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Application of deep eutectic solvents in biomass valorization

Yang G.H., Wu T.Y., Loow Y. L., Ang L. Y.

LIVEWASTE

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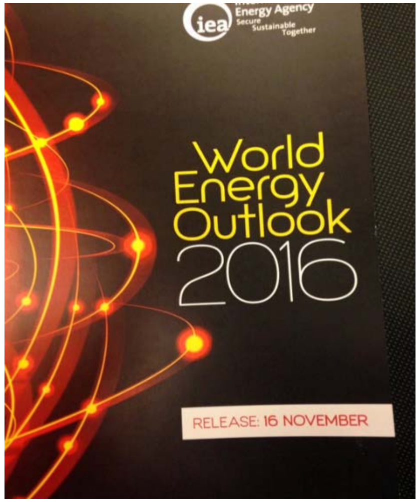
01

Introduction

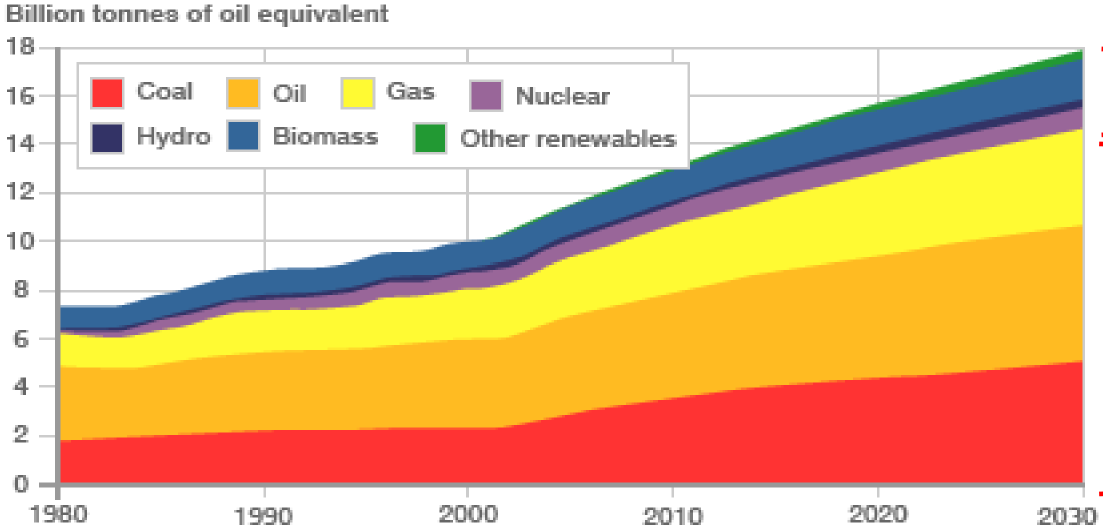
Problem Statement

Introduction of DES

Introduction



Projected Growth in Global Energy Demand

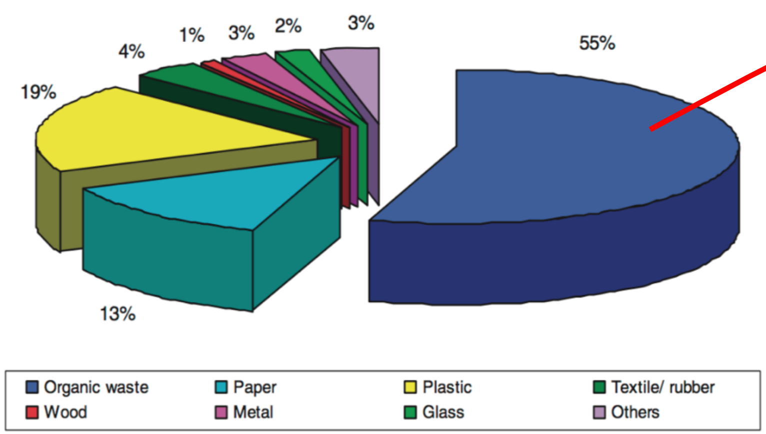


Renewable

Non-renewable

Fig. 1 Projected Growth in Global Energy Demand (adopted from IEA, 2016)

Breakdown of solid waste generated in Malaysia



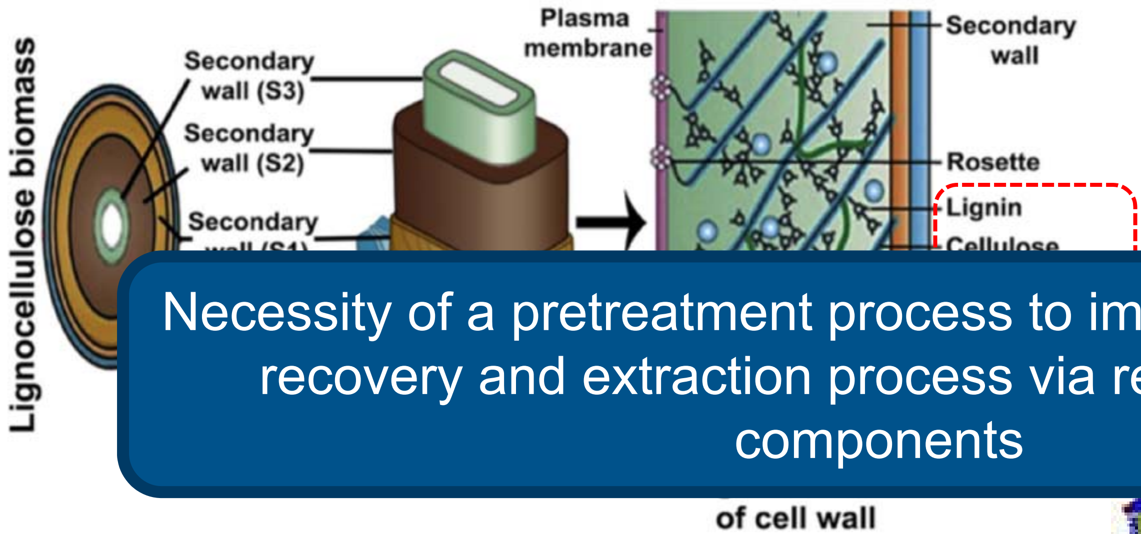
Organic waste
- Plant biomass

- Organic waste → Sugars → Energy
- Renewable source of energy
- Potential sustainable solution

