MONASH University Malaysia

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

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Outline of Content

1. Introduction

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)

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!!!**

Dwindling fossil fuel reserves

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Search for alternative energy sources

Current trend: Fermentation of biomass into more useful products

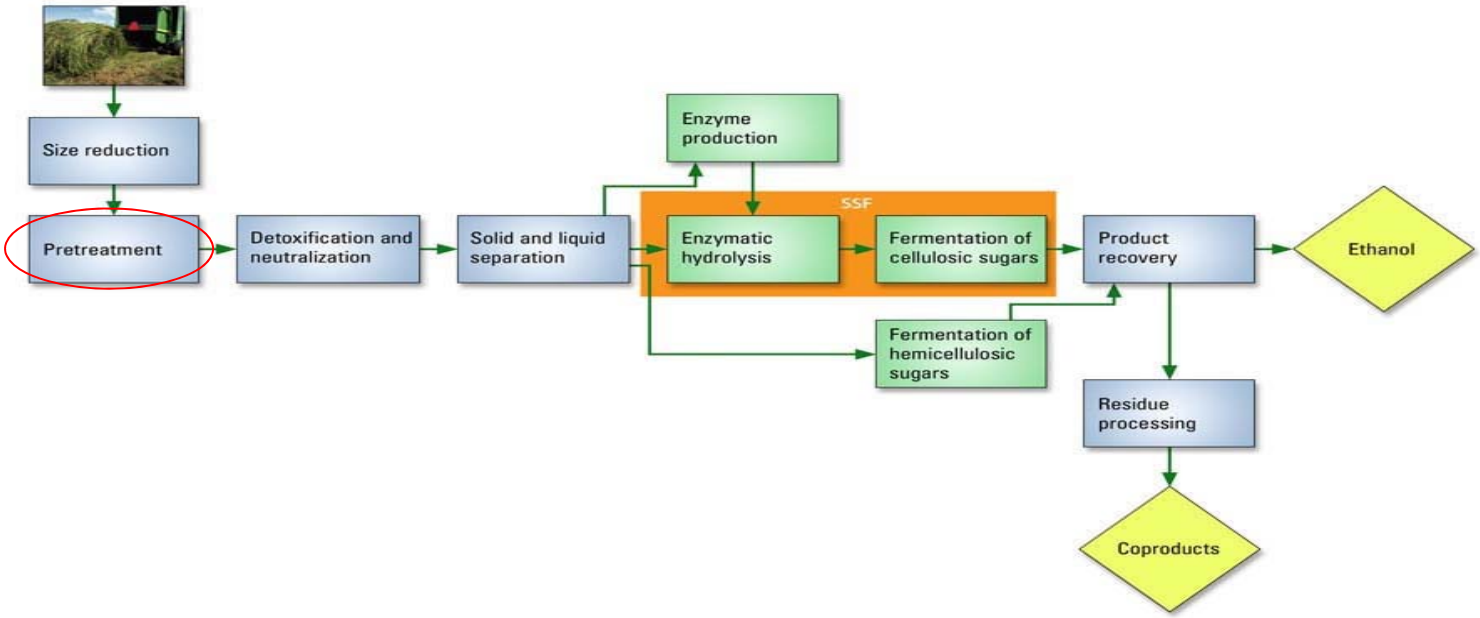


Fig. 2 Process block diagram of a biorefinery system, consisting of biomass pretreatment and fermentation (adapted from https://public.ornl.gov)

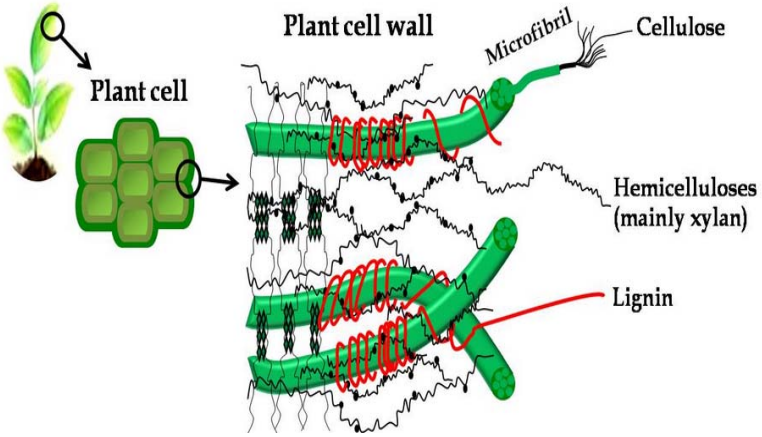


Fig. 3 Lignocellulosic biomass structure

(adapted from Tomme et al., 1995)

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

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)

Oxidizing agent-assisted pretreatment

Addition of oxidizing agent:

- H_2O_2 : Source of OH• radicals

  Non-selective oxidation process

  Proven to improve sugar hydrolysis

- Diaz et al. (2014) : Addition of H_2O_2 = sugar recovery ↑ 75%

- Kato et al. (2014) : $H_2O_2 + Fe^{2+}$ = enzymatic hydrolysis ↑

Oxidizing agent-assisted pretreatment

Addition of oxidizing agent:

