Design of Catalysts for Hydrodeoxygenation of Biomass

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Tailor Made Fuels from Biomass (TMFB)
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http://biofuels.che.wisc.edu/
Huber Research Group (http://biofuels.che.wisc.edu/)

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

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The Institute for Atom-efficient Chemical Transformations (IACT) is supported by the US Department of Energy, Office of Basic Energy Sciences, as part of an Energy Frontier Research Center
• 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 that change depending on market conditions.

• Goal of Huber research group: Replace the entire barrel of oil with catalytic technologies that allow us to economically and efficiently convert our renewable resources into liquid fuels and chemicals.
Range of Liquid Fuel Blendstocks can be made by HDO of Biomass

Petroleum derived Feedstocks are a Mixture of Product

M. G. Al-Shaal, A. Dzierbinski, R. Palkovits; Solvent-free γ-valerolactone hydrogenation to 2-methyltetrahydrofuran catalysed by Ru/C: a reaction network analysis; Green Chem.; 16, 1358-1364; 2014
INTEGRATED CATALYTIC PROCESS TO PRODUCE RENEWABLE DISTILLATE FUELS FROM BIOMASS
Project Goal and Key Technical Challenges

Convert 80% carbon present in the biomass to \( \text{C}_8^+ \) alkanes using stable, catalytic processes with residence times below 1 hour.

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**Project Goal and Key Technical Challenges**

Convert 80% carbon present in the biomass to \( \text{C}_8^+ \) alkanes using stable, catalytic processes with residence times below 1 hour.

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**Project Goal**

Gasification → Fischer-Tropsch Synthesis → C2-C80 alkanes

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**Breakdown of Biomass Polymers**

- Cellulose
- Hemicellulose
- +Lignin

**Hydrolysis**

- Sugars

**Catalytic Conversion**

- Syn-gas

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**C-C Bond Formation**

- \( \text{C}_8^+ \) Alkanes

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\(^2\)Chevron, Typical carbon number distribution - No. 2-D Diesel Fuel
Background on Hydrolysis-Based Upgrading

**Sugar Production**
- Lignocellulosic Biomass
  - Pretreatment
  - Hydrolysis
  - C5 Sugars
  - C6 Sugars

**Sugar Conversion**
- Sugars
  - Aqueous Phase Reforming
  - Biphasic Dehydration
  - Hydrodeoxygenation
  - Furanics, Levulinic Acid
  - Gasoline

**Conversion of Platform Chemicals**
- Furanics, Levulinic Acid
  - C-C Bond Formation
    - Aldol condensation
    - Oligomerization
    - Diels-Alder Reaction
    - Hydrocycloaddition
    - Decarboxylation
    - Hydrodeoxygenation
    - Hydrogenation
  - Heavier Alkanes

**Sources**
- Dumesic & co-workers, Science, 2005, 308, 1446
- Wyman & co-workers, Carbohydrate Research, 2013, 92, 3334
- Dumesic & co-workers, Science, 2010, 327, 1110
- Huber & co-workers, Green Chem., 2010, 12, 1933-1946
- Huber & co-workers, Energy Environ. Sci., 2013, 6, 205
Reaction Chemistry

Cellulose → Glucose → Formic Acid

Hemicellulose → Xylose → Furfural

Liquid Alkanes C₈⁺ → Butene Oligomers C₈⁺

Ru/Al₂O₃ + H₂

Silica-Al₂O₃

Amberlyst

RuSn/C + H₂

gamma-Valerolactone

Liquid Alkanes C₅ – C₃₁ → H-Dimer → F-Ac-F Dimer

Pt/SiO₂-Al₂O₃ + H₂

- H₂O

H₂O

H₂O

Acetone

OH⁻
Petroleum derived feedstock made from biomass

- 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).

