PRODUCTION OF TRANSPORTATION FUELS RANGE HYDROCARBONS FROM PYROLYSIS OIL VIA A LOW HYDROGEN CATALYTIC DEOXYGENATION

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Abstract:

Biomass derived fast pyrolysis oil is a potential alternative replacement for conventional fuels. But the negative properties such as lower energy density, higher water content and acidity prevent the direct use of pyrolysis oil as a fuel. Conversion of pyrolysis oil to hydrocarbons has been successfully performed by deoxygenation with hydroprocessing catalysis with high heat and pressure. However, rapid deactivation of the catalysts and consumption of a large amount of expensive hydrogen have remained a problem for this technology and have prevented commercialization. Therefore, development of an efficient and reduced hydrogen deoxygenation method would be desirable. In this study, we have developed recently a bio-oil pretreatment method patent pending by oxidation to produce an acidified product. This pretreatment of raw bio-oil process allowed to performance of partial deoxygenation step with a low amount of hydrogen during the hydroprocessing of bio-oil. This partially deoxygenated product was then fully deoxygenated with pure hydrogen to produce mixed hydrocarbons. Properties of the resultant hydrocarbon fuels were analyzed by ASTM standards for transportation fuels. The hydrocarbon mixture obtained by our process was analyzed by gas chromatography mass spectroscopy (GC-MS) to identify all compounds in the fuel. Detailed hydrocarbon analysis (DHA) was performed to provide the carbon numbers associated with the hydrocarbons. Simulated distillation was performed to analyze the gasoline, jet fuel and diesel fractions comprising the hydrocarbon mixture.

Keywords: Pyrolysis oil, oxidation, deoxygenation, hydroprocessing, GC-MS and DHA.

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Biography:

Sathishkumar Tanneru is a graduate student in the Department of Forest Products at Mississippi State University. He graduated with a B.Sc in Industrial Chemistry from Kakatiya University and M.Sc in Organic Chemistry from Osmania University, India. He worked as a Research Assistant in the Natural Products Research Laboratory, India. Currently, he is working in Dr. Philip H. Steele research in bio-oil group as a Graduate Research Assistant.

Introduction:

Fast pyrolysis is one of the known and efficient methods for producing bio-oil from biomass. Fast pyrolysis includes heating the biomass at elevated temperatures of in the range of 400 to 550°C in the absence of oxygen. Bio-oil may also be produced by slow pyrolysis, liquefaction or other alternative method. Regardless of the method utilized for its production bio-oils share some similar characteristics. More specifically, bio-oil is a dark brown liquid with pungent phenolic odor; bio-oil chemical properties vary with material utilized for its production or the conditions under which it is produced [Bridgwater et al. 1999, Mohan et al. 2006]. It has environmental advantages when compared to fossil fuels because, when burned, bio-oil produces less pollution than fossil fuels, specifically, half the NOx, negligible quantities of SOx emissions and it is CO2 neutral [Mckendry 2002, Huber et al. 2006]. However, there are still some disadvantages with using untreated bio-oils. For example, untreated bio-oil has significant water content, high acidity, immiscibility with petroleum products, viscosity increase over time, and a distinctive odor. In addition, when tested for use as an engine fuel, bio-oil has caused engine damage in many types of engines. In light of the many disadvantages of using untreated bio-oil as a fuel, it has not been adopted for widespread commercial use [Bandi et al. 2001, Czernik et al. 2004].

