi et al., 2013). The production temperature was 480 °C and the oil yield 65.8%. In order to minimize changes in its properties, the bio-oil was stored at 4 °C and all tests were completed within 3 months since its production. The bioethanol was produced from barley at Biocombustibles CLM - Acciona (Santa Olalla, Toledo, Spain). The petrodiesel was supplied by Repsol (Spain).

The properties of the fuels were determined according to the following standard methods: viscosity at 40 °C (ASTM D445); acid number (ASTM D974); base number (ASTM D2896); water content (UNE EN 12937); elemental analysis (ASTM D5291); carbon residue (ASTM D4530); corrosiveness to copper (ASTM D130); anti-rust properties (ASTM D665); flash point and fire point (ASTM D92); pour point (ASTM D97); relative density (ASTM D4052); higher and lower heat of combustion (ASTM D240). All tests were performed at least in duplicates. The thermal properties of the bio-oil were investigated using thermogravimetric analysis (TGA) under inert (nitrogen) and oxidizing (air) atmospheric conditions. The bio-oil (30 mg) was heated at 10 °C/min under 75 ml/min of purge gas.

2.2. Materials compatibility tests
Compatibility tests were performed according to standard method UNE EN 53510. The fuels investigated include two bio-oil /bioethanol blends, referred to as BO75 (75/25 v/v %) and BO50 (50/50 v/v %). Similar compatibility tests were performed on conventional petrodiesel (PD) for comparative purposes. The materials investigated include five synthetic polymers widely used in fuel systems. These include three synthetic plastics: High Density Polyethylene (HDPE); Polypropylene (PP); Polyvinyl Chloride (PVC); and two synthetic elastomers: Styrene Butadiene Rubber (SBR) and Viton®. The polymers were supplied in sheets of size 1.5 m × 2 m × 2.0 mm, from which test stripes of standard size and shape were produced.
UNE EN 53510 involves static immersion tests of the standard test stripes in 80 ml of the fuel under investigation. The tests were conducted in stainless steel (SS316) reactors under constant temperature (70 °C) and autogenic conditions. Test stripes were removed from the reactors after certain periods of time (168, 336, 504, 672 hours), washed in liquid detergent diluted in distilled water and dried at room temperature. Degradation of the polymers was investigated by measuring strain stress and hardness in the test stripes. Strain stress was characterized in terms of breaking strength (N) and elongation (%) according to standard method ASTM D751 using an Instrom Series 3365 (200 mm/min). Hardness was determined according to standard method ASTM D2240 using a Hildebrand MACRO IRHD-2 Type A Shore Durometer. Each analysis was conducted in triplicate and the results reported represent the mean value.

3. RESULTS AND DISCUSSIONS.

3.1. Characterization of fuels
The bio-oil employed in this work had a homogeneous appearance, and exhibited a dark brown color and a pungent smoky odor. Table 1 shows the fuel characteristics of this material and two other fuels widely used for transportation. The results show notable differences between the three fuels in most parameters, which may be associated with the chemical nature of the fuels. Bioethanol is essentially a pure substance of molecular composition \( \text{C}_2\text{H}_5\text{OH} \), while petrodiesel consists of a mixture of aliphatic, olefinic and aromatic hydrocarbons of molecular size ranging between \( \text{C}_9-\text{C}_{25} \). In contrast, the bio-oil is usually described as a micro-emulsion of an aqueous phase containing lighter oxygenated organic compounds and a non-aqueous phase containing heavier water insoluble aromatic compounds (Oasmaa et al., 2010).

<table>
<thead>
<tr>
<th></th>
<th>Pyrolysis bio-oil</th>
<th>Bioethanol</th>
<th>Petrodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher heating value (kJ/kg)</td>
<td>19600</td>
<td>29670</td>
<td>45605</td>
</tr>
<tr>
<td>Lower heating value (kJ/kg)</td>
<td>15630</td>
<td>26810</td>
<td>42925</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>124</td>
<td>16.6</td>
<td>69</td>
</tr>
<tr>
<td>Elemental analysis (dafb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>47.4</td>
<td>52.2</td>
<td>85.8</td>
</tr>
<tr>
<td>H</td>
<td>11.5</td>
<td>13.1</td>
<td>23.0</td>
</tr>
<tr>
<td>N</td>
<td>0.40</td>
<td>-</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>S</td>
<td>0.01</td>
<td>-</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>O</td>
<td>40.9</td>
<td>34.7</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Water content (wt %)</td>
<td>29.8</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>TAN (mg KOH/g sample)</td>
<td>12.3</td>
<td>-</td>
<td>undetected</td>
</tr>
<tr>
<td>TBN (mg KOH/g sample)</td>
<td>6.1</td>
<td>-</td>
<td>undetected</td>
</tr>
<tr>
<td>Carbon residue (g)</td>
<td>0.02</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>Corrosiveness to copper</td>
<td>light (1a)</td>
<td>-</td>
<td>1a</td>
</tr>
<tr>
<td>Rust-Preventing</td>
<td>light</td>
<td>-</td>
<td>undetected</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-17</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Density (kg/dm3)</td>
<td>1.16</td>
<td>0.794</td>
<td>0.830</td>
</tr>
<tr>
<td>Viscosity (mm2/sg)</td>
<td>14.7</td>
<td>1.52</td>
<td>2.68</td>
</tr>
</tbody>
</table>

daafb = dry ash free basis

The reduced heating values (HHV and LHV) and high flash point exhibited by the bio-oil may be attributed to its high oxygen (40.9 wt %) and water content (29.8 wt %). The bio-oil also exhibited significantly higher mass density, viscosity, and TAN and TBN values.
than the other two fuels analyzed. The high TAN and TBN values have been related to the high concentration of carboxylic acids, aldehydes and other acidic compounds.

