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

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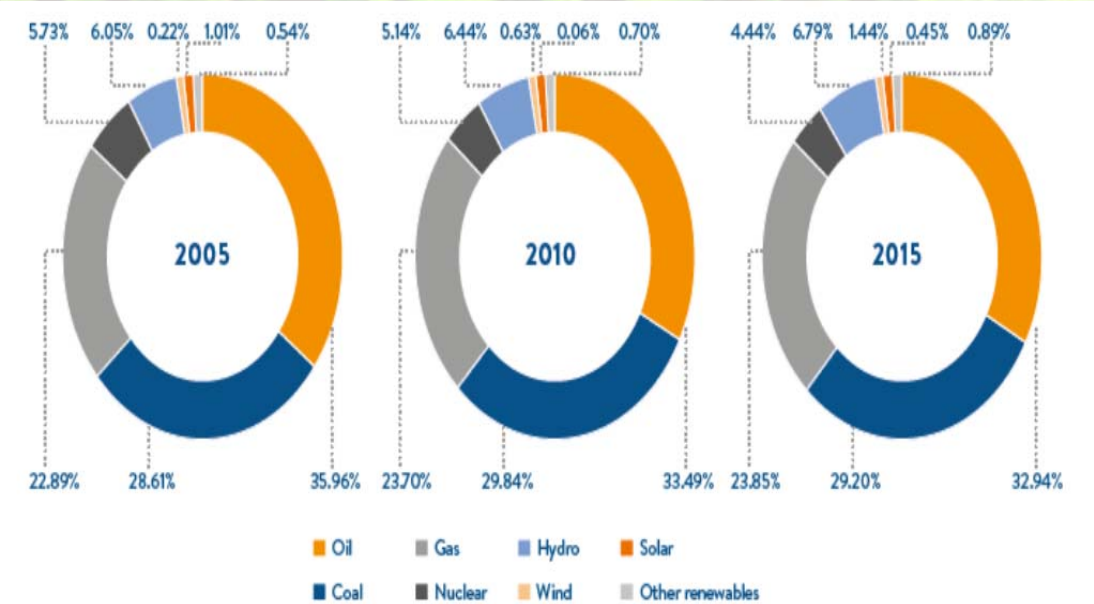
Outline of Contents

1 Introduction



(World Resource Council, 2016)

Bio-refinery:

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

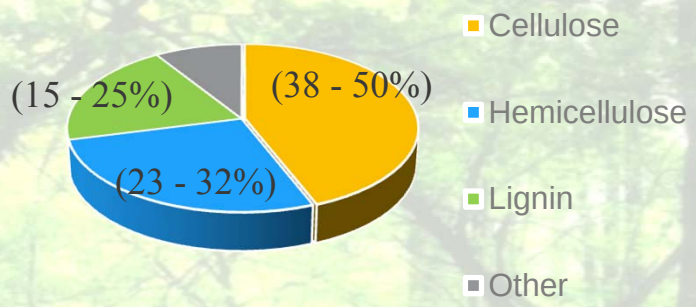
Waste Valorization – Any processes or activities that **utilize** or **convert** normally neglected **waste** to highly useful and value added **products** or **energy** sources. (Kabongo 2013)

Outline of Contents

2 Problem Statement

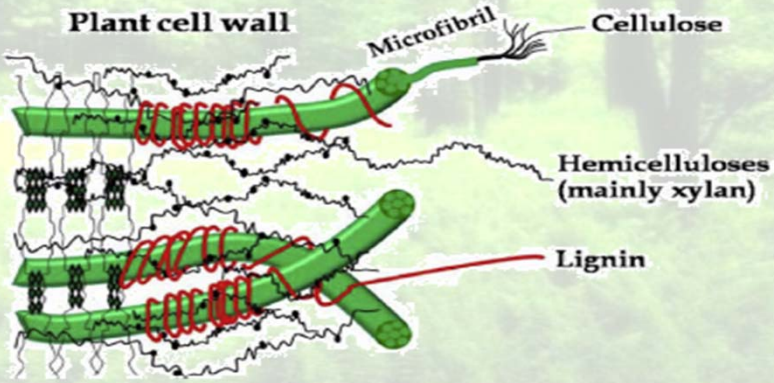
Lignocellulosic biomass waste:

- Hundreds billion tonnes produced annually
- Usually **neglected**
- Potential **feedstock** for waste valorization



