Potential use of alkaline hydrogen peroxide in biomass pretreatment and valorization – a review

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Supervisor: A/P Wu Ta Yeong
Date: 14th June 2018
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2. Problem Statement
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4. Reaction Mechanism
5. Recent Applications
6. Advantages & Limitations
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1 Introduction

Bio-refinery:
- Process to convert biomass to bio-based products and energy
- Biomass – Food crop / Energy crop / Agro-industry waste

Waste Valorization – Any processes or activities that utilize or convert normally neglected waste to highly useful and value added products or energy sources. (Kabongo 2013)

(World Resource Council, 2016)
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Lignocellulosic biomass waste:
- Hundreds billion tonnes produced annually
- Usually neglected
- Potential feedstock for waste valorization

Challenge in Utilizing Lignocellulosic Biomass:
- Recalcitrant nature
- Lignin-carbohydrate complex
- Physical and Chemical Resistant

(Yang et al, 2015)
2 Problem Statement

Existing Pretreatment Methods

Various Pre-Treatment

- Chemical
  - Dilute Sulphuric Acid
  - Sodium hydroxide
  - Alkaline hydrogen peroxide

- Acid organosolv
- Ionic liquid
- Liquid hot water
- Microbes

Physical
- Disk Milling
- Extrusion
- Supercritical carbon dioxide
- Steam explosion

Physiochemical

Alkaline Hydrogen Peroxide:
- Extraordinary performance
- Little sugar degradation
- Mild conditions
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Hydrogen Peroxide:
- Pulping and Bleaching solvent
- React with **aliphatic** part of lignin under **normal circumstances**
- Expose phenolic ring and causes macromolecular structure alteration under alkaline condition and elevated temperature

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HO}^- &\rightarrow \text{HOO}^- + \text{H}_2\text{O} \\
\text{H}_2\text{O}_2 + \text{HOO}^- &\rightarrow \text{HO}^\bullet + \text{O}_2^\bullet^- + \text{H}_2\text{O}
\end{align*}
\]

Hydroperoxyl anion:
- Intermediate products under **alkaline condition**
- Carbonyl and ethylene oxidation
- **Initiator** for radicals forming

Hydroxyl radical (\(\text{HO}^\bullet\)) and Superoxide anion radical (\(\text{O}_2^\bullet^-\)):
- Strong oxidants
- **Oxidization** of lignin
- **Fragmentation** of biomass
- **Destruction** of ester, ether cross-links and cleavage of \(\beta\)-O-4 bonds
- Hemicellulose **solubilisation** and cellulose **depolymerisation**
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Alkaline Hydrogen Peroxide

- **Dependent** on operational variables
- **Optimization** required targeting different biomass or applications
- Efficiency depend on the promotions of radicals
**Recent Application**

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Initial pretreatment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid poplar</td>
<td><em>CuII</em>(bpy)-catalyzed alkaline hydrogen peroxide</td>
<td>Li et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>Solid loading = 1:10 (w/v)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>T</em> = Ambient temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time = 48 h</td>
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<tr>
<td></td>
<td>pH = 11.5</td>
<td></td>
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<tr>
<td></td>
<td><em>H₂O₂</em> concentration = 10 g/L</td>
<td></td>
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<tr>
<td></td>
<td>Catalyst concentration = 5 mM</td>
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</tbody>
</table>

**Key findings:**
- **Catalyst** is essential in **hardwood** pretreatment
- Maximum **lignin solubilisation** of **50.2%**
- Uncatalysed lignin solubilisation **36.6%**
- Disproportional reactions due to highly ordered cell wall matrix
- Diffusible homogeneous catalyst provide alternative route to improve site-specific reactions
### Recent Application

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<tbody>
<tr>
<td>Jerusalem artichoke</td>
<td><em>Ultrasonic assisted alkaline hydrogen peroxide</em></td>
<td>Li et al. (2016)</td>
</tr>
</tbody>
</table>

- Ultrasonic frequency = 40kHz
- Ultrasonic power = 500 W
- Solid loading = 1:20 (w/v)
- $T = 50 \, ^{\circ}C$
- Time = 120 min
- $\text{NaOH concentration} = 2\%$ (w/v)
- $\text{H}_2\text{O}_2$ concentration = 5% (w/v)

