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Alcohol Injection into the Pyrolytic Vapor Stream as a Method to Rapidly Produce Esterified Bio-oil
Bio-oil is a dark brown water emulsion containing a complex mixture of organic compounds.

Biomass

Absence of O₂
0.5-2 sec

350 – 600 °C

Vapors & aerosols
(CO₂, H₂, CO, CH₄)

Solid products
(char)

Cool and condense

Liquid (Bio-oil)
Introduction

- Bio-oil negative properties:
  - high acidity;
  - increased viscosity over time;
  - low energy density;
  - 40-50% oxygen content.
Objective

- Develop a rapid, low-cost method to produce esterified bio-oil for boiler fuel.
Materials and Methods -- Bio-oil Production

- Loblolly pine wood
- Pine lumber, kiln dried: 12 to 17% MC, chipped to 1-2 inch. grinding to 1-3mm; drying to 8-10% MC
- Auger reactor
- Pyrolyzing feedstock at a rate of 7 kg/h.
- Pyrolysis temperature: 450°C
Materials and Methods – Esterification Reaction

- $\text{R-COOH} + \text{R’-OH} \xrightarrow{\text{catalyst}} \text{R-COOR’} + \text{H}_2\text{O}$
  - Where $\text{R-COOH}$ is carboxylic acid
  - $\text{R’-OH}$ is alcohol
  - $\text{R-COOR’}$ is ester
Materials and Methods -- Injection schematic

Biomass → Pyrolysis reactor → Condenser

Alcohol injection

Esterified Bio-oil
Materials and Methods

- Alcohols and acid catalyst were injected into the pyrolysis vapor zone prior to the auger reactor condenser
- Pump and fuel injector: calibrated via a linear calibration formula
- The planned injection rate: 3 kg/hr bio-oil production rate
## Materials and Methods -- Treatments

<table>
<thead>
<tr>
<th></th>
<th>Treatment</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>Methanol, 1-Butanol</td>
<td>10, 20</td>
</tr>
<tr>
<td>Acid catalyst</td>
<td>Sulfuric acid</td>
<td>1</td>
</tr>
</tbody>
</table>
Materials and Methods -- Chemical and physical properties

<table>
<thead>
<tr>
<th>Property (unit)</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid value (mg/KOH g)</td>
<td>ASTM D664</td>
</tr>
<tr>
<td>Water content (mass %)</td>
<td>ASTM E203</td>
</tr>
<tr>
<td>Kinematic Viscosity (mm²/s)</td>
<td>ASTM D445</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>ASTM D240</td>
</tr>
</tbody>
</table>
## Result – Actual injected amount

<table>
<thead>
<tr>
<th>Actual injected (wt%)</th>
<th>20% Methanol</th>
<th>10% Methanol</th>
<th>20% 1-Butanol</th>
<th>10% 1-Butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.1</td>
<td>9.1</td>
<td>18.9</td>
<td>9.1</td>
</tr>
</tbody>
</table>
Result -- Acid value of control and after alcohol injection

Acid Value (mg/ KOH g)

- Raw Bio-oil: 90.00
- 20% Methanol: 75.00
- 10% Methanol: 80.00
- 20% 1-Butanol: 85.00
- 10% 1-Butanol: 90.00
Result -- Water content of control and after alcohol injection

Water Content (wt%)
Result -- Initial viscosity of control and after alcohol injection

**Viscosity (cSt)**

- Raw bio-oil
- 20% Methanol
- 10% Methanol
- 20% 1-Butanol
- 10% 1-Butanol
Result -- Higher heating value of control and after alcohol injection

Higher Heating Value (MJ/kg)

- Raw bio-oil
- 20% Methanol
- 10% Methanol
- 20% 1-Butanol
- 10% 1-Butanol

Higher Heating Value (MJ/kg):
- Raw bio-oil: 14.00
- 20% Methanol: 15.00
- 10% Methanol: 16.00
- 20% 1-Butanol: 19.00
- 10% 1-Butanol: 18.00
Injecting alcohol into the pyrolytic vapor zone provides a fast and cost-effective method to esterify bio-oil.

Treatments with higher amounts of alcohol injection produced more highly upgraded bio-oil.

Treatments with 1-butanol injection had lower water content and higher energy value than methanol injected treatments.

Treatments with methanol injection have lower acid value and viscosity.
Acknowledgement

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