Fig. 2 Segregation of solid waste in Malaysia (adopted from *Agamuthu and Fauziah, 2010*)

Introduction (Continued…)

Structural Component of Lignocellulosic Biomass



Necessity of a pretreatment process to improve overall sugar recovery and extraction process via removal of lignin components

Fig. 3 General components in lignocellulosic biomass (adopted from Loow et al., 2015)

Cellulose	40 - 50%
Hemicellulose	34 - 38%
Lignin	20 - 21%

Glucose

Xylose

Arabinose

Physical seal that protects cellulose and hemicellulose

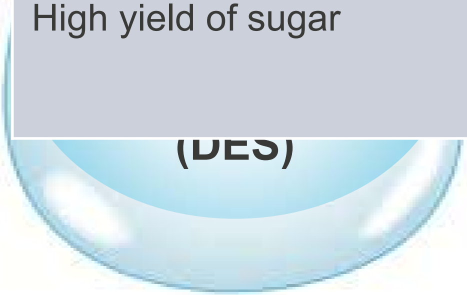
Fig. 4 Structural arrangement of lignin, hemicellulose and cellulose (adopted from Loow et al., 2015)

Introduction (Continued…)

Pretreatment method

Table 1 Comparison of conventional pre-treatment methods of lignocellulosic biomass (adopted from Amirkhani et al., 2015)

Advantages	Pretreatment	Disadvantages
Low cost of alkaline materials	Alkaline pretreatment	Formation of inhibitors Energy intensive Harsh operating condition
Simple pretreatment procedure	Dilute acid pretreatment	Production of inhibitors Hazards due to strong acid use
Mild operating conditions High yield of sugar	Ionic Liquid	Expensive Difficult to synthesize High toxicity Non-biodegradable



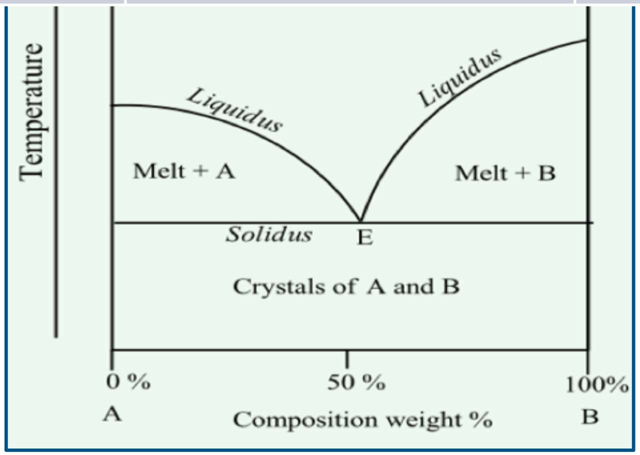


Fig. 5 Phase diagram showing the eutectic composition of DES (adopted from Abbott, 2007)

Sharp decrease in melting point than its constituents

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02

Literature Review

Synthesis of DES

Types and Properties of DES

Recent Developments of DES in Biomass Processing

Synthesis of DES (Heating with agitation)

Choline chloride

Urea

(HBD)

Mixing of a Hydrogen bond donor (HBD) and Hydrogen bond acceptor (HBA) in solid phase

Molar ratio: 1:2

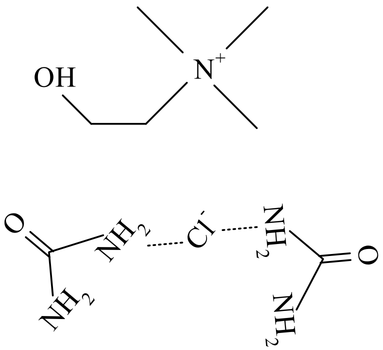
eed: 150 – 200 rpm

ture: 60 - 80°C

ion: 2 hours

Gentle agitation of 150 - 200 rpm at moderate temperature of 60 - 80°C for 2 hours

Formation of liquid DES



Types of DES

Table 2 Types of DES segregated into 4 groups (adopted from Smith et al., 2014)

Type	Terms	General Formula	Example
1	Metal salt + organic salt	$Cat^{+} X^{-} zMClx$; M = [illegible] In	[illegible] hCl
2	Metal salt hydrate + organic salt	$Cat^{+} X^{-} zMClx \cdot yH2O$; [illegible] Ni, Fe	[illegible] $_2$O + ChCl
3	Hydrogen bond donor + organic salt	$Cat^{+} X^{-} zRZ$; Z = $CONH_2$, COOH, OH	urea + ChCl
4	Zinc/Aluminium chloride + Hydrogen bond donor	$MCl_x + RZ = MCl_{x-1}{}^{+} \cdot RZ + MCl_{x+1}{}^{-}$; M = Al, Zn & Z = $CONH_2$, OH	$ZnCl_2$ + urea