Presently, bio-oil upgrading techniques include hydrodeoxygenation, catalytic pyrolysis, and steam reforming mainly to reduce the oxygen content present in the bio-oil [Furimsky 2000, Elliott 2007]. Hydroprocessing is an upgrading process for reducing heavy molecules into lighter hydrocarbons through the catalytic addition of hydrogen. Hydroprocessing of bio-oil has been demonstrated to reduce the oxygen content of bio-oil and produces a liquid hydrocarbon mixture that can be utilized as a transportation fuel. In general, hydroprocessing can be performed in either one, two, or more steps. It has become traditional to hydroprocess liquid intermediates (particularly fast pyrolysis oil) by an initial 1st stage hydrotreating step to prevent polymerization at mild temperatures (200-400 °C) at a hydrogen pressure of 4 to 10 MPa in the presence of a heterogeneous hydrotreating catalyst. In the 2nd stage, a hydrocracking step is performed at more severe temperatures (300-500 °C) but at the same general pressure of 4 to 10 MPa in the presence of a heterogeneous hydrocracking catalyst [Elliott 2007, Jones et al. 2009, Wildschut et al. 2010, Bulushev et al. 2011, Elliott et al. 2012].

Bio-oil aldehydes play a vital role in bio-oil stability from thermal application or stability over time. Aldehydes readily react with phenols and sugars to form higher molecular weight resins and oligomers via polymerization and condensation; oligomerization reactions lead to coke formation [Gagnon et al. 1988, Diebold 2000, Shanks et al. 2009, Hu et al.2012]. Aldehydes present in the raw bio-oil can be converted to carboxylic acids by subjecting them to oxidation [Xu et al. 2011]. Scheme 1 is a schematic of the chemical reaction for the conversion of bio-oil aldehydes to carboxylic acids in the presence of an oxidizing agent reaction pathway.
**Scheme 1.** Oxidation pretreatment pathway of bio-oil aldehydes to carboxylic acids [Xu et al. 2011].

Deoxygenation is a method by which oxygen is removed from oxygenated compounds. Deoxygenation can be applied by hydrodeoxygenation (HDO) or decarboxylation [Elliot et al. 2007 and 2012, Wildschut et al. 2009 and 2010, Gagnon et al. 1988, Furimsky 2000, Czernik et al. 2002, Subramaniam et al. 2011]. The general deoxygenation reactions are shown in Scheme 2 below.

**Scheme 2.** Deoxygenation process reactions to form hydrocarbons [King et al. 1992, Wildschut 2009, Jones et al. 2009].

However, hydroprocessing requires a large volume of expensive hydrogen to deoxygenate the bio-oil. In addition, practitioners continue to encounter rapid coke formation and catalyst deactivation as major problems in present bio-oil deoxygenation processes. [Elliot 2007, Wildschut et al. 2009 and 2010, Gagnon et al. 1988, Furimsky 2000, Czernik et al. 2002, Subramaniam et al. 2011]. Therefore, there is a need to upgrade bio-oil to a fuel by additional methods. New methods may solve the problems encountered during hydroprocessing. In the current research a novel deoxygenation process was performed as an alternative to conventional hydroprocessing to produce a quality transportation fuel. We have developed a novel process (patented recently) that can partially deoxygenate acidified bio-oil by oxidation in the presence of pressurized syngas. The syngas contains approximately 18.0% of hydrogen, 22.0% carbon monoxide, 11.0% carbon dioxide, 2.0% methane and 47.0% nitrogen [Street et al. 2012]. The carbon monoxide present in the syngas by reacting with water present in acidified product produces additional hydrogen during the partial deoxygenation via water gas shift (WGS) reaction [Nagai et al. 2010, Akgul et al. 2012]. The full deoxygenation step utilizes 100% hydrogen to obtain the hydrocarbon mixture from the partially deoxygenated product produced in the presence of syngas.

