Catalytic Processes for the Production of Fuels and Chemicals from Lignocellulosic Biomass

Prof. George W. Huber
University of Wisconsin-Madison
2013 German-American Frontiers of Engineering Symposium
Irvine, CA, April 27, 2013
http://biofuels.che.wisc.edu/
• Petroleum refinery is an integrated complex system of different unit operations.

• Modern refineries have allowed us to extract more value from a barrel of oil.

• Produce a variety of products.

• Processing dirtier feeds
Lignocellulosic biomass is cheapest and most abundant form of biomass

- Vegetable oils – pure oils i.e. soy bean oil (7-14 boe/ha-yr), and waste oils (yellow grease and brown grease).
- Starches – primarily from corn in US (20 boe/ha-yr) sugarcane in Brazil.
- Lignocellulosic biomass – non-edible form of biomass i.e. grasses, woody biomass (40-70 boe/ha-yr).

- Cost on an energy basis decreases: Vegetable Oils > Starches > Cellulosic biomass.
- Ease of conversion decreases: Vegetable oils < Starches < Cellulosic biomass.
Some Predictions in 1968…

- "the battle to feed all of humanity is over"
- “In the 1970s and 1980s hundreds of millions of people will starve to death in spite of any crash programs embarked upon now."
- "India couldn't possibly feed two hundred million more people by 1980,"
- "I have yet to meet anyone familiar with the situation who thinks that India will be self-sufficient in food by 1971."
Technology is Game Changing

Hybrid genetics & biotechnology have driven a five-fold increase in average U.S. corn yields since 1940.

Source: USDA
If we use our agricultural resources more efficiently we can feed the world’s population and produce bioenergy.

<table>
<thead>
<tr>
<th>Country</th>
<th>1990</th>
<th>2000</th>
<th>2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>World Average</td>
<td>59</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>USA</td>
<td>113</td>
<td>137</td>
<td>149</td>
</tr>
<tr>
<td>Argentina</td>
<td>60</td>
<td>93</td>
<td>109</td>
</tr>
<tr>
<td>China</td>
<td>74</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>Brazil</td>
<td>33</td>
<td>47</td>
<td>54</td>
</tr>
<tr>
<td>India</td>
<td>23</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td>Sub-Saharan Africa</td>
<td>22</td>
<td>24</td>
<td>25</td>
</tr>
</tbody>
</table>

Source: Monsanto/Doane Forecast

Slide from Richard Hamilton, CEO Ceres
Selective conversion of a highly functionalized oxygenated molecule, into a flammable liquid product that fits into current infrastructure.

Biomass-derived Feedstocks
High functionality
Low Thermal Stability

Liquid Fuel
Low functionality
High Thermal Stability

Challenges
• Yields
• Economics
• Products that fit into existing infrastructure
• Capital Cost
• Decrease number of process steps
Biomass Feedstocks
Cellulosic Biomass (wood, wood wastes, corn stover, switchgrass, agricultural waste, straw, etc.)
Chemical Structure: cellulose, hemicellulose, lignin

3 Major Routes to Cellulosic Biofuels:
1. Syn-gas routes
2. Bio-oil routes
3. Depolymerization routes

Key: Black - Chemical Conversion
Green - Biological Conversion
Blue - Both Chemical & Biological Conv.
Chemical Engineering Toolbox

- Heterogeneous (Inorganic) Catalysis
- Reaction Engineering
- Process Design/Economics
- Process Chemistry
- Transport Effects
- Process Intensification
- Heat Integration

Chemical Engineers concern themselves with conversion of inexpensive raw materials into more valuable products.

- Design and operation of processes
- Lots of new computational and experimental tools have been developed that can aid chemical engineers to more quickly develop and scale up new processes.
Pyrolysis Based Technologies for Biomass Conversion
Pyrolysis Video
ENSYN Commercial Fast Pyrolysis Plant

Processes 100 metric ton of biomass/day.

Plant located in Western Ontario.

Formed joint venture with UOP to license technology
Bio-oil: Characterization

**Elemental Composition**

- C: 47.0%
- H: 8.2%
- O: 44.8%

**Oak Wood Bio-oil**

- **Viscosity:** ~150 cP
- **pH:** 2.75
- **Acidity**
- **Viscometry**
- **Solubility**

**Non-Combustibles**

- **Ash:** 0.03 wt%

**Solubility**

- Water: 62%
- Methanol: 98%
- Toluene: 14%
- Diesel Fuel: 4%

---

Catalytic Fast Pyrolysis: Process Development Unit

Feed: Pine Wood Sawdust

Process Development Unit (Continual flow of catalyst and biomass on stream since April 2011)

Raw Liquid Product (Contains aromatics and water)

Aromatic Products

GCMS of raw liquid only observe aromatics
$120 billion aromatics market raw materials to make plastics.
Production of Renewable Aromatics by Catalytic Fast Pyrolysis of Biomass

All chemistry occurs in one single reactor.