Composed of environmentally and economically benign materials

Properties of DES

Melting point

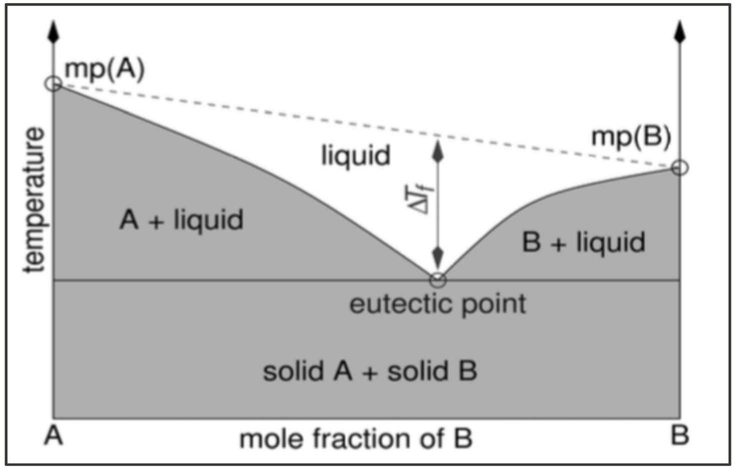


Fig. 6 Schematic representation of eutectic point on a two component phase diagram (adopted from Smith et al., 2014)

- Sharp decrease in melting point
- Example:

  Pure ChCl: 302ºC

  Pure urea: 135ºC

  ChCl-urea DES: 12ºC

Delocalization of charge due to hydrogen bonding between HBD and halide ion.

Dependent variables

Types of HBD and HBA used

Composition of HBD in mixture

Properties of DES

Surface Tension

- Higher surface tension than most ILs
- **Surface tension** is closely related to intermolecular forces

Dependent variables

Type of cation in HBA

Presence of hydroxyl groups in cation led to high surface tension

Temperature of system

Increase of temperature resulted in decrease of surface tension.

Gain of energy by halide salt that broke up the intermolecular forces i.e. hydrogen bonding

Properties of DES

Density

- Higher density than water
  (Type IV DES density > 1.3 g/cm^3)

Dependent Variables

Types of HBD and HBA used

Temperature of system

Water content

Viscosity

- Higher viscosity than ILs
  (except ChCl-ethylene glycol)
- High viscous property accompanied with a low **conductivity**

Hole Theory

Formation of DES resulted in decrease of average hole radius as it is composed of holes and empty vacancies, hence affecting density and viscosity considerably upon formation.

Recent Developments of DES in Biomass Processing

Solubilization of Lignin

Extraction of Phenolic Compound

Table 3 Summary of lignin solubilization methods with different DES reagents

DES reagent	Mol ratio	Lignocellulosic Biomass	Operating Conditions	wt% Delignification	References
Lactic acid - Betaine	2:1	Rice straw	60°C for 12 h in with agitation of 100 rpm in a screw capped conical flask.	52 ± 6	Kumar et al., 2015
	5:1			56 ± 3	
Lactic acid – ChCl	2:1			51 ± 1	
	5:1			60 ± 2	
	9:1			59 ± 3	
Formic acid – ChCl	-	Corn stover	130°C for 2 h with agitation of 100 rpm in a three necked flask.	23.8	Xu et al., 2016
Imidazole – ChCl	2:1	Corncob	115°C for 15 h in an oil bath.	70	Procentese et al., 2015
Urea – ChCl	2:1			24.8	
Glycerol - ChCl	7:3			4.4	

