Biochemicals and biofuels from lignocellulose via catalytic conversion

Xuebing Li

Apr. 10th, 2017, Montreal
Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass
Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass
# Renewable energy sources

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar energy</td>
<td><img src="image1" alt="Solar Energy" /></td>
</tr>
<tr>
<td>Wind</td>
<td><img src="image2" alt="Wind Energy" /></td>
</tr>
<tr>
<td>Hydroenergy</td>
<td><img src="image3" alt="Hydroenergy" /></td>
</tr>
<tr>
<td>Ocean energy</td>
<td><img src="image4" alt="Ocean Energy" /></td>
</tr>
<tr>
<td>Geothermal</td>
<td><img src="image5" alt="Geothermal Energy" /></td>
</tr>
<tr>
<td>Biomass</td>
<td><img src="image6" alt="Biomass Energy" /></td>
</tr>
</tbody>
</table>
### Renewable energy sources

<table>
<thead>
<tr>
<th>Solar energy</th>
<th>Wind</th>
<th>Hydroenergy</th>
</tr>
</thead>
</table>

- **《World Energy Outlook 2017》**: Over the next 20 years, China will be the largest source of renewable energy growth.
- From 2016 to 2020 (the 13th Five Year Plan), the total investment on renewable energy will reach 2.5 trillion RMB in China, the development and utilization of renewable energy will greatly improve the environment problems.
- **Xiong-An New Area** will be established on the basis of clean and renewable energy.
- By the end of 2016, Shandong province has new energy and renewable energy installed capacity of 15.805 GW, accounting for 14.4% of the total electricity generating.
Renewable energy sources

Compete the goals of the 12th Five-Year Plan

- Hydroelectricity 320 GW
- Wind power 120 GW
- Photovoltaic power 40 GW
- Renewable resources 32.7%
Energy structure adjustment

The coal consumption ratio continued to decline

- The proportion of non-fossil energy consumption
- The proportion of coal consumption

2014
- 11.20%

2015
- 12%

2020
- 15%

2014
- 66.10%

2015
- 64.40%

2020
- 62%
By the end of 2016, the cumulative photovoltaic installed capacity in China has reached 43.18 GW, growing to be the largest in the world.
By 2020, the wind power installed capacity of Shandong province will reach 14 GW, accounts for the proportion of 8.6% of the total electricity generating.
Geothermal and ocean energy distribution

Geothermal resources distribution
Ocean energy distribution

Geothermal resources: Widely distributed
Ocean energy: Littoral
Biomass energy

There are abundant biomass resources in China, 70% of rural energy comes from biomass. More than 600 million tons of crop stalks are generated every year.
Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass
**Biomass application**

- **Lignocellulose resources**
  - **Cropland application**
    - Returning directly, Decomposing and returning, Rotten returning
  - **Feedstuff**
    - Physical treatment, Chemical treatment, Biotechnology treatment
  - **Energy utilization**
    - Directly-burning for heating, Gasification and gas supply, Charcoal, Biogas fermentation
  - **Industrial application**
    - Disposable tableware, Building materials, Industrial raw materials (ethanol, newtol, furfural et al.), Fungus culture medium, Papermaking, Knitting
Lignocellulose
Lignocellulose

Lignocellulose plants
Cellulose  40-80%,
Hemicellulose  15-30%,
Lignin  10-25%

Cellulose → Glucose
Hemicellulose → Xylose, Mannose, Acetic acid
Lignin → Oxygen containing aromatic hydrocarbons, Cycloalkanes
Lignin utilization
Lignin is a cross-linked amorphous copolymer with random polymerized structure of the three primary phenylpropane monomers (syringyl (S), guaiacyl (G) and p-hydroxyphenyl units (H)), which are bonded together through several different C–O–C and C–C interunit linkages.

The energy density of lignin is 30% greater than that of polysaccharide polymers and it is one of the few natural large-scale sources of aromatic compounds.
Lignin depolymerization

Depolymerization by alkaline organosolv

Depolymerization in supercritical water

Not exceed yields of approximately 20 -23 wt.% of product oil

• The re-polymerization of the highly reactive products with formation of higher molecular compounds, defined as unconverted lignin.
• CHN analysis of the above unconverted lignin showed a different chemical composition than the original lignin.
Lignin depolymerization

Aqueous reaction mixture (products & unconverted lignin)

Dissolve in THF and filtrate

Lignin
High molecular products

Unconverted lignin
High molecular products
Coke

Coke

Mono-, di- and trimers

Org. Solvent & products

Aqueous reaction mixture (products & unconverted lignin)