- $Na_2S_2O_8$: Source of SO_4^{-}• radicals

  Stronger oxidants than OH•

  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

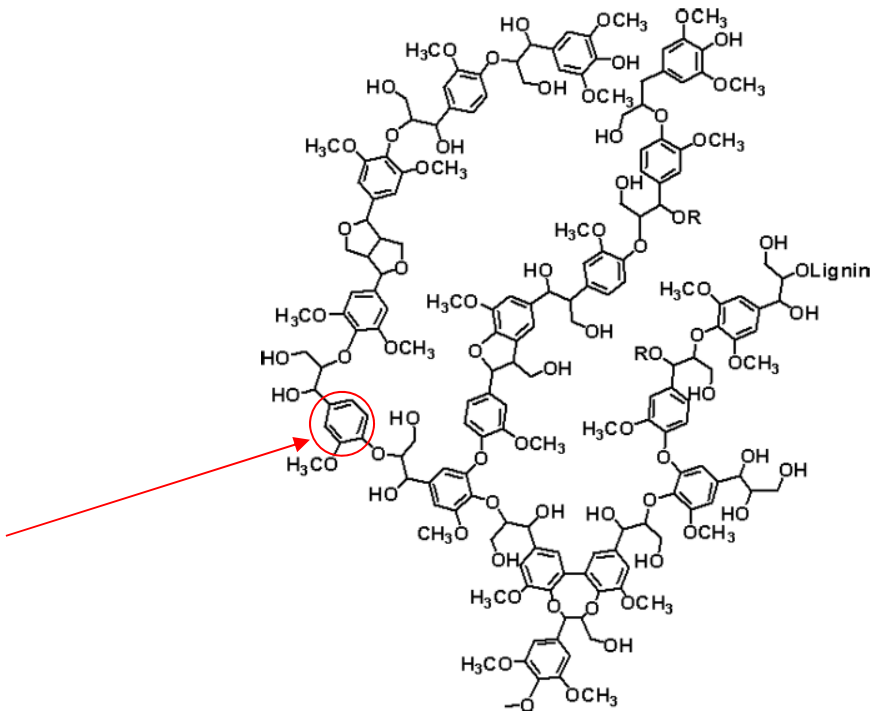


Fig. 4 Chemical structure of lignin (adapted from http://www.lignoworks.ca)

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
$CuSO_4.5H_2O$ (0.2M-0.8M)

Stage 2

Mixture solution + H_2O_2 / $Na_2S_2O_8$
(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

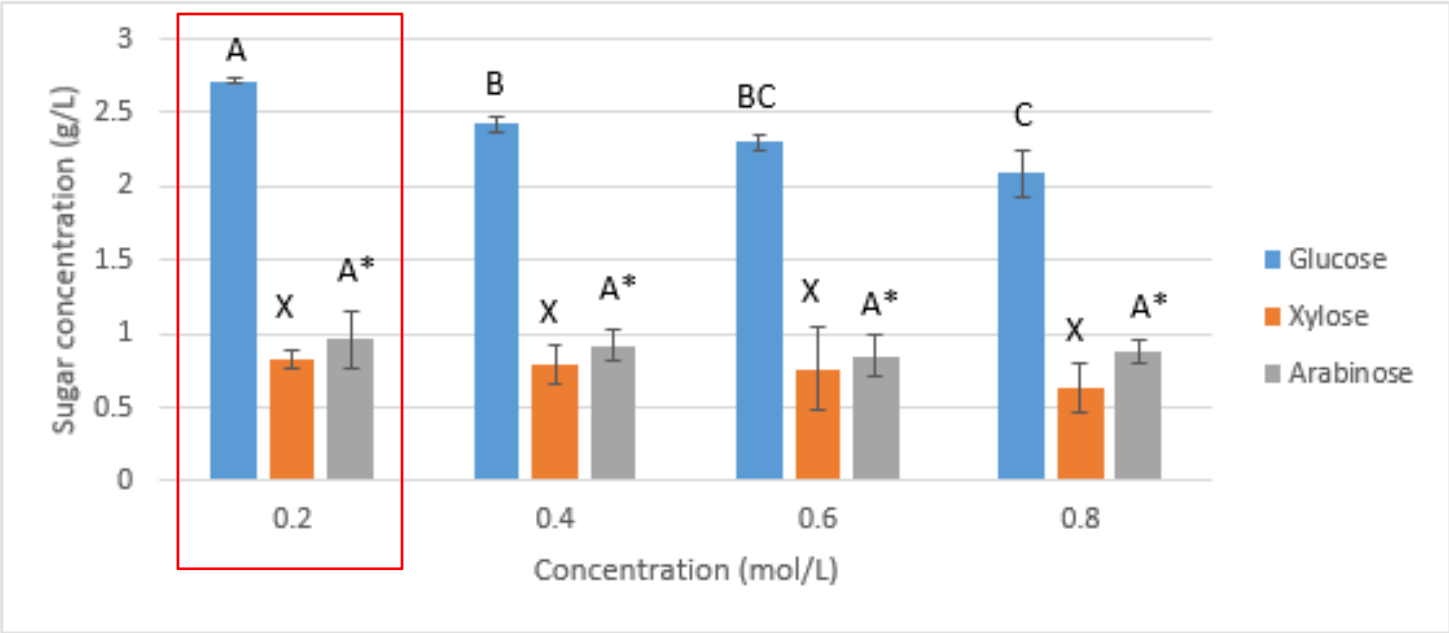


Fig. 5 Sugar recovery from OPF using $CuSO_4.5H_2O$. Different letters signify different significance levels