Recent Developments of DES in Biomass Processing

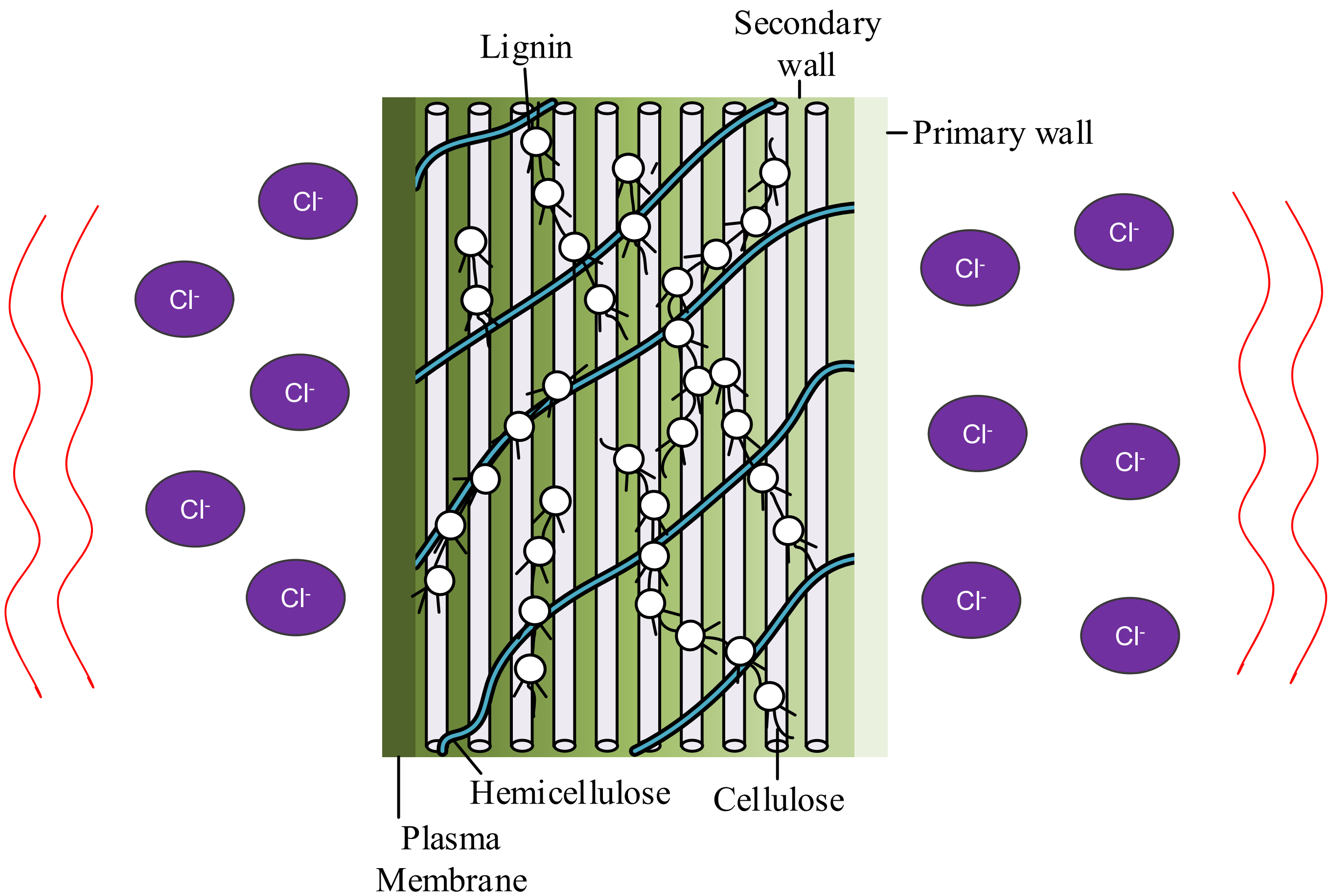


Fig. 7 Reaction mechanism of DES in extraction of lignin compound

Recent Developments of DES in Biomass Processing

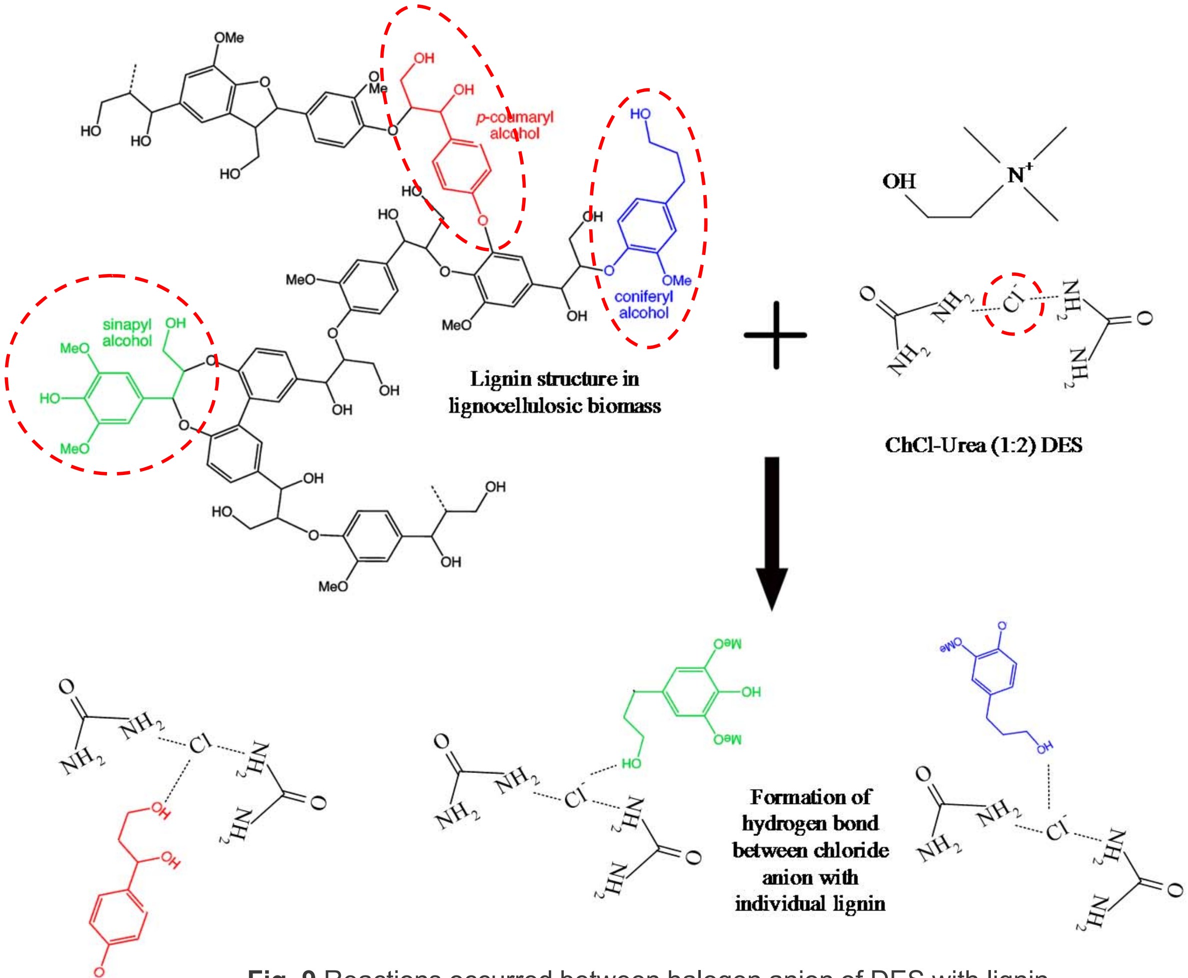
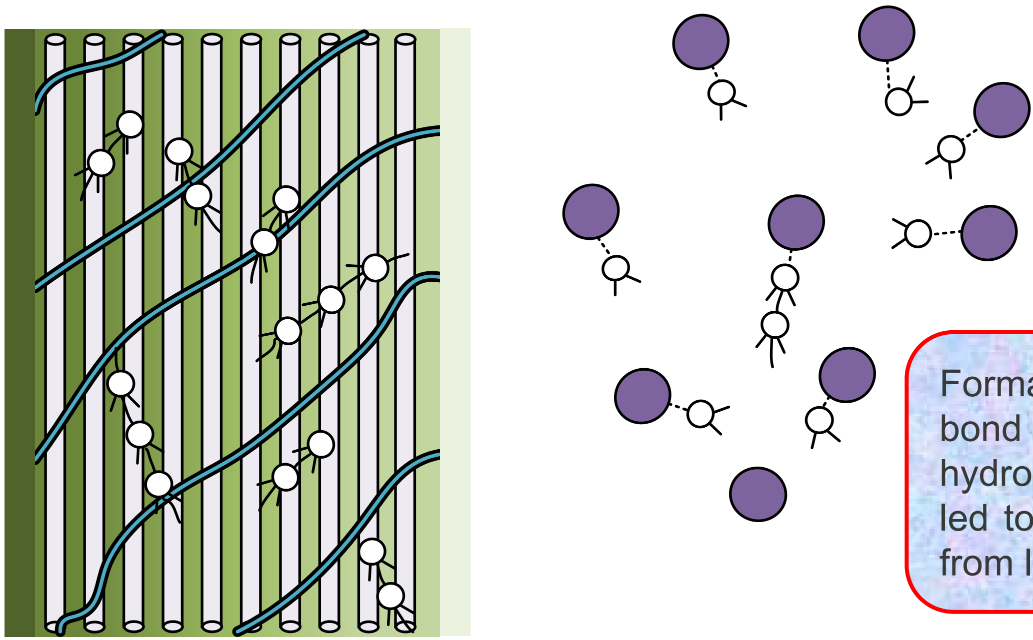


