Biomass Torrefaction for Sustainable Biochar Production and its Applications

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Outline

- Bioenergy:
  - Current status of development
- Torrefaction:
  - Principle
  - Biomass property variation
  - Kinetics
  - Applications
- Conclusions
Bioenergy
Biomass

Solid
- Firewood, biochar, charcoal
- Powder, pellet, block, briquette ...

Liquid
- Biodiesel
- Bioethanol
- Bio-oil
- Biobutanol ...

Gas
- Syngas
- Biogas
- Biohydrogen ...

Fuel
(Carbon Neutral)
Disadvantages

Biomass

- Large Volume
- High Moisture
- Higher Biodegradability
- Low Energy Density
- Low Grindability
- Hygroscopic nature

Difficulty in storage
High cost in transport
Low utilization efficiency
Torrefaction
Coffee roast (180-275 °C, 3-30 min)

Thermal treatment of wood (170-230°C)

Enhancing the flavor and improving organoleptic properties of food
Global Research Article

Total: around 1430 papers with average citation of 15.79

Web of Science
Nov. 23, 2018
Torrefaction is a mild pyrolysis process for biomass pretreatment. It involves heating biomass in a nitrogen or inert atmosphere at temperatures between 200-300°C. This process reduces the moisture content and improves the grindability, calorific value, and homogeneity of the biomass.
Color Change

(a) Lightness $L^*$ vs. Mass loss (%) for Poplar and Fir.

(b) Redness $a^*$ vs. Mass loss (%) in CIELAB color space.

(c) yellowness $b^*$ vs. Mass loss (%) for Yellow.

(d) Total color difference $\Delta E^*$ vs. Mass loss (%) for Poplar and Fir at different temperatures (200°C, 210°C, 220°C, 230°C).
Untreated poplar

230 °C of treatment

Contact angle

Poplar

200 °C
210 °C
220 °C
230 °C
Structure of Lignocelluloses

- **Cellulose**: a linear homopolysaccharide with crystalline and amorphous structures.
- **Hemicellulose**: a branched mixture of various polymerized monosaccharides.
- **Lignin**: a three-dimensional, highly branched and polyphenolic substance.
Thermogravimetric Analysis (TGA)

Raw coconut fiber

240 °C (mild), 2h

275 °C (severe), 2h

SEM Images

Oil palm fiber (fibrous biomass)

Raw

In N₂

In air

1K  5K  30K

Eucalyptus (ligneous biomass)

Grindability

(a) 220 °C

(b) 250 °C

- Four-blade cracker
- Rotation speed of 24,000 rounds per min (rpm) for one min
- Three different sieves (i.e. 100, 200 and 325 mesh)

Volatile Matter vs. Fixed Carbon

- Devolatilization
- Carbonization

van Krevelen Diagram

http://www.google.com/patents/US20130232856

## Higher Heating Value

<table>
<thead>
<tr>
<th>Material</th>
<th>Volatile matter (wt%)</th>
<th>Fixed carbon (wt%)</th>
<th>Higher heating value (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw biomass</td>
<td>67-88</td>
<td>0.5-20</td>
<td>15-20</td>
</tr>
<tr>
<td>Torrefied biomass</td>
<td>34-85</td>
<td>13-45</td>
<td>16-29</td>
</tr>
<tr>
<td>Coal</td>
<td>0.5-50</td>
<td>46-92</td>
<td>25-35</td>
</tr>
</tbody>
</table>
Kinetics
Torrefaction Kinetics

Isothermal torrefaction

Non-isothermal torrefaction

Scenedesmus obliquus CNW-N
Torrefaction Kinetics

\[ \frac{dX}{dt} = k (1 - X)^n \]
\[ X = \frac{W_i - W}{W_i - W_f} \]
\[ k = A \exp \left( -\frac{E_a}{RT} \right) \]

**Isothermal torrefaction**

\[ \ln \left( \frac{1-X_0}{1-X} \right) = k(t-t_0) \quad \text{if} \quad n = 1 \]
\[ (1 - X)^{1-n} - (1 - X_0)^{1-n} = k(n-1)(t-t_0) \quad \text{if} \quad n \neq 1 \]
\[ \ln(k) = \ln A - \frac{E_a}{RT} \]

**Non-isothermal torrefaction**

\[ \frac{dX}{dT} = \left( \frac{1}{\beta} \right) A \exp \left( -\frac{E_a}{RT} \right) (1-X)^n \]

\[ \frac{\ln \left[ -\frac{\ln(1-X)}{T^2} \right]}{\ln \left[ \frac{1 - (1-X)^{1-n}}{(1-n) \times T^2} \right]} = \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT} \quad \text{if} \quad n = 1 \]
\[ \ln \left[ \frac{1 - (1-X)^{1-n}}{(1-n) \times T^2} \right] = \ln \frac{AR}{\beta E_a} - \frac{E_a}{RT} \quad \text{if} \quad n \neq 1 \]
Torrefaction Kinetics

Isothermal torrefaction

\[ \ln k = -6918.7 \cdot T^{-1} + 8.016 \]

\[ R^2 = 0.9897 \]

\[ \ln [\ln(1-X)/T^2] \]

Non-isothermal torrefaction

\[ Y = -8485.6 \cdot T^{-1} + 2.6729 \]

\[ R^2 = 0.9872 \]