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 $CuSO_4.5H_2O$
- 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_2O_2 concentration

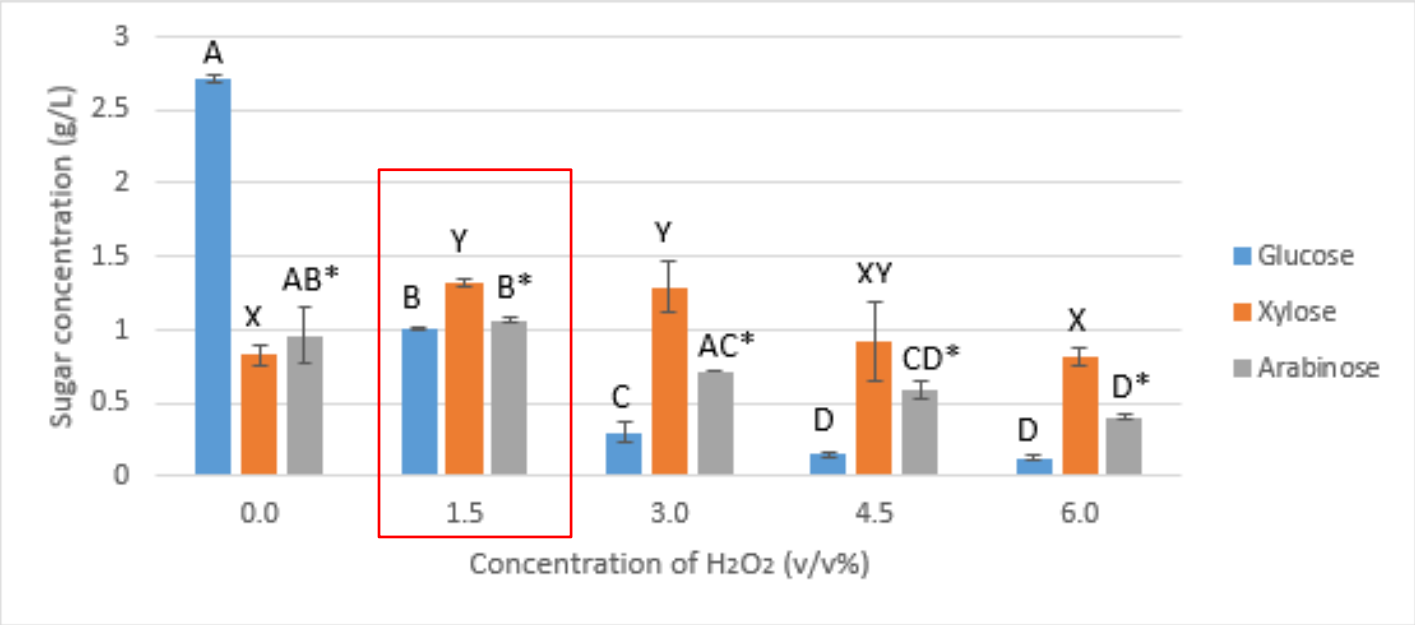


Fig. 6 Sugar recovery from OPF using $CuSO_4.5H_2O$ assisted with H_2O_2. Different letters signify different significance levels

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) H_2O_2, pentose sugars increased slightly
- Source of hydroxyl (OH•) radicals in presence of copper ions (Peng et al., 2012)
- Excessive amounts of H_2O_2 caused secondary reactions (Zazo et al., 2005)