Multiple Phenomena involved in Catalytic Fast Pyrolysis

Phenomena occurring in CFP
1. Fluidization of particles
2. Heat transfer to biomass particles
3. Solid biomass pyrolysis
4. Bubbles formation and growth
5. Mass transfer between phases
6. Reactions in gas phase
7. Catalytic reactions
Hydrolysis based Technologies for Biomass Conversion
Biomass can undergo hydrolysis reaction to make carbohydrates and other products

- **Challenge:** Complex reaction scheme

Conceptual Process Design of Aqueous Phase Hydrodeoxygenation Technology

Feedstocks:
- Carbohydrates
- Bio-oils
- Hydrolysis products

Low temperature hydrogenation

H$_2$

Reactor 1

Aqueous phase hydrodeoxygenation

Reactor 2

Separation system

Unreacted feedstocks & by-products (ie: sorbitan, isosorbide)

Waste water treatment facility

Liquid Products:
- C4-C6 Alkanes
- C1-C6 Alcohols
- C2- C4 Polyols
- Tetrahydrofurans (Ketones)

Non-condensable gases:
- H$_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, CO

Concepts:

Reactor 1 catalysts: High rate of C=O Hydrogenation

Reactor 2 catalysts: High rates of Hydrogenation (C=O; C=C; C-O-C)
- High rates of Dehydration (alcohols; diols)
- Low rates of C-C bond cleavage (decarbonylation; retro-aldol)

Petroleum derived feedstock made from biomass

- Refineries would prefer mixtures rather than single components.
- Red and Blue process optimized for tridecane production.
- Red process optimized for production of a petroleum refinery feedstock: mixture of C7-C30 mostly cyclic alkanes.
- Red is a high quality petroleum feedstock similar to heavy cycle oil (HCO) or light cycle oil (LCO).

Engineers are critical to solve our energy challenges
Conclusions

- Everything that is made from petroleum can be made from biomass and other renewable resources.
- Basic catalytic studies aid in the design of more efficient processes.
- Biomass can be converted by three main routes: gasification, pyrolysis, and hydrolysis.
- Catalytic fast pyrolysis allows the direct production of aromatics and olefins from solid biomass in a single catalytic step.
- Hydrodeoxygenation can be used to convert solubilized biomass into a liquid fuels, alcohols, and polyols.
- Chemical Engineers will be key to help prevent an energy crisis and solve our problems created by fossil fuels.
Green Gasoline: A Renewable Petroleum Alternative From Plants

**Source**
- Plants are composed of carbohydrates such as cellulose & other molecules

**Breakdown**
- Gasification
- Pyrolysis
- Deconstruction
- Glucose (Sugar in water)
- Levoglucosan (Organic liquid)

**Catalysis**
- Fisher-Tropsch Synthesis
- Hydrotreating
- Aqueous Phase Reforming
- Catalysts help recombine molecular components

**End Use**
- Aromatic hydrocarbons and alkanes

**Plant biomass:** poplar, switchgrass, corn stover, and others

**Gasification**
- High heat
- Syngas
- Fisher-Tropsch Synthesis
- Refinery

**Pyrolysis**
- Medium heat
- Biocrude
- Hydrotreating
- Aqueous Phase Reforming
- Sugar in water

**Deconstruction**
- Low heat

**End Products:**
- Jet fuel
- Diesel
- Plastics
- Gas

Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels
www.ecs.umass.edu/biofuels
• Funding Agencies: DOE-EFRC CCEI (Catalysis Center for Energy Innovation), NSF-MRI, NSF-EFRI, NSF-Career, and DARPA-SurfCat

Collaborators:
UMass-Amherst: W. Curt Conner, T. J. Mountziaris, W. Fan, P. Dauenhauer, S. Auerbach

UC-Riverside: Charlie Wyamn, Bin Yang;

Delaware: Dr. Michael Klein, B. M. Moreno.

Wisconsin: J.A. Dumesic

Disclosure: I have financial interest in Anellotech (www.anellotech.com).

Former Huber Team Members: Dr. Y. Lin; Dr. T. Carlson; Dr. K. Routray; Dr. H. Zhang; Dr. W. Shen; Dr. R. Xing; Dr. H. Olcay; Dr. T. Vispute, Dr. Ning Li, Dr. G. Tompsett, Dr. J. Cho, Dr. V. Agarawal, Dr. J. Jae, Dr. Y. Cheng, J. Shi, S. Green.

Current Huber Group Members
Post-doc: Dr. H. Kim, Dr. Y. T. Kim, Dr. Jinzhao Duan, Dr. Run Xu, Dr. Jungmei Cai
Graduate Students: R. Weingarten; R. Coolman; A. Upadhye; P. Karanjkar; C. Gilbert; I. Roo, Z. Xu, J. Lee.