H. Olcay, A. V. Subrahmanyam, R. Xing, J. Lajoie, J. A. Dumesic, G. W. Huber; Production of Renewable Petroleum Refinery Diesel and Jet Fuel Feedstocks from Hemicellulose Sugar Streams; Energy and Environmental Science, 2013, 6, 205-216.
Formation of Heavy Compounds during Hydrogenation

H. Olcay, A. V. Subrahmanyam, R. Xing, J. Lajoie, J. A. Dumesic, G. W. Huber; Production of Renewable Petroleum Refinery Diesel and Jet Fuel Feedstocks from Hemicellulose Sugar Streams; Energy and Environmental Science, 2013, 6, 205-216.
Process Flow Diagram of Lignocellulosic Biorefinery

Hemicellulose (C5 sugars) → Decanter → Biphasic Hydrolysis/Dehydration → Aqueous Phase

Organic Phase → Acetic Acid Column → Furfural, HMF Column → NaOH → Dimer, H-dimer

Aqueous stream (to waste water treatment) → THF Column → Acetic Acid Column

Acetic Acid, Furfural, HMF → Make-up THF → Acetic Acid

Acetic Acid → THF recycle → H2 recycle → Alkanes

Furfural → HMF → Decanter → Dimer, H-dimer

Dimer, H-dimer → H2 recycle → Alkanes

LA Hydrogenation → LA Extraction → H2 recycle

LA, SBP → GVL column → Butene, CO2

CO2 → Alkenes

H2 recycle → H2 recycle → Alkanes

Water Wash → Sulfuric acid recycle → Acid, Salt

Cellulose, Lignin → Pre-treatment

Red Maple → Water → Water Wash

Cellulose Deconstruction

Lignin, C6 Humins → FA, water (waste water treatment) → FA, LA, Lignin, Humins

FA Evaporator → H2 recycle

H2 recycle → H2 recycle

H2 recycle → H2 recycle

H2 recycle → H2 recycle

H2 recycle → H2 recycle

H2 recycle → H2 recycle

Lignocellulosic Biorefinery

Red Maple (271 MW)

Overall Energy Conversion Efficiency = 31%

Biorefinery Energy Efficiency = 33%

Overall Primary Energy Efficiency (%) = \( \frac{\text{Energy renewable fuels and chemicals}}{\text{Primary Energy Input (biomass, natural gas)}} \times 100\% \)

Sankey Diagram for Carbon Yields and Capital Costs

Equipment and Operating Cost

Total Equipment Costs = $208.8 M

Total Reactor and Catalyst Costs = $85.2 M

Total Operating Costs = $138.9 M/yr

Economic Analysis: MSP of jet fuel = $4.75 per gallon

- Value of diesel and jet fuel adjusted to set NPV=0
- Current Jet fuel spot price= $3 per gallon

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<table>
<thead>
<tr>
<th>Category</th>
<th>Parameter</th>
<th>Assumption</th>
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<tr>
<td>Project Financing</td>
<td>Equity</td>
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<tr>
<td></td>
<td>Depreciation Method</td>
<td>Variable Declining Balance (VDB)</td>
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<tr>
<td></td>
<td>Depreciation Period</td>
<td>7 yrs</td>
</tr>
<tr>
<td></td>
<td>Construction Period</td>
<td>3 yrs</td>
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<tr>
<td></td>
<td>Discount Rate</td>
<td>6.74 %</td>
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<tr>
<td></td>
<td>Income Tax Rate</td>
<td>35 %</td>
</tr>
<tr>
<td></td>
<td>Operating Hours</td>
<td>8400 hrs per yr</td>
</tr>
<tr>
<td></td>
<td>Cost Year of Analysis</td>
<td>2010</td>
</tr>
<tr>
<td></td>
<td>Inflation</td>
<td>2 % per yr</td>
</tr>
</tbody>
</table>

| Calculation of Fixed Costs and Working Capital | Inside Battery Limits (ISBL) Costs | Estimated from Aspen Simulation |
| | Outside Battery Limits (OSBL) Costs | 30% of ISBL Costs |
| | Direct Costs | ISBL + OSBL Costs |
| | Engineering and Supervision | 30% Of Direct Costs |
| | Construction and Fee | 30% Of Direct Costs |
| | Contingency | 20% Of Direct Costs |
| | Fixed Capital Investment | 2.34* ISBL Costs |
| | Working Capital | 5 % of FCI |