✓ Effect of $Na_2S_2O_8$ concentration

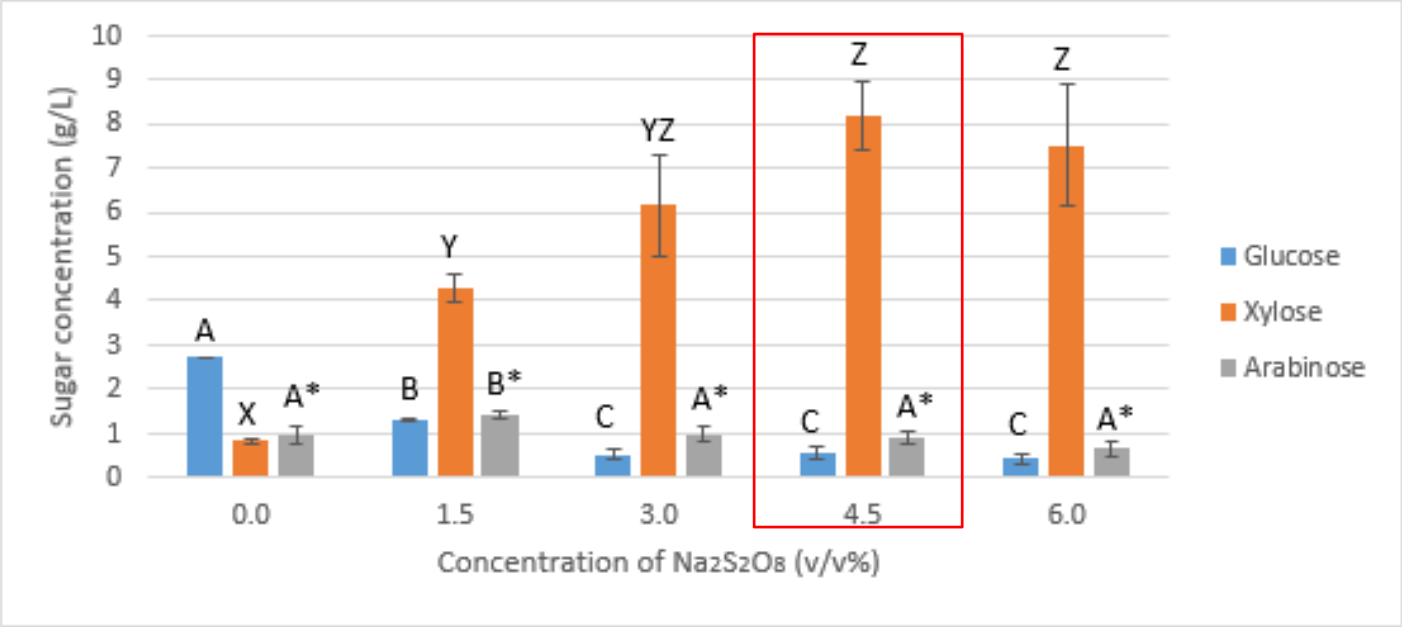


Fig. 7 Sugar recovery from OPF using $CuSO_4.5H_2O$ assisted with $Na_2S_2O_8$. Different letters signify different significance levels

Xylose yield of 8.2 g/L at 41.0%.

Arabinose yield of 0.9 g/L at 33.1%.

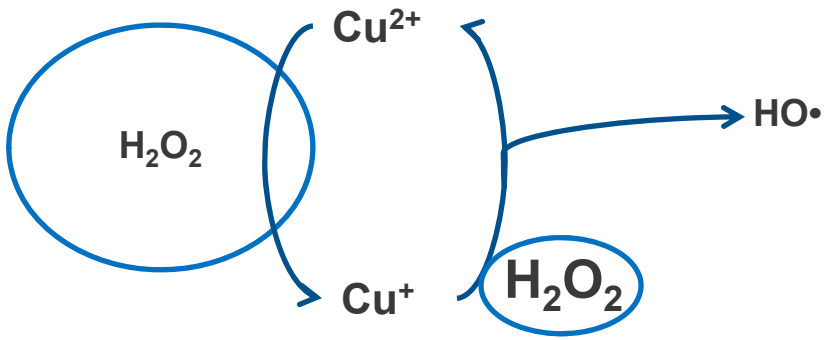
Observations

- At 4.5% (v/v) $Na_2S_2O_8$, pentose sugars increased significantly
- Source of sulfate (SO_4^{-}•) radicals (Zhang et al., 2015)
- Excessive $Na_2S_2O_8$ caused unwanted reactions that compete to consume SO_4^{-}• (Rastogi et al., 2009)