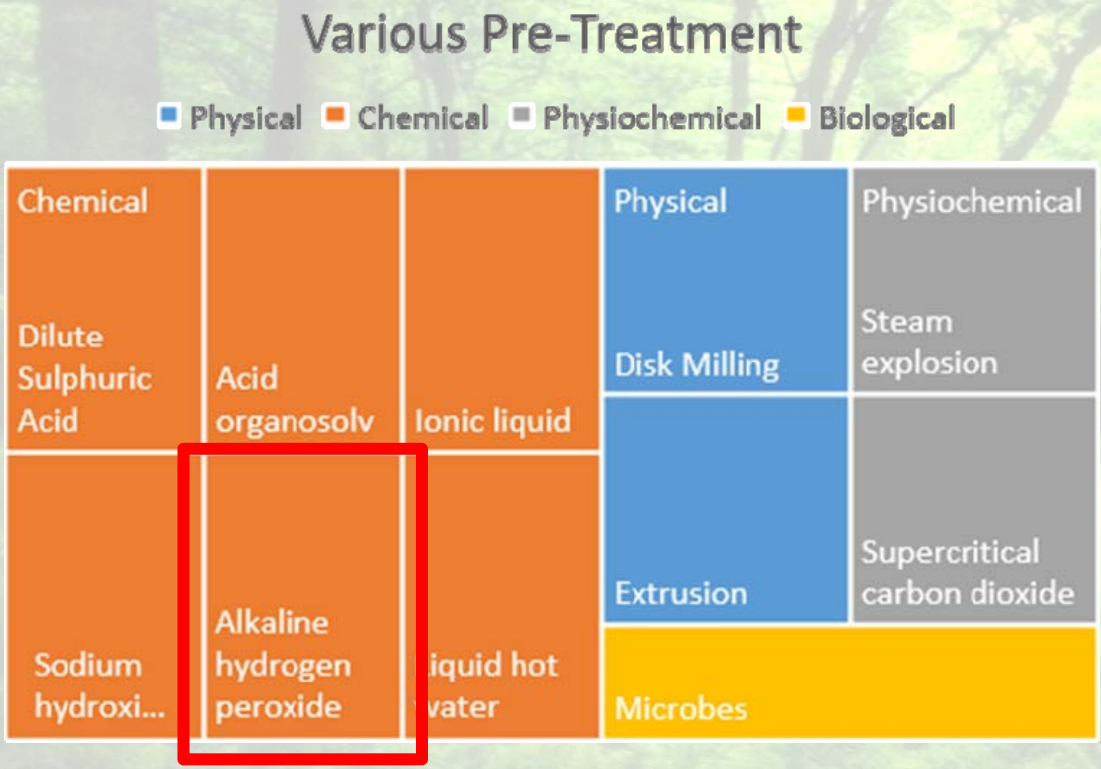
Challenge in Utilizing Lignocellulosic Biomass:

- **Recalcitrant** nature
- Lignin-carbohydrate complex
- Physical and Chemical Resistant



(Yang et al, 2015)

Existing Pretreatment Methods



Alkaline Hydrogen Peroxide:

- **Extraordinary** performance
- Little sugar degradation
- **Mild** conditions

Outline of Contents

Background Information

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

Hydroperoxyl anion:

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

$$H_2O_2 + HO^- \xrightarrow{\text{Alkaline}} HOO^- + H_2O$$

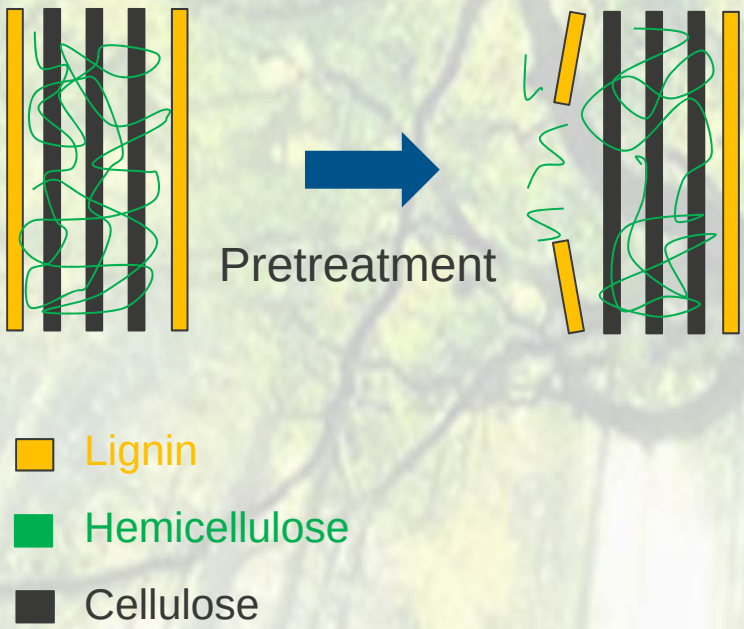
$$H_2O_2 + HOO^- \longrightarrow HO\bullet + O_2^{-}\bullet + H_2O$$