| Important Raw Material and Utility Costs | Red Maple | 51 $/MT |
| | Hydrogen | 2000 $/MT |
| | Ru-based catalyst | 540 $/kg |
| | Pt/SiO2-Al2O3 | 2000 $/kg |
| | Amberlyst | 150 $/kg |
| | SiO2-Al2O3 | 5 $/kg |
| | Catalyst Refurbishing Cost | 10% of Total Catalyst Cost per year |
| | Waste Water Treatment | 36 $/MT |

| By-Product Costs for Revenue Calculations | Acetic Acid | 772 $/MT |
| | HMF | 1580 $/MT |
| | Light Ends | 2 $/gal |
| | Naptha | 2.5 $/gal |

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1www.eia.gov
Conclusions and Directions for Future Research

• Minimum Selling Price (MSP) of jet fuel from lignocellulosic biorefinery was estimated as $4.75 per gallon

• Advantages
  – Drop in distillate fuels produced with 33% energy conversion efficiency
  – Demonstrated each technology on lab scale reactors with feed derived from biomass

• High value platform chemicals (such as LA, FA, Acetic Acid, Furfural, HMF) can be alternatively sold to improve the economic feasibility of the process

• Opportunities for cost reduction
  – Low yield step LA production (75% yield of LA)
  – Lignin conversion: Currently, the lignin is combusted for process energy
    • Need technologies to convert lignin and humins to useful fuels and chemicals
  – Hydrodeoxygenation reactor which utilizes Pt based catalyst is the most expensive step
    • Need for cheaper catalyst (most promising alternative)
  – Waste water treatment is a major operating cost
    • Need for better processes which would allow recycle of water

Hydrodeoxygenation (HDO) of Biomass

- Selective removal of oxygen (as H$_2$O or CO$_2$) from biomass derived feedstocks
- Make targeted products (alkanes, alcohol, polyols, ethers) that fit into existing infrastructure
- Process a range of biomass derived feedstocks (carbohydrates, pyrolysis oils, hydrolysis products)
- Lots of water present (up to 95 wt% H$_2$O)
- Minimize hydrogen consumption
- Design of Catalyst is crucial (requires an understanding of chemistry)
Design of Catalysts for HDO of Biomass

**Metal Functionality**
- Monometallic vs. Bimetallic
- Hydrogenation (aldehyde, ketones, ethers, acids, carbohydrates)
- C-C bond cleavage (decarbonylation, retro-aldol condensation)
- C-O-C bond hydrogenolysis

**Bifunctional Metal-Acid Catalysts**
- Dehydration (C-O bond cleavage)
- Location of acid sites
- Brønsted vs. Lewis Isomerization

**Support**
- High surface area
- Hydrothermally stable
- Regenerable
- Acidity
EFFECT OF ACIDITY, SOLVENT AND WATER ON DEHYDRATION AND HYDROLYSIS REACTIONS
There are several (aqueous-phase) acid catalyzed reactions in biomass conversion

- **Hydrolysis**

  ![Hydrolysis Reaction]

- **Isomerization**\(^1\)

  ![Isomerization Reaction]

- **Dehydration**\(^2\)

  ![Dehydration Reaction]

- **Rehydration**

  ![Rehydration Reaction]

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Low product selectivity is a key challenge in biomass conversion.
Kinetic Model for Conversion of Xylose into Furfural with Mineral Acid

All reactions are first order with respect to reactants.

<table>
<thead>
<tr>
<th>reaction parameters</th>
<th>( \log_{10} A )</th>
<th>( E_A (kJ/mol) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_k_1 (min^{-1}) )</td>
<td>13.17 ± 0.72(^a)</td>
<td>123.91 ± 6.00</td>
</tr>
<tr>
<td>( b_k_2 (M^{-1} \cdot min^{-1}) )</td>
<td>7.63 ± 1.97</td>
<td>72.47 ± 16.28</td>
</tr>
<tr>
<td>( b_k_3 (min^{-1}) )</td>
<td>5.44 ± 1.18</td>
<td>67.58 ± 9.66</td>
</tr>
<tr>
<td>( k_4/k_{-4} )</td>
<td>7.1</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) 95% confidence interval in parameter estimation.
\( ^b \) 1st and 2nd order rate parameters that are lumped with acid concentration; \( k_n = k'_n[H_3O^+] \)