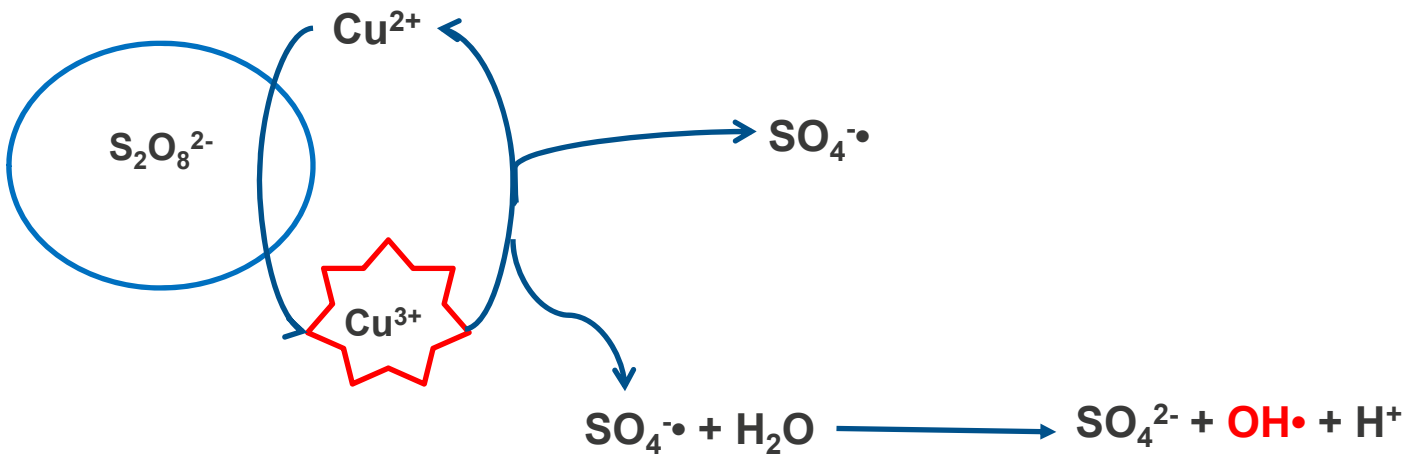
(2) Proposed mechanism

Mechanism of H_2O_2/ $Na_2S_2O_8$ action on inorganic salt

1) $Cu^{2+} + H_2O_2 \rightarrow Cu^{+} + HO_2\bullet + H^{+}$
$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + OH\bullet + OH^{-}$ (Simpson et al., 1988)



2) $Cu^{2+} + S_2O_8^{2-} \rightarrow Cu^{3+} + SO_4^{-}\bullet + SO_4^{2-}$ (Liu et al., 2012)