Fig. 9 Reactions occurred between halogen anion of DES with lignin

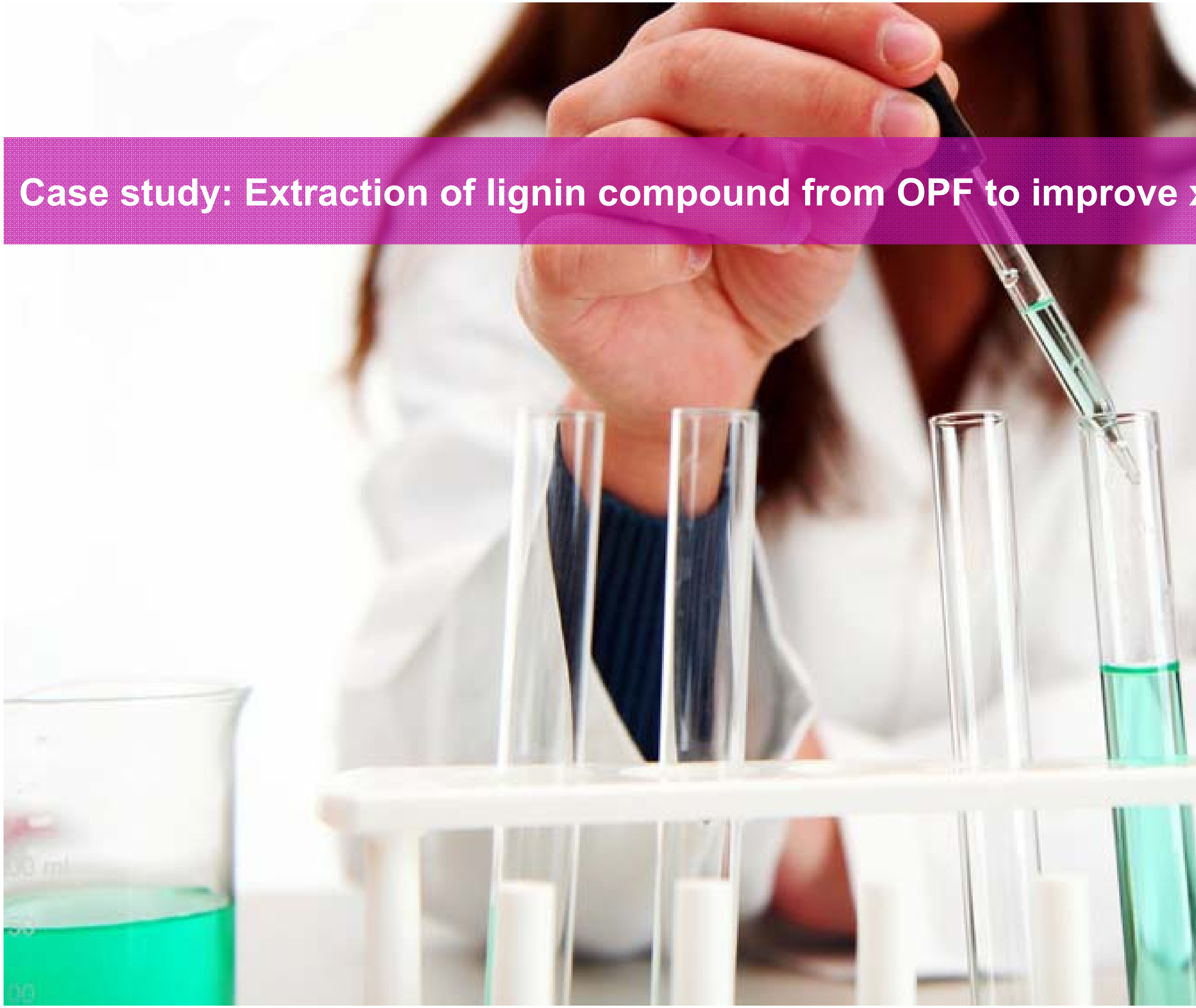
Recent Developments of DES in Biomass Processing

DES delignification damaged the protection barrier provided by lignin via dissolution of lignin



Formation of hydrogen bond between Cl^- and hydroxyl group of lignin led to dissolution of lignin from lignocellulose

Fig. 8 Structural change of DES and solid biomass after proposed reaction mechanism



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Case study: Extraction of lignin compound from OPF to improve xylose recovery

Case study: Delignification of OPF via DES in improving xylose extraction from Oil Palm Fronds (OPF)

