Photocatalytic bioethanol production as future green energy solution

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Convensional biofuel production using waste biomass

- Mechanical - Milling, grinding, chipping
- Hydrothermal - Hot water, Steam pressure (160-260 °C, 0.69-4.83 MPa)
- Acid, Alkali, oxidising agents
- Biological - Fungi & Bacteria

Fermentation

Distillation and Evaporation

Biofuel

Cellulose Biomass

Conventional biofuel production using waste biomass

Proposed photocatalytic biofuel production

Photocatalytic (visible light) breakdown of waste biomass

Fermentation

Membrane separation of Biofuel
Photocatalytic Bioethanol Production
Project overview

- Natural irradiation or low power illumination
- Release of fermentable sugars
- Microbial Fermentation
- Energy demand - EtOH Supply

- Visible light nanoparticulate catalyst to release of fermentable sugars from waste biomass.
- Engineer cost and energy efficient cellulosic photocatalytic saccharification reactor
- Select or manipulate microorganism(s) those ferments the photocatalytic by-products
### Content of cellulose in common agricultural residue and wastes

<table>
<thead>
<tr>
<th>Lignocellulosic biomass</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood stems</td>
<td>45-50</td>
<td>24-40</td>
<td>18-25</td>
</tr>
<tr>
<td>Softwood stems</td>
<td>45-50</td>
<td>25-35</td>
<td>25-35</td>
</tr>
<tr>
<td>Nut shells</td>
<td>25-30</td>
<td>25-30</td>
<td>30-40</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>45</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Grasses</td>
<td>25-40</td>
<td>35-50</td>
<td>10-30</td>
</tr>
<tr>
<td>Paper</td>
<td>85-99</td>
<td>0</td>
<td>0-15</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30</td>
<td>50</td>
<td>15</td>
</tr>
<tr>
<td>Sorted refuse</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Leaves</td>
<td>15-20</td>
<td>80-85</td>
<td>0</td>
</tr>
<tr>
<td>Cotton seed hairs</td>
<td>80-95</td>
<td>5-20</td>
<td>0</td>
</tr>
<tr>
<td>Newspapers</td>
<td>40-55</td>
<td>25-40</td>
<td>18-30</td>
</tr>
<tr>
<td>Waste papers from chemical pulps</td>
<td>60-70</td>
<td>10-20</td>
<td>5-10</td>
</tr>
<tr>
<td>Primary waste water solid</td>
<td>8-15</td>
<td>NAb</td>
<td>24-29</td>
</tr>
<tr>
<td>Swine waste</td>
<td>6.0</td>
<td>28</td>
<td>NAb</td>
</tr>
<tr>
<td>Solid cattle manure</td>
<td>1.6-4.7</td>
<td>1.4-3.3</td>
<td>2.7-5.7</td>
</tr>
<tr>
<td>Coastal Bermuda grass</td>
<td>25</td>
<td>35.7</td>
<td>6.4</td>
</tr>
<tr>
<td>Switch grass</td>
<td>45</td>
<td>31.4</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Prasetyo and Park, 2013
Photocatalysis

Conduction Band (CB)

Photo-excitation

Recombination

A\(^+\) (\(\cdot\)O\(_2\)\(-\))

Reduction

A (O\(_2\))

E\(_{bg}\) > ~3.0 eV = UV
E\(_{bg}\) < ~3.0 eV = Visible

E\(_{bg}\) of common catalyst:
- TiO\(_2\) P25 – 3.2 eV
- ZrO\(_2\) – 5.0 eV
- CdS – 2.5 eV

Valence Band (VB)

D (H\(_2\)O)

Oxidation

D- (H\(^+\), \(\cdot\)OH)
The importance of hydroxyl radicals (OH·)

Cellulose photodegradation is a **Solid-Solid photocatalysis**

Cellulose will not adsorb, so:
- very close contact with catalyst
- Or migrating OH·

radius of diffusion will dictate the reaction zone.

From ~ 1 μm to ~2 mm:


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Choi, W.; Kim, S.; Cho, S.; Yoo, H.-I. & Kim, M.-H.

## Cellulose photodegradation

![Cellulose degradation diagram](image)

<table>
<thead>
<tr>
<th>Organism</th>
<th>Characteristics</th>
<th>Advantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td>Facultative anaerobic yeast</td>
<td>Naturally adapted, High alcohol yield, High alcohol tolerance, genetic modification</td>
<td>Girio et al., 2010,</td>
</tr>
<tr>
<td><em>Zymomonas mobilis</em></td>
<td>Ethanologenic Gram-neg bacteria</td>
<td>High ethanol productivity (five-fold more than <em>S. cerevisiae</em>)</td>
<td>Balat &amp; Balat, 2008</td>
</tr>
<tr>
<td><em>Esherichia coli</em></td>
<td>Mesophilic Gram-neg bacteria.</td>
<td>Ferments pentoses &amp; hexoses, Amenability for genetic modifications</td>
<td>Zayed et al., 1996</td>
</tr>
<tr>
<td><em>Thermoanaerobacterium saccharolyticum</em>, <em>Thermoanaerobacter ethanolicus</em>, <em>Clostridium thermocellum</em></td>
<td>Extreme anaerobic bacteria</td>
<td>Resistance to an extremely high temperature of 70 °C Ferment a variety of sugars Amenability to genetic modification</td>
<td>Georgieva et al., 2008, Kumar et al., 2009</td>
</tr>
</tbody>
</table>
**HPLC-ELSD analysis of celloextrins**