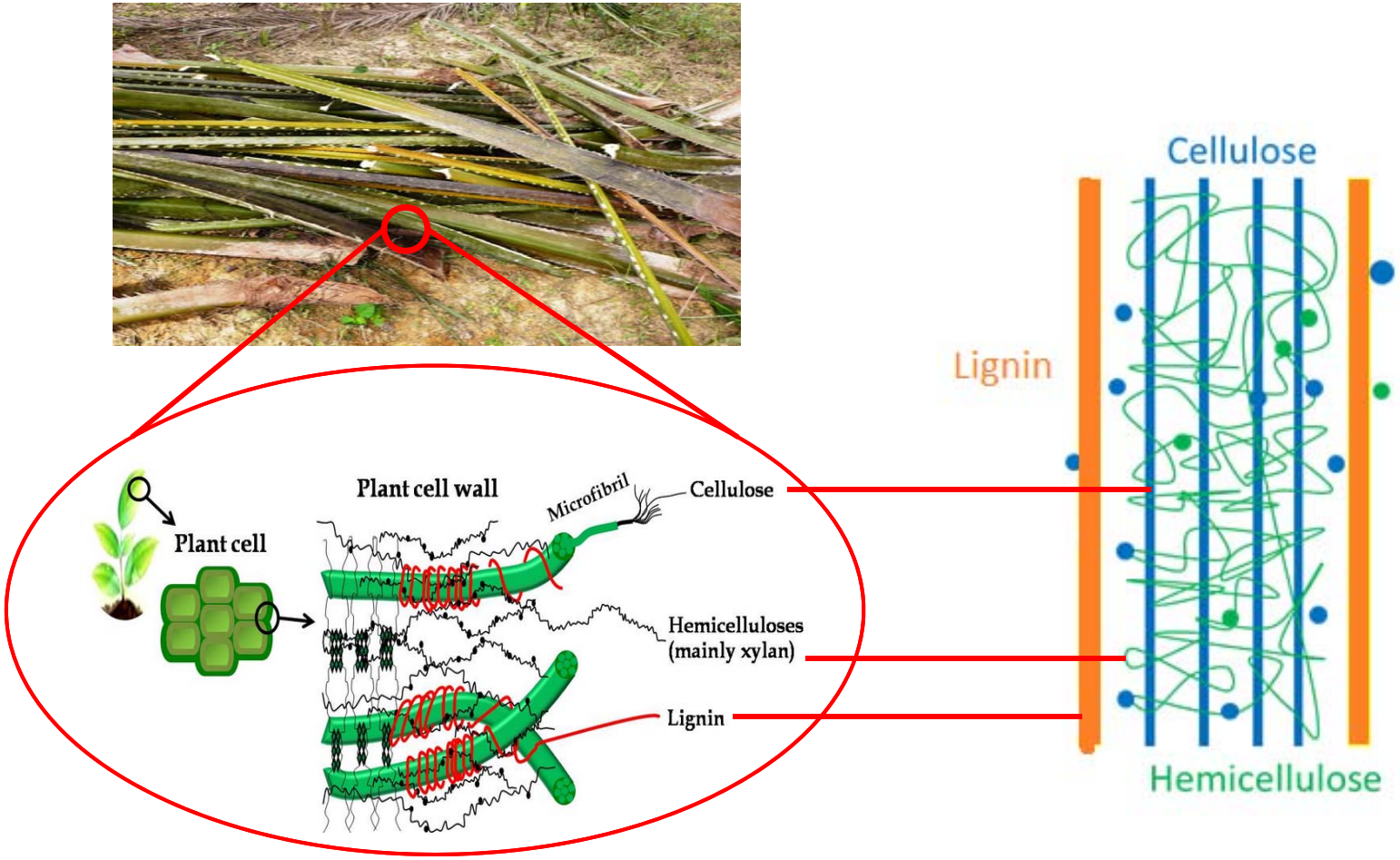


Fig. 8 Schematic illustration of the lignocellulosic components in biomass

Proposed Mechanism

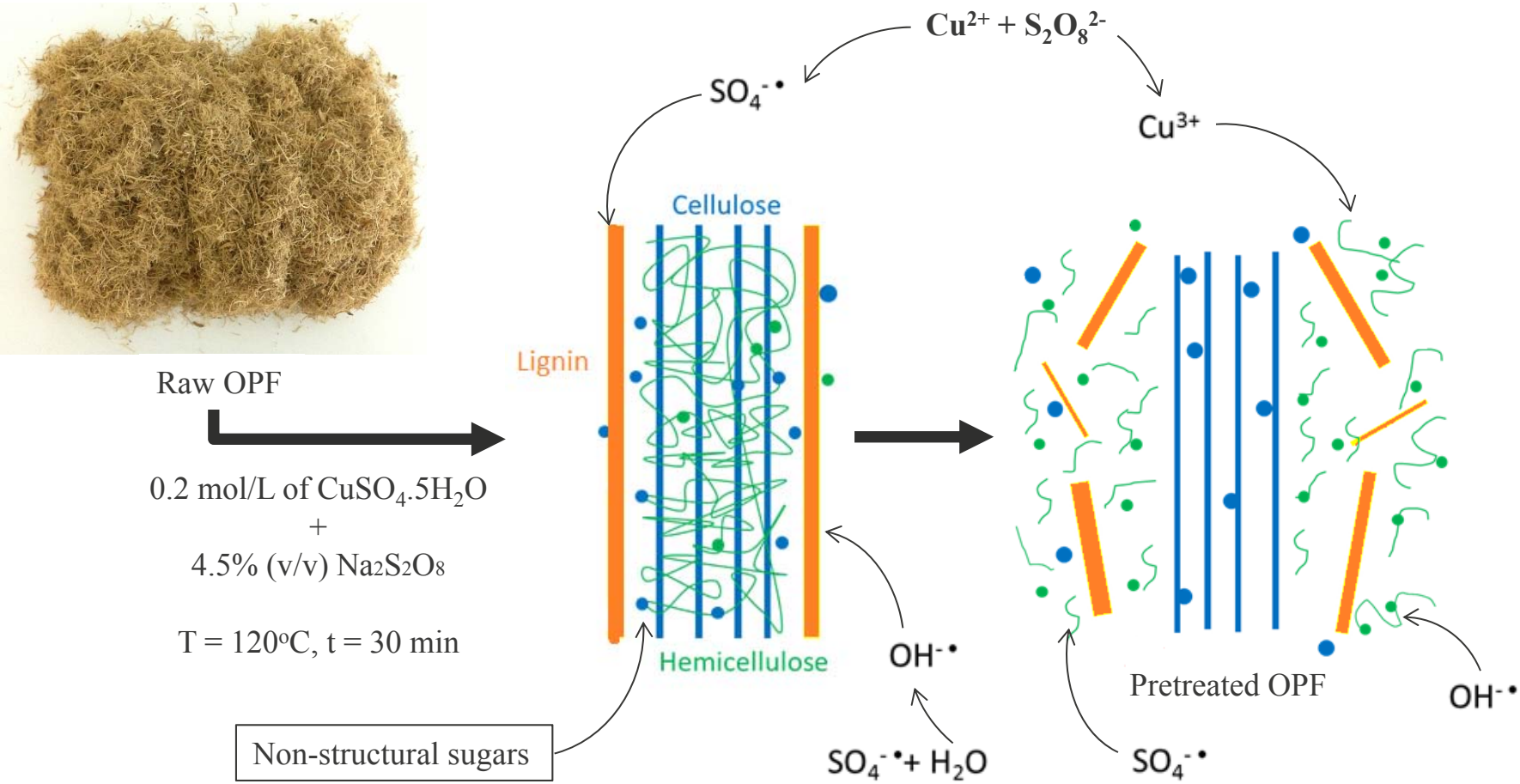


Fig. 9 Proposed mechanism for the synergistic action of hydroxyl/sulfate radicals and inorganic salt during pretreatment of OPF