Methodology

Quantitative Results

OPF Characterization (XRD, FT-IR, FE-SEM)

Overview

Fig. 10 Oil palm fronds (OPF), with leaflets removed (adapted from http://www.mightyjacksparrow.com)

Type of lignocellulosic biomass: Oil Palm Fronds (OPF)

Type of DES used: ChCl-urea with molar ratio of 1:2

Aim: To determine the recovery of xylose sugar via inorganic salt hydrolysis enhanced by DES delignification

Control set

OPF → **Inorganic salt pre-treatment** → **Xylose recovery**

Real sets

OPF → **Delignification of OPF via DES** → **Inorganic salt pre-treatment** → **Xylose recovery**

Case study (Continued…)

Methodology

ChCl-Urea DES (25 ml)

Supernatant liquid (DES + Lignin)

Characterization (FE-SEM, FT-IR, XRD)

Grinding of OPF

- Equipment: Siever / Grinder
- Particle Size < 0.5 mm

Synthesis of DES

- Equipment: Magnetic Stirrer
- Raw feedstock: ChCl and Urea
- Mix at molar ratio of 1:2

Delignification of OPF

- Equipment: Oil Bath
- Biomass loadings at 10 w/v% to DES

Inorganic salt pre-treatment

- Equipment: Autoclave
- Biomass loadings at 10 w/v% to 0.4 M $CuCl_2$ solution

Monomeric sugars analysis

- Equipment: HPLC
- Quantification of xylose

Characterization of OPF

- Equipment: FESEM, FT-IR
- Compare the morphology, crystallinity index and functional groups of OPF before and after each stage of pre-treatment

Characterization (FE-SEM, FT-IR, XRD)

0.4 M CuCl2 solution (10 ml)

Monomeric sugar recovery (HPLC)

Grinding of OPF ✓	*Synthesis of DES* ✓	*Delignification of OPF* ✓	*Inorganic salt pre-treatment* ✓	*Monomeric sugars analysis* ✓	*Characterization of OPF* ✓

se study (Continued…)

antitative Result (Xylose Recovery from OPF)

Fig. 11 Effec f tempe

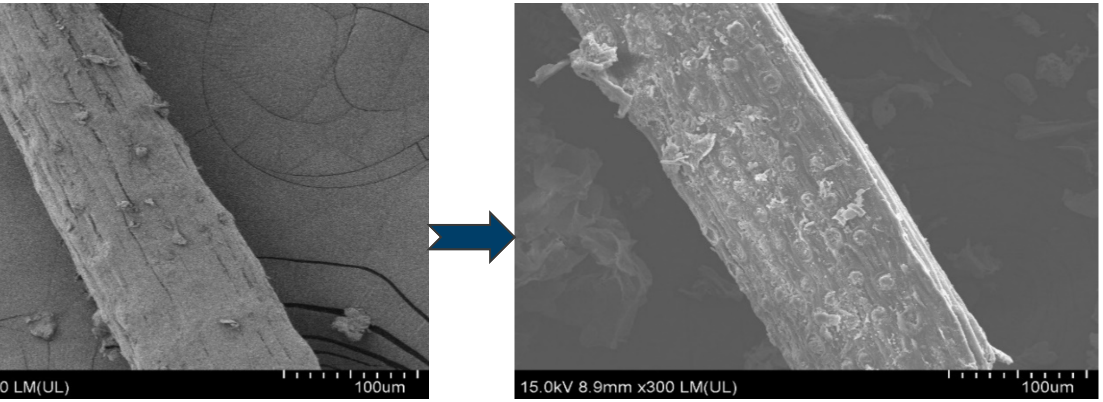
Removal percentage of lignin: 28.42%

Operating condition: **120°C, 4 hours**

se study (Continued…)

F Characterization (FE-SEM)

ol - (0.4 M $CuCl_2$ inorganic salt pre-treatment)

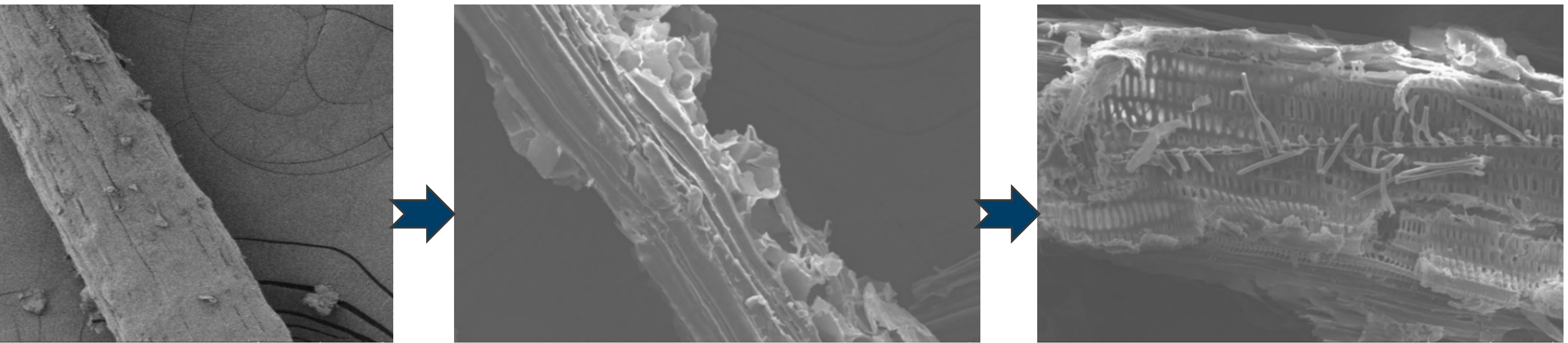


Raw OPF

After inorganic salt pre-treatment

Fig. 10 Morphology of OPF in control set

l-urea DES delignification + 0.4 M $CuCl_2$ inorganic salt pre-treatment)



se study (Continued…)

