Thermal evolution of biochar and its physicochemical properties during hydrothermal gasification

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Thermal Evolution of Biochar and its Physicochemical Properties during Hydrothermal Gasification of Biomass

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Introduction

- Dependence on fossil fuels as the main energy sources has led to serious energy crisis and environmental problems.

- **Waste biomass** is a potential renewable energy source to meet the increasing energy demands.

- Biomass can be converted to biofuels by BTL (pyrolysis, liquefaction and fermentation) and BTG (gasification) technologies.

- Hydrogen is renewable, non-toxic, clean fuel and highly energy efficient source.
Definition: Any plant grown as a low-cost and low-maintenance harvest used for making biofuels or combusted for its energy content to generate heat or electricity.

Ideal traits of an energy crop:
- Fast growing, short rotation and high yield
- Be able to grow in marginal or degraded lands
- Low requirement of intensive agricultural practices
- No competition with food crops for land and nutrients

Examples:
Wood-based energy crops: Willow and poplar
Grasses: switch grass, elephant grass and timothy grass
Supercritical water gasification

Water at temperature > 374 °C and pressure > 22.1 MPa is called supercritical water.

Physical and chemical characteristics such as ion product, density, dielectric constant and viscosity of supercritical water are greatly different from either extreme state of the gas phase or the liquid phase.

Advantages:
- No biomass drying required
- Better solvation of organics
- Negligible or no toxic byproducts
- Hydrogen-rich synthesis gas products
Timothy grass: Biochemical characterization

- High cellulose and hemicellulose (~64.3 wt.%) indicates high sugar content. Good for bioconversion
- Extractives include tannin, terpens, terpenoids, lipids, fatty components etc.
Timothy grass: Thermogravimetric analysis

Moisture and volatiles evolution

Char production

Weight % vs. Temperature (°C)
Experimental

Objectives

➢ To study the gasification potentials of timothy grass as a model biomass for energy crops.

➢ To study the effects of different gasification parameters:
  o Temperature (450-650°C)
  o Feed concentration (1:4 and 1:8 biomass-to-water ratio)
  o Reaction time (15-45 min)

➢ To enhance H₂ yields by the application of homogeneous alkali catalysts and study the effect of their concentrations (1-3 wt%)
  o KOH
  o NaOH
  o K₂CO₃
  o Na₂CO₃

➢ Characterize the biochar generated at different temperatures to determine their thermal and physicochemical properties.
Supercritical water gasification
Effects of temperature and feed concentration (45 min)

- H₂ yield: 1:4 BTW (1.04-4.08 mmol/g) < 1:8 BTW (1.14-5.15 mmol/g).
- Higher gas yields at 650°C than at 450°C.
- CO yield decreased at 650°C due to water-gas shift reaction.
Effect of temperature (45 min, 1:8 BTW ratio)

- Total gas yields increased from 7 mmol/g at 450°C to 17.2 mmol/g at 650°C
- LHV increased from 541 kJ/Nm³ at 450°C to 2207 kJ/Nm³ at 650°C
Effect of reaction time and feed concentration (650°C)

- H$_2$ yield: 1:4 BTW (1.75-4.08 mmol/g) < 1:8 BTW (2.7-5.15 mmol/g)
- H$_2$ yield increased at 45 min than 15 min due to hydrogenation reaction.
- Better water-gas shift reaction at 45 min.
Effect of reaction time (650°C, 1:8 BTW ratio)

- Total gas yields increased from 11 mmol/g at 15 min to 17.2 mmol/g at 45 min
- LHV increased from 1451 kJ/Nm³ at 15 min to 2207 kJ/Nm³ at 45 min
Effect of catalysts (650°C, 45 min, 1:8 BTW ratio)

KOH
Better hydrogenation, water-gas shift reaction

NaOH
Better methanation reaction
Effect of catalyst (650°C, 45 min, 1:8 BTW ratio)

Total gas yield: KOH > K₂CO₃ > NaOH > Na₂CO₃

LHV: NaOH > KOH > K₂CO₃ > Na₂CO₃
## Proximate and ultimate analysis of timothy grass biomass and biochars (45 min, 1:8 BTW ratio)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Timothy grass</th>
<th>Biochar-450°C</th>
<th>Biochar-550°C</th>
<th>Biochar-650°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis (wt%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>6.2</td>
<td>3.5</td>
<td>2.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Ash</td>
<td>4.1</td>
<td>8.6</td>
<td>10.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>71.4</td>
<td>58.4</td>
<td>46.6</td>
<td>37.4</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>18.3</td>
<td>29.5</td>
<td>40.4</td>
<td>47.4</td>
</tr>
<tr>
<td><strong>Ultimate analysis (wt%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>47.4</td>
<td>61.2</td>
<td>69.7</td>
<td>75.1</td>
</tr>
<tr>
<td>H</td>
<td>6.8</td>
<td>5.4</td>
<td>4.1</td>
<td>3.7</td>
</tr>
<tr>
<td>N</td>
<td>1.4</td>
<td>1.2</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>O(^b)</td>
<td>40.4</td>
<td>23.6</td>
<td>15.1</td>
<td>7.3</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>18.6</td>
<td>24.9</td>
<td>26.2</td>
<td>28.9</td>
</tr>
</tbody>
</table>
SEM analysis of biochars
(45 min, 1:8 BTW ratio)

More cracked surface
FTIR analysis of biochars
(45 min, 1:8 BTW ratio)

- High gasification temperature led to the removal of alkanes, alkynes, alcohols, esters, ethers and carbonyls from biomass in biochars due to dehydration of organic functional groups (C–O, C=O and C–H).
- Biochar at 650°C become more aromatic with the increase in C–C and C–H groups.
- High temperature led to formation of aromatic biochars due to dehydration, dehydrogenation, demethanation, decarboxylation and decarbonylation of organic components.
Raman spectroscopy of biochars (45 min, 1:8 BTW ratio)

Band Assignment

<table>
<thead>
<tr>
<th>Band</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>C–H Hydroaromatic rings</td>
</tr>
<tr>
<td>$S_L$</td>
<td>C–C Aromatic rings</td>
</tr>
<tr>
<td>D</td>
<td>C–C Highly ordered carbon</td>
</tr>
<tr>
<td>$V_L$</td>
<td>C–H Methylene or methyl</td>
</tr>
<tr>
<td>$G_R$</td>
<td>Amorphous carbon structure</td>
</tr>
<tr>
<td>G</td>
<td>C=C Alkenes, Crystalline carbon structures</td>
</tr>
</tbody>
</table>

- Biochar at 650°C showed the removal of hydroaromatic rings ($S$ band), and methylene groups ($V_L$ band).
- Thermal cracking and dehydrogenation caused aromatization of biochar with the increase in crystalline carbon structures, e.g. C–C ($D$ band), C=C ($G$ band).
Conclusions

- Temperature played a major role leading to hydrothermal cracking of timothy grass with highest gas yields at 650°C.

- The carbon content in the biochar and heating value increased with the rise in temperature.

- Lower feed concentration (1:8 BTW ratio) resulted in higher H₂ yields due to free-radical mechanism and water-gas shift reaction.

- Reaction time of 45 min was optimal for higher H₂ yields, total gas yields with greater LHV of the gas products.

- 3 wt% KOH resulted in highest yields of H₂ due to higher water-gas shift reaction, while 3 wt% NaOH enhanced methanation reaction with higher CH₄ yields.

- As the temperature increased from 450 to 650°C, extreme thermal denaturation of biochar through dehydration, bond breakages and formation of transformational products resulted in their aromatization.
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