The thermal behavior of the fast pyrolysis bio-oil is shown in Figure 1. The results show an area of weight loss at temperatures up to 400 °C, attributable to progressive devolatilization of the fuel components. Weight loss at that temperature represents around 74 wt % of the original mass. The oxidizing effect of oxygen is evidenced at temperatures between 400 and 600 °C, resulting in complete combustion of the carbonized residue. When heating was conducted under inert atmospheric conditions, the residue at 600 °C still represented 15.4 wt% of the original mass, which looked like a tar. Heating up to 800 °C resulted in progressive volatilization of this material.

3.2. Compatibility tests
Test stripes exposed to the fuels under investigation were analyzed to determine degradation of their physical properties. The graphs describe the evolution in specific physical properties (breaking strength; elongation; hardness) as a result of increasing exposure time to the fuel. Values registered as zero (0 min) of exposure time represent the physical properties of the polymer as received.

3.2.1. Stress strain tests
The results in Figure 2 illustrate that the plastic polymers (mainly PVC and PP) exhibited comparatively higher resistance to rupture (around 350 N) than the elastomers (SBR and Viton). In contrast, Figure 3 shows that the elastomers exhibited a higher elongation capacity (up to 286 % in SBR) prior to rupture than the plastic polymers (8 % in PP).

The results in Figures 2 and 3 showed that PP was not significantly affected by exposure to diesel. However, the breaking strength and, most importantly, the elongation capacity upon stress increased dramatically upon exposure to bio-oil blends. This means that PP became highly ductile. In contrast, PE was not affected in terms of resistance to rupture (stress) when exposed to bio-oil blends but some changes were observed in terms of elongation capacity. Exposure to bio-oil mixtures had a very limited effect on the stress strain capacity of the two elastomers investigated: SBR and Viton. Resistance to rupture and elongation capacity remained constant even after very prolonged contact times.

Figure 1: Thermogravimetric analysis of fast pyrolysis bio-oil under oxidizing (left) and inert atmospheric conditions.
Figure 2: Breaking strength of synthetic polymers exposed to bio-oil/bioethanol blends (BO50, BO75) and conventional petrodiesel (PDiesel) over different time periods.

Figure 3: Elongation tests of synthetic polymers exposed to bio-oil/bioethanol blends (BO50, BO75) and conventional petrodiesel (PDiesel) over different time periods.

3.2.2. Hardness tests
Hardness describes the resistance of the material to permanent shape changes when a force is applied. The results in Figure 4 show that hardness values of some polymeric plastics (PE, PP) remained largely unaffected upon exposure to bio-oil/bioethanol mixtures. Some changes were observed in the case of PVC, primarily when exposed over very long time periods (15% hardness reduction after 672 hours). Similar results were observed in the case of petrodiesel for the three plastic materials.
In contrast, exposure to bio-oil mixtures had a more noticeable effect on the hardness properties of the elastomers (SBR and Viton), primarily after exposure times above 400 minutes. For instance, the hardness of SBR and Viton after exposure to BO50 over 672 hours had been reduced by 45% and 33%, respectively. No significant differences were observed in the deleterious capacity of bio-oil blends with different proportions of bioethanol (BO50 and BO75). The only material that was affected by exposure to conventional diesel (PDiesel) was Viton. The other materials were largely unaffected.

4. CONCLUSIONS
- The properties of fast pyrolysis bio-oil differ significantly from those of conventional liquid fuels, which is attributed to high water content and high concentration of oxygenated species.
- Materials compatibility tests describe that the mechanical properties of synthetic polymers are degraded to very different extents upon exposure to the fuels under investigation.
- The hardness of synthetic plastics (PP, PVC, PE) was not affected when they were exposed to bio-oil/bioethanol blends and diesel. However, breaking strength and elongation values where highly affected according to the following order: PE > PVC > PP.
- The hardness of elastomers (mainly SBR but also Viton) was reduced significantly after long exposure to bio-oil blends. In contrast, exposure of elastomers to bio-oil blends had a limited effect on breaking strength and elongation capacity of the elastomers.

ACKNOWLEDGEMENTS
The authors are grateful to the Spanish Ministry for Science and Innovation (Ministerio de Ciencia e Innovación-MICINN) for economic support under Plan Nacional (INNPACTO). We are also grateful to Ikerlan IK4 for supplying the fast pyrolysis bio-oil employed.

REFERENCES
Bridgwater A.V. Upgrading biomass fast pyrolysis liquids, Environmental Progress & Sustainable Energy, 31 (2); (2012); 261–268

Chiaromonti D., Oasmaa A., Solantausta Y. Power generation using fast pyrolysis liquids from biomass, Renewable and Sustainable Energy Reviews, 11 (6); (2007); 1056-1086


Fazal M.A., Haseeb A.S.M.A., Masjuki H.H. Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. Fuel Processing Technology, 91; (2010); 1308-1315


Flitney B. Which elastomer seal materials are suitable for use in biofuels? Seal Technology, (2007); 8-11


Trakarnpruk W., Pornthongjitkit S. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renewable Energy 33; (2008); 1558-1563