**Materials and Methods:**

Bio-oil required for this research was produced from the pine wood particles by the fast pyrolysis process at a rate of 7-kg/h by the department of Forest Products, Mississippi State University (MSU) auger-feed pyrolysis reactor. A fast pyrolysis bio-oil with approximately 30% water content was produced. Oxidation pretreatment and partial and full deoxygenation experiments were performed in a stainless steel, high-pressure batch autoclave equipped with
an overhead magnetic stirrer, a pressure indicator with a maximum capacity of 5000 psig and a thermocouple for temperature monitoring in the range of 0-450 °C. The autoclave is equipped with an electrical heating and cooling system to control the temperature inside the reactor. Oxidation pretreatment was applied to raw bio-oil by treating with an oxidizing agent to convert the aldehyde compounds to carboxylic acids at an ambient reaction conditions. Catalytic deoxygenation experiments were performed in two stages. The 1st stage of partial deoxygenation of the acidified product in the presence of a heterogeneous catalyst was treated at moderate temperatures in the range of 250-400 °C and under pressurized syngas conditions of 500-1000 psi. In the 2nd stage, partially deoxygenated product was fully deoxygenated by a heterogeneous catalyst at high temperature in the range of 300-450 °C and under pressurized hydrogen conditions of 750-1500 psi.

Results and Discussion:

As shown in Table 1 the acid number increased from 90.28 to 161.0 mg KOH/g. Viscosity decreased by 45.16%; water content increased by about 11%. The HHV of the acidified product decreased from 16.01 to 15.40 MJ/kg probably due to the water content increase. Density decreased from 1.22 to 1.14 g/ml and pH was reduced to 2.87 from 3.16. Oxygen content increased somewhat from 53.58 to 58.96. This resulted from both increased acid and water content.

The acidified product was then partially deoxygenated in the presence of pressurized syngas of 800 psi and a Ni-based MSU developed proprietary heterogeneous catalyst. Reaction temperature was 360 °C and time of reaction was 90 min. After cooling the partially deoxygenated product had an aqueous phase at the bottom of the vessel and an oil phase at the top. The aqueous fraction was separated from the oil fraction. A portion of the oil fraction was maintained for testing as a boiler fuel product. The remainder of the oil fraction was subjected to full deoxygenation under hydrogen pressure of 1500 psi at a temperature 425 °C for 150 min. The resulting liquid contained both hydrocarbons as a top layer and a small percentage of an aqueous phase at the bottom.

Table 1. Comparison of raw bio-oil and acidified product physical and chemical properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Raw bio-oil</th>
<th>Acidified product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/mL</td>
<td>1.22</td>
<td>1.14</td>
</tr>
<tr>
<td>HHV, MJ/kg</td>
<td>16.01</td>
<td>15.40</td>
</tr>
<tr>
<td>Oxygen, wt%</td>
<td>53.58</td>
<td>58.96</td>
</tr>
<tr>
<td>Total acid number, mg KOH/g</td>
<td>90.28</td>
<td>161.0</td>
</tr>
<tr>
<td>pH</td>
<td>3.16</td>
<td>2.87</td>
</tr>
<tr>
<td>Water content, vol%</td>
<td>30.45</td>
<td>33.75</td>
</tr>
<tr>
<td>Kinematic viscosity, 40°C, cSt</td>
<td>12.09</td>
<td>6.63</td>
</tr>
</tbody>
</table>

The properties of the acidified product, the resultant boiler fuel following partial deoxygenation and the hydrocarbon mixture produced by full deoxygenation are given in Table
2. The HHV of the boiler fuel at 35.40 MJ/kg was more than double the 15.40 MJ/kg value of the acidified product. Boiler fuel oxygen content was dramatically reduced from 58.96 to 14.0. Acid number was reduced from 161.0 to 51.6. pH was increased from 2.87 to 4.24. Water content of the boiler fuels was only 2.7 vol% compared to that of the acidified product at 33.75 vol%. Density was reduced to 1.04 for boiler fuel compared to 1.14 for the acidified product. Viscosity increased greatly from 6.63 to 28.25 cSt.

The properties of the hydrocarbon mixture were greatly improved above those of the boiler fuel. HHV was increased to 45.10, rivaling the value of most petroleum fuels. Oxygen content and acid value were zero. pH was on the basic side at 9.5. Water content was only 0.08. Density and viscosity were considerably lowered at 0.88 g/ml and 2.38 cSt, respectively.

