Transformation of oil palm fronds into pentose sugars using copper (II) sulfate pentahydrate with the assistance of chemical additive

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1. Introduction
In 2010 (Yunus et al., 2010), per million ton FFB processed:

- OPT = 7 million tons, EFB = 0.23 million tons
- **OPF = 26.2 million tons!!!**

**Lignocellulosic biomass**

- Agricultural residues
  (corn stover, wheat straw, etc…)
- Energy crops
  (switchgrass, miscanthus straw, etc…)
- Forestry residues
  (wood chips, poplar, etc…)

![Fig. 1 Oil palm fronds (OPF), with leaflets removed](adapted from http://www.mightyjacksparrow.com)
Introduction

Dwindling fossil fuel reserves

Search for alternative energy sources

**Current trend**: Fermentation of biomass into more useful products

![Process block diagram of a biorefinery system, consisting of biomass pretreatment and fermentation](https://public.ornl.gov)

*Fig. 2* Process block diagram of a biorefinery system, consisting of biomass pretreatment and fermentation (adapted from https://public.ornl.gov)
Introduction (Continued…)

• Biomass recalcitrance
• Difficult to be converted into fermentable sugars
• Without pretreatment → low sugar yield

Fig. 3 Lignocellulosic biomass structure
(adapted from Tomme et al., 1995)
Biomass pretreatments:

• Chemical (acid hydrolysis, alkali, ionic liquid, etc)
• Physical (grinding, milling, etc)

Constraints:

• Operate at extreme conditions (150-180°C, high pressures)
• Energy intensive
Inorganic salt pretreatment

i. **Tested:** NaCl, MgCl$_2$, CuCl$_2$, FeCl$_3$, AlCl$_3$, etc…

ii. **Comparable to acid hydrolysis:**

   Effective hydrolysis rates and sugar yields of hemicellulose

**Mechanism:-**

- Complex cation $[M(H_2O)_n]^{z+}$ acts as nucleophile (**Lewis acid**)
- Production of $H_3O^+$ ion, better effect than acid (**Bronsted acid**)

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**Introduction (Continued…)**
Addition of oxidizing agent:

- \( \text{H}_2\text{O}_2 \): Source of \( \text{OH}\bullet \) radicals
  
  Non-selective oxidation process
  
  Proven to improve sugar hydrolysis

- Diaz et al. (2014): Addition of \( \text{H}_2\text{O}_2 \) \( \Rightarrow \) sugar recovery \( \uparrow \) 75%

- Kato et al. (2014): \( \text{H}_2\text{O}_2 \) + \( \text{Fe}^{2+} \) \( \Rightarrow \) enzymatic hydrolysis \( \uparrow \)
Oxidizing agent-assisted pretreatment

Addition of oxidizing agent:

• $\text{Na}_2\text{S}_2\text{O}_8$ : Source of $\text{SO}_4^{\cdot}$ radicals
  
  Stronger oxidants than $\text{OH}^{\cdot}$
  
  Degrade organic compounds

• Never tested in biomass pretreatment
2. Research Aims
Research Aims

To develop a novel pretreatment system using inorganic salt and oxidizing agent, and to evaluate its efficiency on pentose sugar recovery under less severe conditions.
Oxidizing agent-assisted pretreatment

Theory: Oxidative delignification of aromatic ring in lignin

Fig. 4 Chemical structure of lignin (adapted from http://www.lignoworks.ca)
3. Research Methodology

Stage A: Inorganic salt pretreatment

Stage B: Oxidizing agent-assisted pretreatment
Methodology

Stage 1
OPF + Salt solution = Mixture solution
S:L ratio = 1:10
CuSO₄·5H₂O (0.2M-0.8M)

Stage 2
Mixture solution + H₂O₂ / Na₂S₂O₈
(1.5 - 6 % v/v)

Reaction at 120°C for 30min

(1) HPLC analysis for sugars
(2) Mechanism
(3) Characterization studies
(Fe-SEM, FTIR, BET, etc....)
4. Pentose Sugar Recovery in Hydrolysate

Stage A: Inorganic salt pretreatment

Stage B: Oxidizing agent-assisted pretreatment
(1) HPLC analysis of liquid fraction
Effect of inorganic salt concentration

Fig. 5 Sugar recovery from OPF using CuSO₄⋅5H₂O. Different letters signify different significance levels

Xylose yield of 0.8 g/L at 4.1%.
Arabinose yield of 1.0 g/L at 35.2%.
Observations

- No significant changes with increase from 0.2M – 0.8M of CuSO$_4$.5H$_2$O
- Inverse relationship between hydration levels and solvating ability (Awosusi et al., 2015)
- Saturation of water molecules around cation (Leipner et al., 2000)
- Divalent salt not as effective as trivalent (Sun et al., 2011)
Effect of H$_2$O$_2$ concentration

![Bar chart showing sugar recovery from OPF using CuSO$_4$.5H$_2$O assisted with H$_2$O$_2$. Different letters signify different significance levels.](chart.png)

Fig. 6 Sugar recovery from OPF using CuSO$_4$.5H$_2$O assisted with H$_2$O$_2$. Different letters signify different significance levels.

Xylose yield of 1.3 g/L at 6.6%.

Arabinose yield of 1.1 g/L at 39.1%.
Observations

• At 1.5% (v/v) H₂O₂, pentose sugars increased slightly

• Source of hydroxyl (OH•) radicals in presence of copper ions (Peng et al., 2012)

• Excessive amounts of H₂O₂ caused secondary reactions (Zazo et al., 2005)
Effect of Na$_2$S$_2$O$_8$ concentration

Fig. 7 Sugar recovery from OPF using CuSO$_4$·5H$_2$O assisted with Na$_2$S$_2$O$_8$. Different letters signify different significance levels.