Acidify

Filtration

Extraction

Solvent removal

Purification

Aqueous phase

Mono-, di- and trimer solution

Virginia M. Roberts, Valentin Stein, Thomas Reiner, Angeliki Lemonidou, Xuebing Li, Johannes A. Lercher
Lignin depolymerization Effect of time

300 °C and 250 bar, 10 wt.% lignin in 4 wt.% NaOH solution
<table>
<thead>
<tr>
<th>Monomer</th>
<th>Chemical formula</th>
<th>Conc.[wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syringol</td>
<td>C$<em>8$H$</em>{10}$O$_3$</td>
<td>40.9</td>
</tr>
<tr>
<td>Syringyl aldehyde</td>
<td>C$<em>9$H$</em>{10}$O$_4$</td>
<td>18.0</td>
</tr>
<tr>
<td>3, 5-dimethoxy-4-hydroxy acetophenone</td>
<td>C$<em>{10}$H$</em>{12}$O$_4$</td>
<td>16.3</td>
</tr>
<tr>
<td>4-methyl-syringol</td>
<td>C$<em>9$H$</em>{12}$O$_3$</td>
<td>6.7</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>C$_7$H$_8$O$_2$</td>
<td>10.5</td>
</tr>
<tr>
<td>Vanillin</td>
<td>C$_8$H$_8$O$_3$</td>
<td>3.5</td>
</tr>
<tr>
<td>4-hydroxy-3-methoxy phenylacetone</td>
<td>C$<em>{10}$H$</em>{12}$O$_3$</td>
<td>2.3</td>
</tr>
<tr>
<td>Ortho-methoxy-catechol</td>
<td>C$_7$H$_8$O$_3$</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Lignin depolymerization Repolymerization

Degradation

Base site dominating

Acid site dominating

H^+ + OH^- \rightarrow H_2O

Lignin depolymerization Repolymerization to form C-C bond
Lignin depolymerization in the Boric acid system

Graph showing the yield (wt.%) as a function of the wt. (Boric acid/Lignin) ratio.

- Non-catalytic hydrothermal treatment
- BCD

Conditions: 300°C, 250 bar
The extraction of the filter cake exhibited very similar product distribution as the oil, and led to oil yield as high as 85 wt.%.

<table>
<thead>
<tr>
<th>wt. (NaOH/Boric acid)</th>
<th>pH</th>
<th>Oil Yield (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.5</td>
<td>36</td>
</tr>
<tr>
<td>0.50</td>
<td>9.6</td>
<td>29</td>
</tr>
<tr>
<td>0.75</td>
<td>13.0</td>
<td>52</td>
</tr>
<tr>
<td>1.00</td>
<td>13.3</td>
<td>47</td>
</tr>
<tr>
<td>1.25</td>
<td>13.4</td>
<td>29</td>
</tr>
</tbody>
</table>
Methylation: DMC

Methylation of active hydroxyl in lignin + Methylated lignin depolymerization on solid base catalyst → Bio-oils

Methylation: DMC

Conversion = 100%

Lignin: Organosolv lignin
Catalyst: 10 wt% Ni-MgO/Al₂O₃
H₂ source: H₂
Solvent: Water, Ethanol, Dodecane

Conversion > 90%

A Highly Efficient, Green, and Cheap Depolymerization Process.

Funded by National natural Science Foundation of China: 21676287
Depolymerization of oxidized lignin under mild conditions in aqueous formic acid results in more than 60wt% yield of low-molecular-mass aromatics.

Lignin depolymerization

Oxidation system

CrO$_3$ + H$_2$SO$_4$

Fe(acac)$_3$/phen/K$_2$CO$_3$/NaOH

Dess-Martin periodinane

4-acetamido-TEMPO

O$_3$ Green, cheap and efficient
Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass
Hydrodeoxygenation of bio-oil  

Background:

- **30% of water**
- **Unstable**
- **HDO with cobalt or nickel doped molybdenum sulfides**
- Sensitive to water, poisoned by the oxygen containing compounds
- Cracking by zeolitic catalysts at 400 °C
- The oxygenates are mostly converted to carbonaceous deposits
By benzene hydrogenation, ether bond hydrolysis and alcohol dehydration, bio-oil derived from lignin depolymerization are transformed into cycloalkanes, which are isolated from water automatically.
Hydrodeoxygenation of bio-oil Bifunctional catalysts

Bifunctional catalysts

Hydrogenation catalysts

Noble metal: Pt/C, Pd/C, Ru/C
Non-noble metal: Raney Ni, Ni-doped catalysts

Hydrolysis and the dehydration catalysts

Mineral acid: Phosphoric acid; Sulfuric acid
Organic acid: Acetic acid
Solid acid: Nafion, Zeolite