F Characterization (FT-IR)

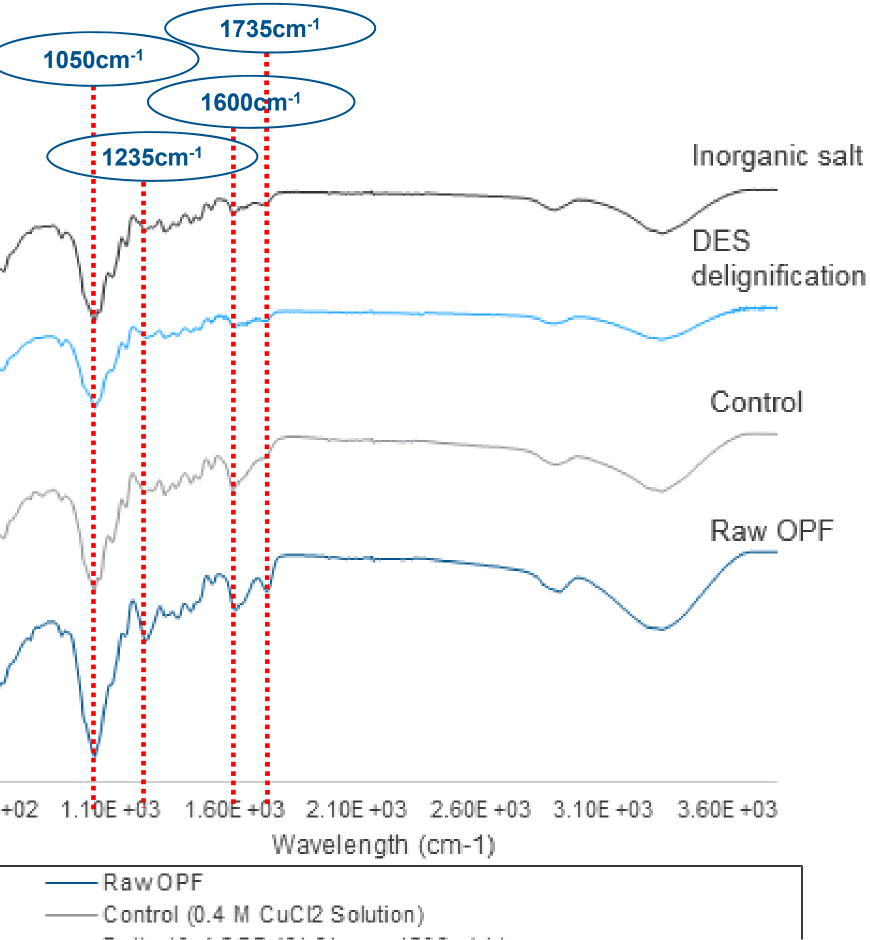
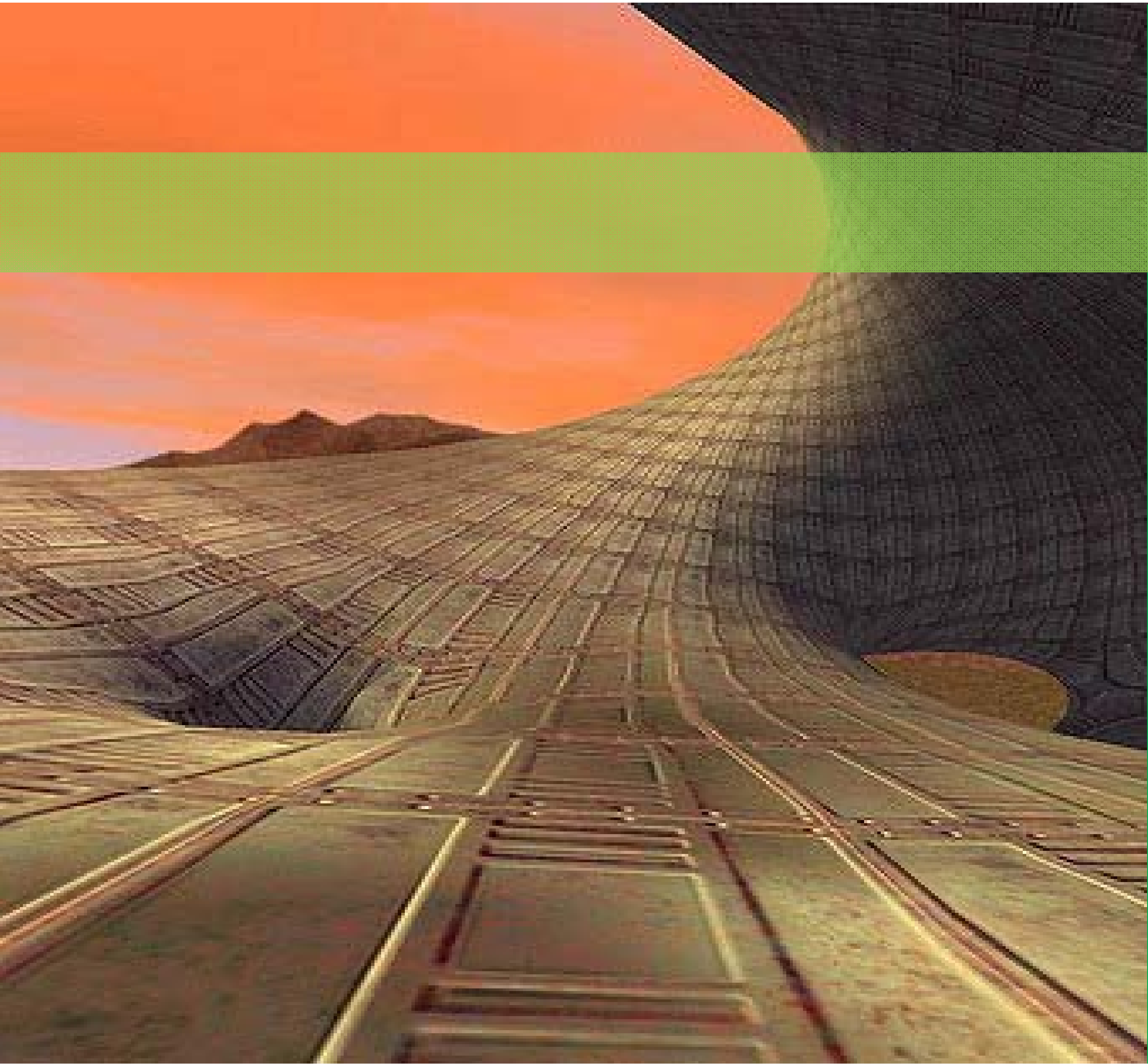