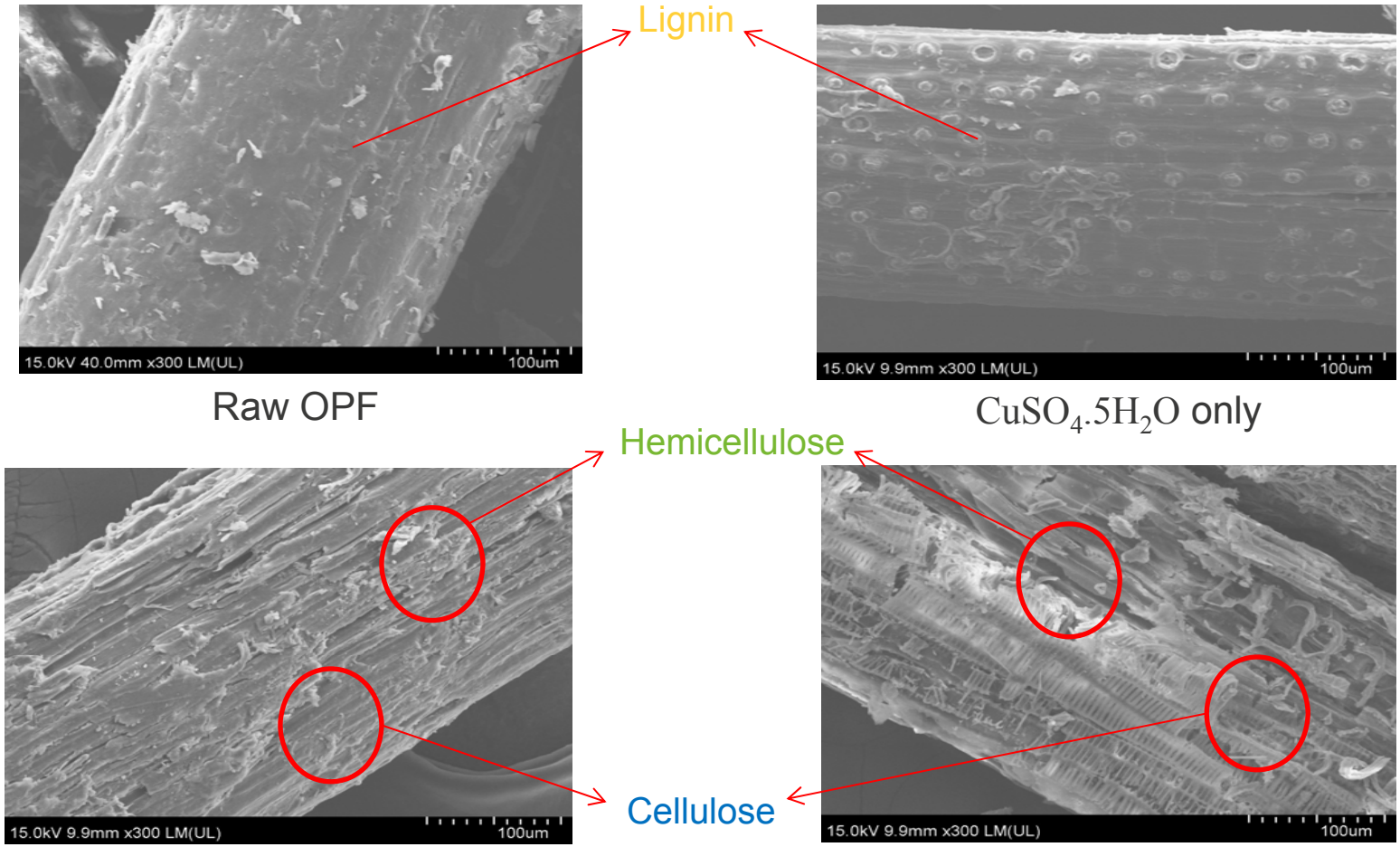
5. Characterization of Solid Residues

Stage A: Inorganic salt pretreatment

Stage B: Oxidizing agent-assisted pretreatment

(3) Characterization of solid fraction

FE-SEM



Raw OPF

$CuSO_4.5H_2O$ only

$CuSO_4.5H_2O + H_2O_2$

$CuSO_4.5H_2O + Na_2S_2O_8$

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

BET

Specific surface area:

- Raw OPF (before pretreatment) = 0.3752 m^2/g
- 0.2M $CuSO_4.5H_2O$ only = 0.4587 m^2/g
- 0.2M $CuSO_4.5H_2O$ + 1.5% H_2O_2 = 0.4872 m^2/g
- 0.2M $CuSO_4.5H_2O$ + 4.5% $Na_2S_2O_8$ = 0.6952 m^2/g