Xylose yield of 8.2 g/L at 41.0%.

Arabinose yield of 0.9 g/L at 33.1%.
Observations

• At 4.5% (v/v) Na$_2$S$_2$O$_8$, pentose sugars increased significantly

• Source of sulfate (SO$_4$•) radicals (Zhang et al., 2015)

• Excessive Na$_2$S$_2$O$_8$ caused unwanted reactions that compete to consume SO$_4$• (Rastogi et al., 2009)
(2) Proposed mechanism
Mechanism of H$_2$O$_2$/ Na$_2$S$_2$O$_8$ action on inorganic salt

1) Cu$^{2+}$ + H$_2$O$_2$ → Cu$^+$ + HO$_2$• + H$^+$
   Cu$^+$ + H$_2$O$_2$ → Cu$^{2+}$ + OH• + OH$^-$ (Simpson et al., 1988)

2) Cu$^{2+}$ + S$_2$O$_8^{2-}$ → Cu$^{3+}$ + SO$_4$•$^-$ + SO$_4^{2-}$ (Liu et al., 2012)
Fig. 8 Schematic illustration of the lignocellulosic components in biomass
Proposed Mechanism

Fig. 9 Proposed mechanism for the synergistic action of hydroxyl/sulfate radicals and inorganic salt during pretreatment of OPF

0.2 mol/L of CuSO$_4$·5H$_2$O $+$ 4.5% (v/v) Na$_2$S$_2$O$_8$

$T = 120^\circ$C, $t = 30$ min

Raw OPF $\rightarrow$ Pretreated OPF

Non-structural sugars
5. Characterization of Solid Residues

Stage A: Inorganic salt pretreatment

Stage B: Oxidizing agent-assisted pretreatment
(3) Characterization of solid fraction
5 Characterization of Solid Residues (Continued…)

FE-SEM

Fig. 10 FE-SEM images of raw and pretreated OPF at x300 magnification

- **Raw OPF**
- **CuSO₄·5H₂O** only
- **CuSO₄·5H₂O + H₂O₂**
- **CuSO₄·5H₂O + Na₂S₂O₈**

**Lignin**

**Hemicellulose**

**Cellulose**
BET

Specific surface area:

• Raw OPF (before pretreatment) = 0.3752 m\(^2\)/g

• 0.2M CuSO\(_4\)·5H\(_2\)O only = 0.4587 m\(^2\)/g

• 0.2M CuSO\(_4\)·5H\(_2\)O + 1.5% H\(_2\)O\(_2\) = 0.4872 m\(^2\)/g

• 0.2M CuSO\(_4\)·5H\(_2\)O + 4.5% Na\(_2\)S\(_2\)O\(_8\) = 0.6952 m\(^2\)/g

Oxidizing agent caused more severe breakage → higher surface area
Characterization of Solid Residues (Continued…)

FTIR

Fig. 11 FTIR spectra of raw and pretreated OPF
### Table 1 Performance of various pretreatment systems utilizing OPF

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Pretreatment conditions</th>
<th>Sugar recovery</th>
<th>Ref.</th>
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</table>
| 841 µm OPF particles | 1) Soaked in 2.0 mol/L of NaOH at room temperature for 24h  
2) Acid hydrolysis with 10.0% (v/v) H₂SO₄ for 121°C and 30 min | 1) Maximum reducing sugar concentration of 0.0811 g/L | Sabihahanim et al. (2012) |
| <1 mm OPF particles | 1) Auto-hydrolysis for 121°C and 1h  
2) Enzymatic hydrolysis using 16 U xylanase for 48h | 1) Maximum xylose concentration of 0.795 g/L | Siti Sabrina et al. (2013) |
| 0.5 mm OPF particles | 1) Auto-hydrolysis for 121°C and 60 min  
2) Enzymatic hydrolysis using 4 U Trichoderma viride endo-(1, 4)-β-xylanase/100mg hydrolysate, at 40°C and 48h | 1) Arabinose and xylose yields of 19.24% (w/w) and 25.64% (w/w), respectively | Sabihahanim et al. (2011) |
| <1 mm OPF particles | 1) Hot compressed water for 175°C and 12.5 min | 1) Highest concentration of 0.4434 g/L xylose and 0.0633 g/L glucose | Goh et al. (2010) |
| 125-706 µm OPF particles | 1) Soaked in 7% (w/w) aqueous ammonia for 80°C and 20h  
2) Simultaneous saccharification and fermentation using 60 FPU Accellerase 1000/g glucan and 30 CBU β-glucosidase/g glucan, at 38°C and 48h | 1) Xylose concentration of 7.6 g/L (62.4% recovery) | Jung et al. (2012) |
| ≤0.5mm OPF particles | 1) 0.2 mol/L of CuSO₄·5H₂O + 4.5% (v/v) Na₂S₂O₅ reaction at 120°C and 30mins | 1) Xylose concentration of 8.2 g/L (41.0% recovery) and arabinose concentration of 0.9 g/L (33.1% recovery) | This study |
6. Communications of Results
Communications of Results

Conference Proceedings:


Submitted Publications:


- **Loow YL**, Wu TY, Yang GH, Jahim JM, Mohammad AW (2016) Role of energy irradiation as an assistive technique during the pretreatment of lignocellulosic biomass for improving reducing sugars recovery. *Cellulose* (Accepted with conditions). Impact factor: 3.573 (Q1)

7. References
References


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Thank You