Table 5 Assignment of bands wavelength of solid biomass at various stage of pre-treatment

Notation	Band wavelength (cm^{-1})	Assignment
A	~900	Small sharp band indicates cellulose
B	~1235	C-O-C indicates ether bond in lignin
C	~1508-1600	C=C double bond indicates the stretching of aromatic ring in lignin
D	~1735	C=O double bond denotes hemicellulose
E	~1033	Represents cellulose and hemicellulose



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Conclusion

Current Limitations & Future Improvements

Contributions of Proposed Research

urrent Limitations & Conclusion

The development of DES in biomass processing is still in its preliminary stage.

The potential of DES in biomass processing has been proven based on literature reviews and case study above.

Main issues – Recyclability issues of DES after pre-treatment
Little yet to be known on the effects of different types of DES on biomass processing

Further investigation will be needed to rectify the issue above.

ontributions of Proposed Research

his study is expected to be able to provide a better understanding nd outcome on the following aspects:

- Valuable knowledge for lignocellulosic residues pretreatment that proves to be beneficial for various industries.
- An introduction to the use of DES as a solvent for delignification and extraction of phenolic compounds from lignocellulosic biomass.
- In alignment with the National Key Economic Area mainly related to entry point project (EPP7) in Agriculture on waste management of fresh fruits/vegetables and their by-products.

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Thank You

PF Characterization (XRD)

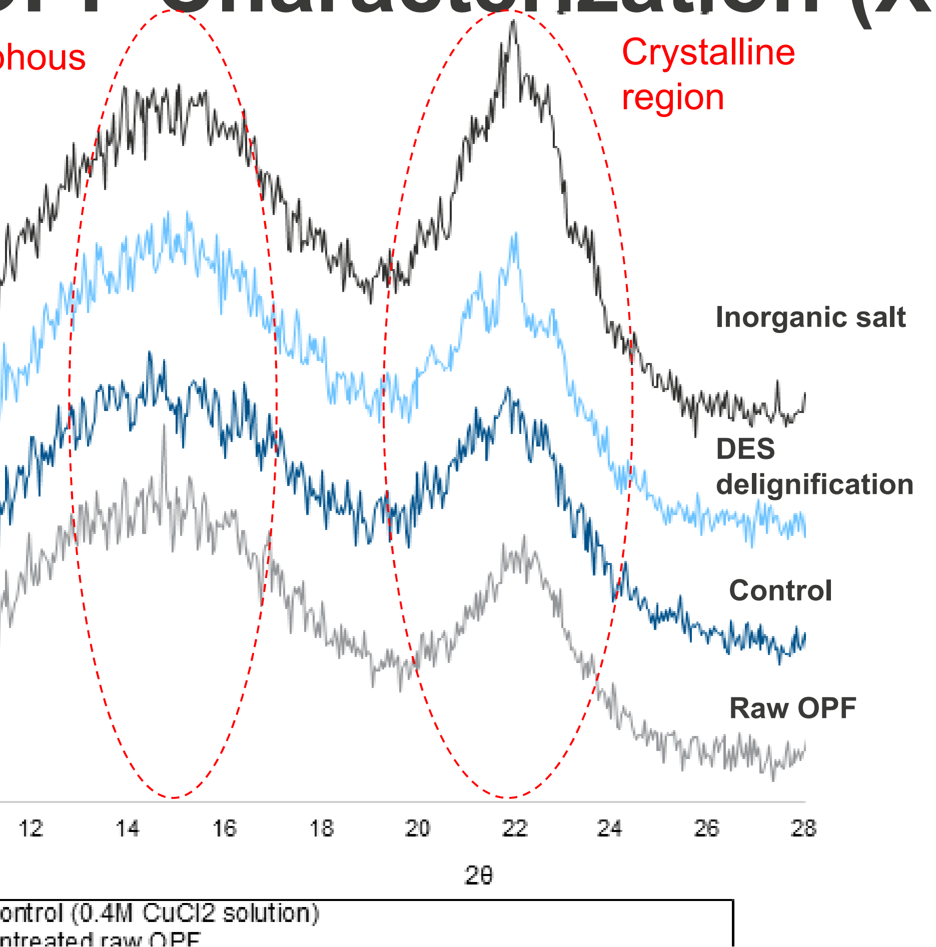

Table 4 Crystallinity index of solid biomass at various stage of pre-treatment

Control (0.4 M $CuCl_2$ inorganic salt pre-treatment)	
Stage of pre-treatment	**Crystallinity Index**
Raw OPF	34.99%
After inorganic salt pre-treatment	36.35%
ChCl-urea DES delignification + 0.4 M $CuCl_2$ inorganic salt pre-treatment	
Stage of pre-treatment	**Crystallinity Index**
Raw OPF	34.99%
After DES delignification	41.02%
After inorganic salt pre-treatment	45.94%