Hydrodeoxygenation of bio-oil

(A) Before reaction

phenols

(B) After reaction

Hydrocarbons

Nafion/SiO₂

Raney Ni
Hydrodeoxygenation of bio-oil

Bifunctional catalysts

- Hydrogenation
- Ketone/enol isomerization
- Hydrolysis
- Dehydration
- Demethoxylation

Chemical reactions involving hydrodeoxygenation and bifunctional catalysts.
## Hydrodeoxygenation of bio-oil

Bifunctional catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Reaction conditions</th>
<th>Conversion (%)</th>
<th>Selectivity to cycloalkanes (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C; H₃PO₃</td>
<td><img src="OH" alt="OH" /></td>
<td>5 MPa H₂, 523 K, 0.5 h</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>Pd/C; H₃PO₃</td>
<td><img src="OMeMeO" alt="OMeMeO" /></td>
<td>5 MPa H₂, 523 K, 0.5 h</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>Pd/C; HZSM-5</td>
<td><img src="OH" alt="OH" /></td>
<td>5 MPa H₂, 473 K, 2 h</td>
<td>95</td>
<td>80</td>
</tr>
<tr>
<td>RANEY Ni Nafion/SiO₂</td>
<td><img src="OH" alt="OH" /></td>
<td>4 MPa H₂, 573 K, 0.5 h</td>
<td>80</td>
<td>86</td>
</tr>
</tbody>
</table>

Note that HZSM-5 showed a high rate of dehydration (1600 mol mol-[H⁺]⁻¹ h⁻¹), two orders of magnitude higher than that of H₃PO₄ (15 mol mol-[H⁺]⁻¹ h⁻¹).
The mechanisms of outstanding dehydration and hydrolysis of acidic zeolite:

- The accumulation effect of zeolite could increase the concentration of reactants, therefore promoting the catalytic reaction.
- The pores of zeolite are suitable for reactants transporting to the acid sites, promoting the equilibrium reaction from alcohol monomer/oligomer to monomer with high reactivity.

C. Zhao, J. He, A. A. Lemonidou, X. Li, J. A. Lercher, J. Catal. 280 (2011) 8;

Outlines

1. Renewable energy utilization in China
2. Lignin depolymerization
3. Hydrodeoxygenation of bio-oils
4. Biochemicals from biomass
Lignocellulose application
Lignocellulose application

Technology roadmap of lignocellulose resources application, cooperated with Xinmu Corporation.
International Cooperation energy
Research Cooperation

Prof. Dr. Johannes A. Lercher
Technical University of Munich
& Pacific Northwest National Laboratory

Prof. Dr. Xuebing Li
QIBEBT, CAS

Prof. Dr. Martin Muhler
Ruhr-University Bochum
Sino-German Project-2016

Mesoporous Carbon Supported Metal Catalysts for Sustainable Hydrogenation Reactions

￥2,535 Million RMB

Financial Support

Research, Training, Exchange, Summer School…
Institute and group
Qingdao Institute of Bioenergy and Bioprocess Technology
Qingdao Institute of Bioenergy and Bioprocess Technology

One of China’s primary national research institutions for renewable energy and green materials, focusing mainly on R&D of the resources, technologies, products and processes for bio-based energy and materials.

Devoted to providing systematic and sustainable solutions to China’s bioenergy needs by integrating science, technology, and engineering in the fields of industrial biology, green chemical technology, and process engineering.

- Co-found by CAS, Shandong and Qingdao
- Officially operated since 2007
- More than 400 research staff
- 180 Postgraduate students
- Unique capabilities
- Synergy innovation with government, industry and universities
Qingdao Institute of Bioenergy and Bioprocess Technology

Renewable Resources

Industrial Biotechnology & Green Chemical Engineering & Process Engineering

Biology

Energy

Process

Biomass Feedstock

Bio-based Materials

Bioenergy

Energy Storage

Energy Process

Product Process

“major breakthroughs” & “top priorities”

Resources Development

Energy Application

Low-Carbon Production

Clean Process
Research and Academic Cooperation

---global partnership for excellence in green energy and materials for a sustainable Earth

Multi-level cooperation with over 40 global and domestic institutes, universities and companies: joint laboratories, academic exchange and training, collaborative research projects, regular seminars and conferences
Heterogeneous Catalytic Conversion

Novel Catalytic Materials

Catalytic mechanism and kinetics

Catalytic Processing technology

Bio-fuels

Bio-chemicals

Emission-control

Biodiesel

Bio-aviation fuel

Lignin-derived

Lubricates

Pyruvic acid

Dicarbontes

DeNOx

DeSOx

VOC
Comments & Questions

lixb@qibebt.ac.cn 15866870310