Range of conditions:
10 wt% xylose; 0.1 M HCl; T = 130-170 °C
Organic solvent: MIBK

Brønsted vs Lewis Sites in the Liquid Phase

- Brønsted acid site: proton (H⁺) donor
- Lewis acid site: electron-pair acceptor (Mⁿ⁺)

The effects of water on solid catalysts is under debate.

Lewis acid sites have been shown to exist in water.¹

Activity and Selectivity of Xylose Conversion is a Function of Lewis-Bronsted Ratio for Homogeneous Catalysts

Reaction conditions: T=160 °C and total acid sites were kept constant at 0.500 mmoles. Feed was 10 wt% xylose aqueous solution. Brønsted : Lewis ratio = 1:0 (■), 1:1 (●), 0:1 (▲).

Brønsted acid: HCl
Lewis Acid: Yb(OTf)_3 (ytterbium triflate)*

Furfural Selectivity Increases with the Brønsted to Lewis Acid Site Ratio

- Brønsted acid sites are more selective to dehydration reactions.
- Lewis acid sites catalyze humin formaions.
- Ion-exchange resins show similar selectivities to Zr-P.
- Strong potential to make solid acid catalysts for aqueous phase conversion of biomass.

Activity and selectivity are a function of the Brønsted to Lewis site ratio for Glucose Conversion.

Brønsted to Lewis acid ratio = 1:0 (■), 3:1 (○), 1:1 (▲), 1:3 (●), and 0:1 (◆). Blank run (dashed line) (★).

**Brønsted acid:** HCl  
**Lewis Acid:** Yb(OTf)$_3$ (ytterbium triflate)

Reaction conditions: 160 °C; 10 wt% glucose; 0.1 M total acid sites

High Carbohydrate Yields can be Obtained from Biomass in GVL Solvents

Proposed reaction scheme

AQUEOUS PHASE

POLAR APROTIC SOLVENT

CELLULOSE $\xrightarrow{\text{H}^+} \text{Levoglucosan} \xrightarrow{\text{H}^+ \text{Solvent}} \text{HMF} \xrightarrow{\text{H}^+ \text{H}_2\text{O}} \text{Levulinic acid}$

HUMINS
Higher HMF yields are obtained in polar aprotic solvents

The rate of cellulose conversion increases as the water content decreases.
METALLIC AND BIMETALLIC CATALYST FUNCTIONALITY
Monometallic Catalysts for Hydrogenation of Carbonyl Groups

- Ru is most active for the APH of all feeds except furfural; Pd is most active for the APH of furfural
- C-binding intermediates play dominant role in APH activity of furfural
- Steric effects are important in hydrogenation (rate of xylose vs. furfural vs. propanal)

Ru is most active for non-furanic carbonyl hydrogenation and C-C bond scission. Pd is most active for hydrogenation of furanic compounds. Ni is active for C-O-C hydrogenolysis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature (°C)</th>
<th>Functionality hydrogenated</th>
<th>Most active metal</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>100</td>
<td>0.6</td>
<td>Ru</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>100</td>
<td>0.5</td>
<td>Ru</td>
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<tr>
<td>C=O</td>
<td>100</td>
<td>4.7</td>
<td>Ru</td>
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<tr>
<td>C=O</td>
<td>100</td>
<td>0.7</td>
<td>Ru</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>100</td>
<td>0.13</td>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>80</td>
<td>0.08</td>
<td>Pd</td>
<td></td>
</tr>
<tr>
<td>C-O-C</td>
<td>250</td>
<td>0.01</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>200</td>
<td>0.09</td>
<td>Ru</td>
<td></td>
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</table>

Bimetallic Catalysts can increase activity for Hydrogenation Reactions

Bimetallic Pd-Fe catalyst is most active catalyst for furfural hydrogenation

Bimetallic Pd-Fe catalyst is most active catalyst for furfural hydrogenation

J Lee, YT Kim, GW Huber, Aqueous phase hydrogenation and hydrodeoxygenation of biomass-derived oxygenates with bimetallic catalysts; Green Chemistry (2014) 16(2) 708-718.
Challenges with Base Metals: Leaching

Up to 55% of cobalt leached out during aqueous-phase hydrogenation of furfuryl alcohol.