**Key findings:**
- Increased **lignin removal** from 37.5% to **40.3%**
- Degree of polymerization **reduced**
- Significantly **increase** crystallinity index from 45% to **62.5%**
- **Improve** accessibility of carbohydrate
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<tr>
<td></td>
<td>Solid loading = 1:10 (w/v)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T = 180 , ^\circ C$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time = 60 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$pH = 11.6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H_2O_2$ concentration = 4% (w/w)</td>
<td></td>
</tr>
</tbody>
</table>

### Key findings:
- Delignification of 22%
- Glucomannan removal of 78%
- Little degradation of cellulose while removing protective barrier
## Recent Application

### Biomass
- **Rice Straw**

<table>
<thead>
<tr>
<th>Initial pretreatment</th>
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</tr>
</thead>
<tbody>
<tr>
<td><em>Alkaline hydrogen peroxide-assisted wet air oxidation</em></td>
<td>Morone et al. (2017)</td>
</tr>
<tr>
<td>Soaking in alkaline hydrogen peroxide</td>
<td></td>
</tr>
<tr>
<td>Time = 14 h</td>
<td></td>
</tr>
<tr>
<td>pH = 11.9</td>
<td></td>
</tr>
<tr>
<td>H₂O₂ concentration = 0.5 % (w/v)</td>
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<tr>
<td>Pressurized with 6 bar air at 190 °C for 20 min with mixing at 200 rpm</td>
<td></td>
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</tbody>
</table>

### Key findings:
- **Reduced** peroxide loadings to 0.5% (w/v)
- Maximum **lignin removal** of 77.29%
- Maximum **cellulose recovery** of 83.01%
- High temperature promote formation of carboxylic acids, eg. Acetic acids
- pH drop to as low as 5.63
## Recent Application

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</thead>
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<tr>
<td>Corn stover</td>
<td><em>Alkaline hydrogen peroxide</em></td>
<td>Mittal et al. (2017)</td>
</tr>
<tr>
<td></td>
<td>Solid loading: 1:10 (w/v)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T = 50 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time = 3 h</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pH = 11.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H2O2 concentration = 250 mg</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H2O2 / g dry biomass</td>
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</table>

**Key findings:**
- Lignin removal of **80%**
- Glucose yield of **90%**
- Xylose yield of **80%**
- Lignin extraction depends on peroxide concentration
Surface Morphology

Biomass after pretreatment
- Noticeable change in colour
- Reduced particle size
- Disorder fibrils and formation of tiny holes
- Cell disjoining with dimmer cell wall

(Morone et al. 2017)  (Mittal et al. 2017)
**Recent Applications**

**Inhibitors**

**Acetic acid** – Yes. Degradation of acetyl group in removed hemicellulose.

**Total phenolic content** – Yes. Inhibitor to fermenting strain.

**Furfural** – None

**5-hydroxymethylfurfural (HMF)** – None
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Advantages & Limitations

Advantages:
- Hydrolysate detoxification
- Less cellulose degradation
- Mild conditions
- Highly fermentable pretreated biomass
- Absent of furfural and hydroxymethylfurfural (HMF)
- Environmentally benign chemicals
- Availability

Limitations:
- High pH to deprotonate hydrogen peroxide
- High peroxide loadings may affect economic viability
- Required relatively long time at ambient conditions
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Conclusion

Alkaline hydrogen peroxide pretreatment is compatible to subsequent bioconversion, safer decomposition products, and flexible in different process requirement, hence provide an alternative sustainable route to effective valorize biomass for biofuels or biochemical productions.

Recommendation

- Ambient temperature in effective biomass processing
- Synergism of alkaline hydrogen peroxide in stage-wise pretreatment strategies
- Recyclability of alkaline hydrogen peroxide


Balat, M 2011, 'Production of bioethanol from lignocellulosic materials via the biochemical pathway: a review', *Energy conversion and management*, vol. 52, no. 2, pp. 858-75.


Li, Z, Chen, CH, Liu, T, Mathrubootham, V, Hegg, EL & Hodge, DB 2013, 'Catalysis with CuII (bpy) improves alkaline hydrogen peroxide pretreatment', *Biotechnology and bioengineering*, vol. 110, no. 4, pp. 1078-86.


Teixeira, LC, Linden, JC & Schroeder, HA 1999, 'Alkaline and peracetic acid pretreatments of biomass for ethanol production', in *Twentieth Symposium on Biotechnology for Fuels and Chemicals*, pp. 19-34.


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Thank you