Regression line

Experimental data

\[ Y = \ln [\ln(1-X)/T^2] \]

Scenedesmus obliquus CNW-N

Activation energy
\[ E_a = 57.52 \text{ kJ mole}^{-1} \]

Activation energy
\[ E_a = 40.14 \sim 88.41 \text{ kJ mole}^{-1} \]
Two-Step Kinetics

Two-step reaction

\[
\frac{dm_A}{dt} = -m_A \cdot (k_1 + k_{V1})
\]

\[
\frac{dm_B}{dt} = k_1 \cdot m_A - m_B \cdot (k_2 + k_{V2})
\]

\[
\frac{dm_C}{dt} = k_2 \cdot m_B
\]

\[
\frac{dm_{V1}}{dt} = k_{V1} \cdot m_A
\]

\[
\frac{dm_{V2}}{dt} = k_{V2} \cdot m_B
\]
Two-Step Kinetics

Spruce

![Diagram showing two-step kinetics with rate constants and mass fraction graphs for Spruce and Birch](image)

<table>
<thead>
<tr>
<th>Rate constant (min⁻¹)</th>
<th>Spruce</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>( 1.04 \times 10^4 \exp\left(\frac{-20792}{RT}\right) )</td>
<td>( 2.25 \times 10^7 \exp\left(\frac{-87705}{RT}\right) )</td>
</tr>
<tr>
<td>( k_{V1} )</td>
<td>( 1.26 \times 10^7 \exp\left(\frac{-90262}{RT}\right) )</td>
<td>( 1.02 \times 10^{10} \exp\left(\frac{-119850}{RT}\right) )</td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 2.76 \times 10^4 \exp\left(\frac{-70605}{RT}\right) )</td>
<td>( 2.39 \times 10^1 \times \exp\left(\frac{-93506}{RT}\right) )</td>
</tr>
<tr>
<td>( k_{V2} )</td>
<td>( 3.84 \times 10^6 \exp\left(\frac{-93473}{RT}\right) )</td>
<td>( 1.03 \times 10^8 \exp\left(\frac{-109617}{RT}\right) )</td>
</tr>
</tbody>
</table>

\( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \), \( T \): absolute temperature (K)

Two-Step Kinetics

Spruce

(A) 220 °C

(B) 260 °C

Torrefaction time (min)

Mass fraction

Exp. Cal. A B C

Applications
Global Patent

(b) Global (2005-2018)

Year

Number

Total no.: 325 (Nov. 2018)
Pulverized Coal Injection around Raceway
R-Factor & Burnout

A higher R-factor implies a better devolatilization extent for fuel particles traveling in a reaction zone.

The higher the burnout, the better the combustibility of a fuel.

Entrained-Bed Gasifier

ITRI 2 ton/day (600 kWth)
Coal-based Pressurized and Slagging Entrained-Bed Gasifier
Syngas Formation

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂</td>
<td>0.6</td>
</tr>
<tr>
<td>Syngas</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- Bamboo
- Torrefied bamboo
- Coal

Mole fraction (CO)
- 0.44
- 0.42
- 0.4
- 0.38
- 0.36
- 0.34
- 0.32
- 0.3
- 0.28
- 0.26
- 0.24
- 0.22
- 0.2
- 0.18
- 0.16
- 0.14
- 0.12
- 0.1
- 0.08
- 0.06
- 0.04
- 0.02
- 0.01

Mole fraction (H₂)
- 0.2
- 0.19
- 0.18
- 0.17
- 0.16
- 0.15
- 0.14
- 0.13
- 0.12
- 0.11
- 0.1
- 0.09
- 0.08
- 0.07
- 0.06
- 0.05
- 0.04
- 0.03
- 0.02
- 0.01

CC and CGE

Carbon conversion (%)

Cold gas efficiency (%)

CC > 90%

29% 50% 68%

Raw bamboo Torrefied bamboo Coal

Feed

Coal Raw bamboo Torrefied bamboo

CC CGE

Pyrolysis of Torrefied Biomass

![Graph](image1)

**Fig. 4.** Effect of torrefaction on the yields of pyrolysis products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content (wt.%)</th>
<th>pH value</th>
<th>Heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil-DCS</td>
<td>62.3</td>
<td>3.16</td>
<td>9.95</td>
</tr>
<tr>
<td>Bio-oil-TCS220</td>
<td>55.7</td>
<td>3.05</td>
<td>10.82</td>
</tr>
<tr>
<td>Bio-oil-TCS250</td>
<td>46.3</td>
<td>3.23</td>
<td>13.19</td>
</tr>
<tr>
<td>Bio-oil-TCS280</td>
<td>37.5</td>
<td>3.28</td>
<td>14.93</td>
</tr>
</tbody>
</table>
Bio-oils produced from the liquefaction of torrefied rice stalk reduced oxygen/carbon ratios and water content.
Torrefaction can **improve the properties** of biomass to a great extent.

Torrefaction produced **coal-like carbon neutral fuels**. The developed substitute fuels make the environment more sustainable.

Torrefied biomass can be used in blast furnaces (ironmaking), combustors (boilers), gasifier, pyrolyzers, and liquefaction reactors for **heat, syngas and bio-oil production**.

Torrefaction is a **promising technology** to enhance biomass utilization.
Thank you very much for your attention