Oxidizing agent caused more severe breakage → higher surface area

FTIR

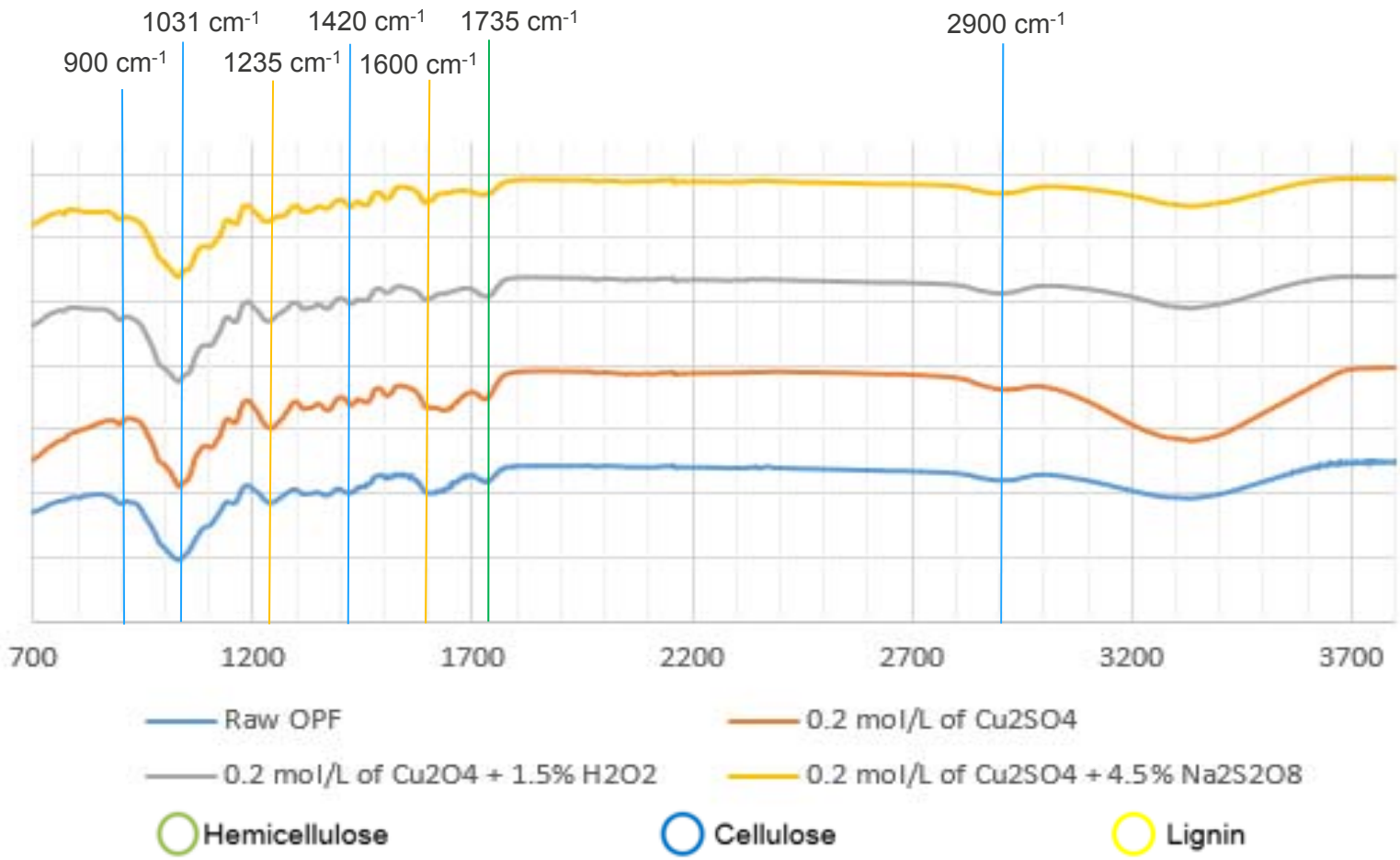


Fig. 11 FTIR spectra of raw and pretreated OPF

Table 1 Performance of various pretreatment systems utilizing OPF

Feedstock	Pretreatment conditions	Sugar recovery	Ref.
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) H_2SO_4 for 121°C and 30 min	1) Maximum reducing sugar concentration of 0.0811 g/L	Sabiha-Hanim 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	Sabiha-Hanim 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 $CuSO_4.5H_2O$ + 4.5% (v/v) $Na_2S_2O_8$ 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

Conference Proceedings:

- **Loow YL**, Wu TY, Jahim JM, Mohammad AW (2015) Sustainable conversion of lignocellulosic biomass into reducing sugars using alkaline pretreatment. In: APCChE 2015, 27 Sept – 01 Oct 2015, Melbourne, Victoria, 2015: 1418-1427.
- **Loow YL**, Wu TY, Jahim JM, Mohammad AW (2015) Using dilute acid hydrolysis pretreatment in transforming lignocellulosic biomass into reducing sugars. In: APCChE 2015, 27 Sept – 01 Oct 2015, Melbourne, Victoria, 2015: 1428-1438.

Submitted Publications:

- **Loow YL**, Wu TY, Tan KA, Lim YS (2015) Recent advances in application of inorganic salt pretreatment for transforming lignocellulosic biomass into reducing sugars. *Journal of Agricultural and Food Chemistry* 63(38): 8349-8363. Impact factor: 2.912 (Q1)
- **Loow YL**, Wu TY, Jahim JM, Mohammad AW, Teoh WH (2016) Typical conversion of lignocellulosic biomass into reducing sugars using dilute acid hydrolysis and alkaline pretreatment. *Cellulose* 23: 1491-1520. Impact factor: 3.573 (Q1)
- **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)
- **Loow YL**, Wu TY, Lim YS, Tan KA, Jahim JM, Mohammad AW (2016) Recovery of Sugars from Oil Palm Fronds using Inorganic Salts assisted with Hydrogen Peroxide/Sodium Persulfate Additives. *Energy and Environmental Science* (Under preparation). Impact factor: 20.523 (Q1)

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Acknowledgement

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- CYPRUS 2016 4th International Conference on Sustainable Solid Waste Management


Thank You