Waters Xbridge Amide column (3.5 µm x 4.6 x 250 mm) – HPLC-ELSD

LOD – 5 µg/ml

ACN : Water

Waters Acquity BEH Amide column (1.7 µm x 2.1 x 100 mm) – UPLC-MS

LOD – 1 µg/ml

- **Glucose**
  - C₆H₁₂O₆
  - MW - 180.16

- **Cellobiose**
  - C₁₂H₂₂O₁₁
  - MW - 342.30

- **Cellotetraose**
  - C₂₄H₄₂O₂₁
  - MW - 666.58

- **Cellopentaose**
  - C₃₀H₅₂O₂₆
  - MW - 828.72

Graph showing the HPLC-ELSD analysis with peaks at different retention times and corresponding LSU values.
Proof of Principle

Cellulose

Dialysis tube

Glucose

TiO$_2$

hv
UPLC-MS analysis of cellulose breakdown products

Glucose analytical standard $180 + Na = 203 \ m/z$

Samples infused into QToF MS
Key features for catalysts

- **Visible light activation**
- **Structure**
  - Increases $e^{-}$ and $h^{+}$ mobility and separation
- **Band gap energy**
  - For solar photon absorption
- **Surface Area**
  - Increases catalyst-reactant surface reaction
- **Particle size**
  - Critical for catalyst interaction with cellulose chains – catalyst needs to ‘penetrate’ cellulose chains
- **Recyclability**
- **Cost**
- **Hydroxyl radical formation**
In-situ growth of CdS QDs on cellulose
- Coupling CdS quantum dots with cellulose increases the stability of CdS and can prevent photo corrosion.

Irradiation under visible light for 24 hrs (420 nm cut-off filter)
- CdS $E_{bg} = \sim 2.5$ eV which corresponds to excitation at $\sim 495$ nm

Analysis by HPLC-RI

Small sugars or organic acids from cellulose decomposition were found out – further detection and identification is currently ongoing.
The effectiveness of any photocatalytic treatment processes depends on:

- Distribution of target molecule and photocatalyst
- Reaction kinetics
- Irradiation characteristics
- **Mass transfer of target molecule and photocatalyst**
  - Maximise interaction between cellulose and OH\(^-\) in order to cleave hydrogen and glycosidic bonds

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The conversion of target species (cellulose) is controlled by the rate of mass transfer

Mass transfer of a reactor is capable of supplying target species to the catalyst surface

In a mass controlled reactor, increasing mixing properties will increase level of conversion
Solar Light is potentially a huge source of energy
- 120,000 TW year\(^{-1}\) solar irradiation reaching Earth’s surface
- Capturing and harvesting light is a major limitation
- Photocatalysis has ability to harness solar light and convert into renewable energy products – Bioethanol production

Concentration of solar light is essential
- Parabolic mirrors and solar concentrators
- Light guiding mirrors can concentrate and direct a focused photon beam towards a target reactor
- Under diffuse weather conditions concentrating solar irradiation is key to drive the photocatalytic release of glucose from cellulose
LED illumination is a low power lab scale alternative to solar irradiation
- Temporary approach for evaluation of catalysts and systems
- Currently in use are 3.8 V LEDs that provide a 30° viewing angle
- Ideal for use in submerged systems to maximise light penetration and flow characteristics
- Range of LEDs can be used to mimic solar irradiation
- Choice of LED is dictated by catalyst development
  - Incorporation of co-catalysts and dopants will change the electronic configuration of the catalyst which can shift the $E_{bg}$ and absorption region
Yields of bioethanol by photocatalytic release of glucose from paper mill waste (% dry weight)

- Dry paper mill waste - 1 tonne (1000 kg)
- Cellulose content in paper mill waste (85%) - 850 kg (Prasetyo and Park, 2013)
- Photocatalytic efficiency (90%) - x 0.90
- Efficiency of glucose harvest (90% RO) - x 0.90
- Ethanol stoichiometric yield - x 0.51 (Badger, 2002)
- Glucose fermentation efficiency (75%) - x 0.75 (Badger, 2002)
- EtOH harvest – membrane separation (80%) - x 0.80

Yield of EtOH from glucose = 210 kg (267 L) per tonne

- Annual paper mill waste produced = ~6000 tonnes
- Dry annual paper mill waste (40%) = 2400 tonnes
- Potential annual EtOH production = 267 L x 2400 = 640,000 L
Acknowledgments