Table 2. Comparison of acidified product, boiler fuel and hydrocarbon mixture physical and chemical properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Acidified product</th>
<th>Boiler fuel</th>
<th>Hydrocarbon mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV, MJ/kg</td>
<td>15.40</td>
<td>35.40</td>
<td>45.10</td>
</tr>
<tr>
<td>Oxygen, wt%</td>
<td>58.96</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>Total acid number, mg KOH/g</td>
<td>161</td>
<td>51.6</td>
<td>0</td>
</tr>
<tr>
<td>pH</td>
<td>2.87</td>
<td>4.24</td>
<td>9.5</td>
</tr>
<tr>
<td>Water content, vol%</td>
<td>33.75</td>
<td>2.7</td>
<td>0.08</td>
</tr>
<tr>
<td>Density, g/ml</td>
<td>1.14</td>
<td>1.04</td>
<td>0.88</td>
</tr>
<tr>
<td>Kinematic viscosity, 40°C, cSt</td>
<td>6.63</td>
<td>28.25</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Figure 1. Shows the elemental composition weight percentages of the acidified product, boiler fuel and hydrocarbon mixture. The carbon content of the boiler fuel of 76.4 wt% increased from that of the acidified product at 33.12 wt%. Carbon content of the hydrocarbon mixture was 87.06. The oxygen content of the acidified product decreased from 58.96 wt% to 14.0 wt% for boiler fuel to zero for the hydrocarbon mixture.
A Detailed Hydrocarbon Analysis (DHA) was performed by ASTM D6730-01. This test is often referred to as the PIANO method (paraffins, iso-paraffins, aromatics, naphthenes and olefins) to classify the hydrocarbons present in the hydrocarbon mixture. The results of the DHA are given in Table 3. These results showed that the hydrocarbon mixture contained n-paraffins of 21.33 mass%, iso-paraffins of 35.9 mass%, olefins of 13.65 mass%, naphthenes of 20.55 mass%, aromatics of 8.56 mass% and oxygenated compounds of 0.005 mass%.

Table 3. Hydrocarbon types and their mass% present in hydrocarbon mixture results analyzed by Detailed Hydrocarbon Analysis by ASTM D6730-01 method.

<table>
<thead>
<tr>
<th>Hydrocarbon type</th>
<th>Total (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td>21.33</td>
</tr>
<tr>
<td>I-Paraffins</td>
<td>35.9</td>
</tr>
<tr>
<td>Olefins</td>
<td>13.65</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>20.55</td>
</tr>
<tr>
<td>Aromatics</td>
<td>8.56</td>
</tr>
<tr>
<td>Oxygenated</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Simulated distillation of the hydrocarbon mixture results are shown in Figure 2. Figure 2 shows the petroleum fuel equivalent based on vaporization temperature. Simulated distillation of the hydrocarbon mixture was performed by the ASTM D2887 method for boiling range distribution of petroleum fractions by gas chromatography. These boiling temperatures are
given below the named petroleum equivalents in the figure. These petroleum equivalents were of the molecular weights of gasoline (45%), jet fuel (20%) and diesel (30%). Not shown in Figure 2 is the 5% of heavy fuel produced at temperatures above 350 °C.

![Figure 2. Gasoline, jet fuel and diesel fuels weight percentages present in hydrocarbon mixture results from simulated distillation analysis by the ASTM D2887.](image)

**Conclusions:**

Our novel approach of pretreatment of raw bio-oil followed by a partial deoxygenation in the presence of pressurized syngas and full deoxygenation with pure hydrogen successfully produced hydrocarbons of transportation fuel quality. The hydrocarbons produced from this process had an HHV of 45.10 MJ/kg. Oxygen content and acid value were zero. pH was on the basic side at 9.5. Water content was only 0.08. Density and viscosity were considerably lowered at 0.88 g/ml and 2.38 cSt, respectively. The energy density of hydrocarbons produced by this method was increased by 181.7% from raw bio-oil. The hydrocarbon mixture was comprised of petroleum equivalent molecular weights of gasoline (45%), jet fuel (20%) and diesel (30%).

**References:**