Hydroxyl radical (HO•) and Superoxide anion radical (O_2^{-}•):

- Strong oxidants
- **Oxidization** of lignin
- **Fragmentation** of biomass
- **Destruction** of ester, ether cross-links and cleavage of β-O-4 bonds
- Hemicellulose **solubilisation** and cellulose **depolymerisation**

Outline of Contents

4 Recent Applications



Alkaline Hydrogen Peroxide

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

Recent Application

Biomass	Initial pretreatment	References
Hybrid poplar 	*Cu^{II}(bpy)-catalyzed alkaline hydrogen peroxide* **Solid loading = 1:10 (w/v)** **T = Ambient temperature** **Time = 48 h** **pH = 11.5** **H_2O_2 concentration = 10 g/L** **Catalyst concentration = 5mM**	Li et al. (2013)

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

Biomass	Initial pretreatment	References
Jerusalem artichoke 	*Ultrasonic assisted alkaline hydrogen peroxide* **Ultrasonic frequency = 40kHz** **Ultrasonic power = 500 W** **Solid loading = 1:20 (w/v)** **T = 50 °C** **Time = 120 min** **NaOH concentration = 2% (w/v)** **H2O2 concentration = 5% (w/v)**	Li et al. (2016)

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

Recent Application

Biomass	Initial pretreatment	References
Douglas fir 	*Alkaline hydrogen peroxide* **Solid loading = 1:10 (w/v)** **T = 180 °C** **Time = 60 min** **pH = 11.6** **H2O2 concentration = 4% (w/w)**	Alvarez-Vasco and Zhang (2013)

Key findings:

- **Delignification** of **22%**
- **Glucomannan** removal of **78%**
- Little degradation of cellulose while removing protective barrier

Recent Application

Biomass	Initial pretreatment	References
Rice Straw 	*Alkaline hydrogen peroxide-assisted wet air oxidation* **Soaking in alkaline hydrogen peroxide** **Time = 14 h** **pH = 11.9** **H2O2 concentration = 0.5 % (w/v)** **Pressurized with 6 bar air at 190 °C for 20 min with mixing at 200 rpm**	Morone et al. (2017)

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

Biomass	Initial pretreatment	References
Corn stover 	*Alkaline hydrogen peroxide* **Solid loading: 1:10 (w/v)** **T = 50 °C** **Time = 3 h** **pH = 11.5** **H2O2 concentration = 250 mg H2O2 / g dry biomass**	Mittal et al. (2017)

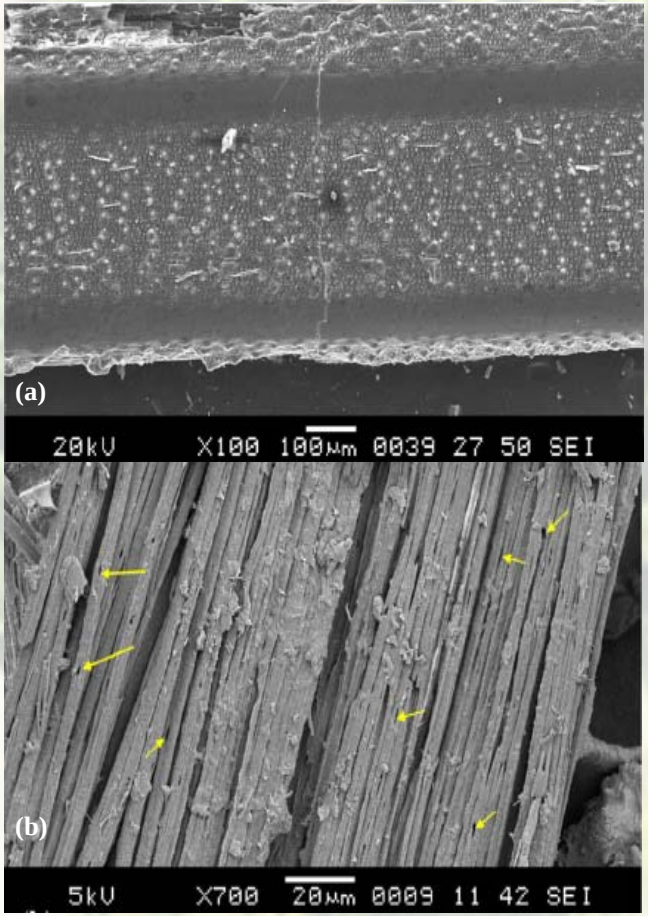
Key findings:

- **Lignin** removal of **80%**
- **Glucose** yield of **90 %**
- **Xylose** yield of **80%**
- Lignin extraction depends on peroxide concentration

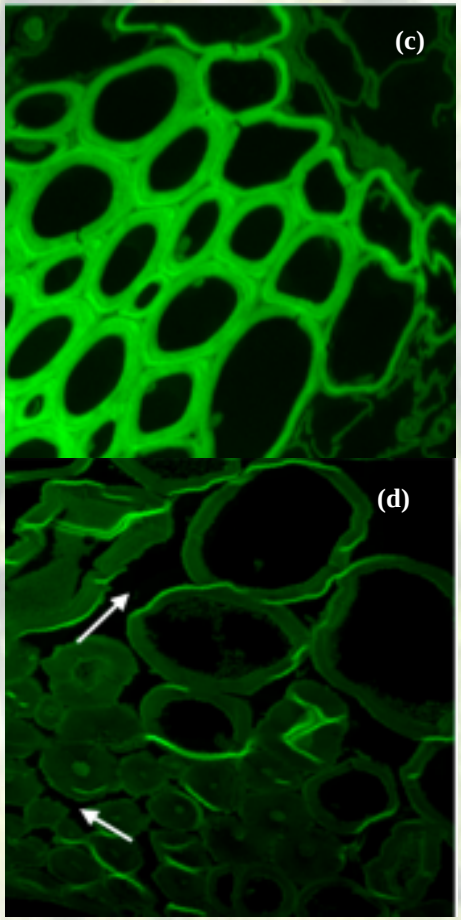
Surface Morphology

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)

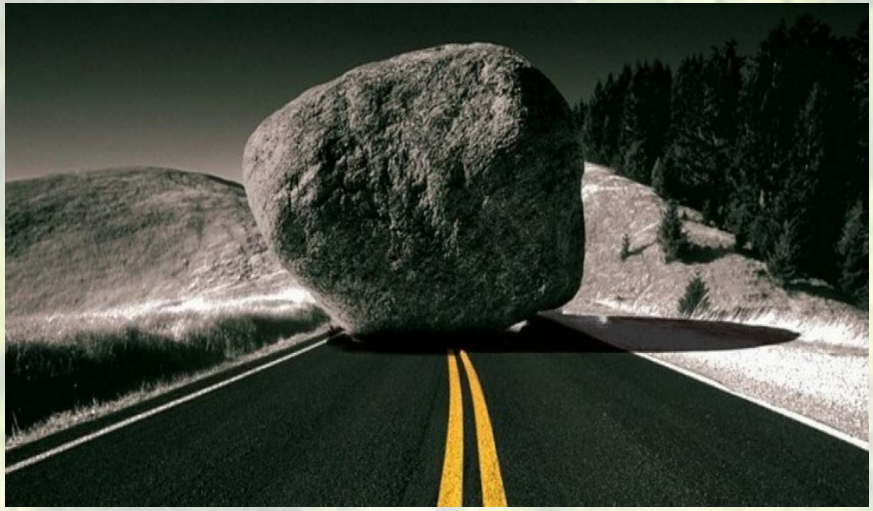
Inhibitors

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

Total phenolic content – Yes. Inhibitor to fermenting strain.

Furfural – None

5-hydroxymethylfurfural (HMF) – None



Outline of Contents

5 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

Outline of Contents

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

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Q&A