How to stabilize base metals in aqueous solutions?

Reaction condition: 140 °C, 300 psig, WHSV = 5.8 h⁻¹, 2 wt% furfuryl alcohol solution as the feed
Continuous flow reactor
Able to stabilize base metal catalysts using a technique called Atomic Layer Deposition (ALD) to prepare catalysts

J. Lee, DHK Jackson, T Li, RE Winans, JA Dumesic, TF Kuech, GW Huber; Enhanced stability of cobalt catalysts by atomic layer deposition for aqueous-phase reactions; Energy and Environmental Science (2014) 7, 1657-1660.
The catalytic performance of TiO$_2$/Co/TiO$_2$ increases compared to classic cobalt catalysts for furfuryl alcohol conversion.

After calcination, ALD TiO$_2$ coating decorates defects and edges of cobalt particles, preventing leaching and sintering.

Reaction conditions:
413 K, 2.34 MPa, WHSV = 5.8 h$^{-1}$
ELECTROCATALYTIC HYDRODEOXYGENATION
Challenge with HDO is Hydrogen Cost

- Cost of hydrogen gas can be as much as as the biomass itself
  - Low near petroleum refineries (~$1/kg)
  - 100 fold increase in remote locations that require trucking and storage of hydrogen

Sources:
- National Renewable Energy Laboratory (NREL), Biomass Resources of the United States
- Padró, C. E. G.; Putsche, V. Survey of the Economics of Hydrogen Technologies; NREL, 1999
Electrocatalytic Conversion of Biomass

**Anode Reactions**

\[ H_2O \rightarrow 2H^+ + 2e^- + O_2 \]

**Cathode Reactions**

\[ 2H^+ + 2e^- + \text{Glucose } (C_6H_{12}O_6) \rightarrow \text{Hexane } (C_6H_{14}) + H_2O \]

**Overall Reaction**: \( H_2O + \text{Glucose} \rightarrow \text{Hexane} + 3.5O_2 \)

S. K. Green; G. A. Tompsett; H. Ju Kim; W. B. Kim; and; G. W. Huber; ChemSusChem (2012)
S. K. Green; J. Lee; H. Ju Kim; G.A. Tompsett; W. B. Kim; and; G. W. Huber; Green Chemistry (2013)
Critical we continue to develop improved catalytic processes for biomass conversion

- Make higher value products in higher yields (Selective bond cleavage: C-C vs. C-O vs. Hydrogenation)
- Improved hydrothermal stability of catalyst supports (stability with minerals in biomass)
- Non-precious metal catalysts that are stable (Cu, Ni)
- Processing of cheaper more realistic biomass based feeds
- Reaction Engineering
- More detailed understanding of reaction chemistry (detailed kinetic models)
- Catalysts designed with precise control of active sites (metal and acid location)
BIFUNCTIONAL ACID METAL CATALYSTS
Bifunctional Catalysts for HDO of Sorbitol
Pt/Zr-P and Pt-ReO$_x$/C

The size of Pt metal particles: Pt/Zr-P: Pt-ReO$_x$/C = 22:1
The amount of acid sites based on the surface area: Pt/Zr-P: Pt-ReO$_x$/C = 110:1

Aqueous-Phase Hydrodeoxygenation of Sorbitol

4 Key Classes Reactions

- **Dehydration**
- **Hydrogenation**
- **Dehydration and Hydrogenation**
- **Dehydrogenation and retro-aldol condensation**
- **Dehydrogenation and decarbonylation**

Light gases

Gasoline-range products

Aqueous-phase products
Tuning HDO Chemistry to Make Commodity Chemicals: 1,6 Hexanediol