The Challenges and Opportunities of Designing Pioneer Catalytic Technologies for the Production of Sustainable Fuels and Chemicals from Biomass

KAUST Future Fuels Workshop
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University of Wisconsin-Madison Chemical & Biological Engineering
http://biofuels.che.wisc.edu/
The discovery of inexpensive oil revolutionized our world.

Aug. 27, 1859 “Colonel Edwin Drake” Strikes Oil for First Time in Titusville, PA
See “The Prize” by Daniel Yergin for a history of oil production.
Cellulosic Biofuels are best technology option for decreasing petroleum usage and greenhouse gas emissions.

CCS = Carbon Capture and Storage
The biomass conversion challenge

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 or Commodity Chemical
Low functionality
High Thermal Stability

Chemical Engineering Challenges
• Economics
• Low overall carbon yield
• Low energy density feedstock (high oxygen content)
• Distributed non-volatile feedstock
• Separations of dilute mixtures
• Unknown chemistry
Integrated Biorefinery Program

- Over $2 billion has been spent to develop 2\textsuperscript{nd} generation biofuel technology in the past decade.
- Goal is to help share cost for 1\textsuperscript{st} generation plants in biomass reforming
- Fund:
  - Pilot plants (up to $20 million)
  - Demonstration Plants
  - Commercial plants (up to $500 million total)
- Provides 20-50% funding from DOE
2nd Generation Biofuel Companies have Struggled

Stock Price KiOR
Stock Price GEVO
Stock Price Amyris

$95/barrel  $94/barrel  $94/barrel  $93/barrel  Average Oil Price
KiOR Columbus, MS Facility built in 2011-2012
KiOR

- Technology to produce renewable transportation fuels from biomass by pyrolysis oil and hydrotreating.
- 2007 - Founded
- 2011 IPO raised $150 million (received $75 million loan from MS)
  - IPO documents claim they can produce 67 gallons of fuel per ton of biomass
- 2011 groundbreaking of Columbus, MS demonstration plant with capacity of 13 million gallons/year
- 2012 CEO claimed yields of 72 gallons per ton of biomass with potential to get 92 gallons per ton of biomass
- 2012 Management claimed that Columbus, MS demonstration facility was online that was going to produce 0.5-1.0 million gallon in 2012
- 2013 Management now says no biofuels have yet shipped but plant will produce 3-5 million gallons soon
- 2013 Columbus facility output was 25% of capacity
- 2014 CEO claim actual yields in Columbus facility in low 30 gallons per ton (whistleblower lawsuit claims 22 gallons per ton)
- 2014 KiOR files for bankruptcy
- Spent over $600 Million with $2 million in revenues

http://fortune.com/kior-vinod-khosla-clean-tech/
Challenges with Pioneer Process Plants


• Rand Study, 1981 prepared for US DOE because of underestimate for costs for coal to liquids technologies in 70s.
• Looked at 44 chemical process plants from 34 companies in chemical, oil, minerals and design
• “The occurrence of cost misestimation and performance shortfalls does not surprise the few people who have experience with first of a kind technologies.”
• Severe underestimation of capital is common in new technology
• Performance problems are common in new technology
• First generation plants will not have a high performance. Over 50 percent of the plants failed to meet production goals in the 2nd six months after start up.
Conventional View of Estimating Project Costs

Fig. 4.1 — The conventional view of how information and project phase affect estimation accuracy

Actual Views of Estimating Project Costs of Pioneer Plants

![Graph showing the ratio of estimated to actual costs for different estimate classes, with data points and error bars.]

**Fig. 4.3 — Experience of the pioneer plants sample with estimation accuracy**

Estimating Plant Performance

\[ \text{Plant Performance} = 85.77 - 9.69 \times \text{NEWSTEPS} + 0.33 \times \text{BALEQS} - 4.12 \times \text{WASTE} - 17.91 \times \text{SOLIDS} \]  

(Eq 1)

NEWSTEPS = Number of new process areas  
BALEQS = Percentage of Material Balances based on commercial data  
WASTE = 0 or 5 factor of waste disposal  
SOLIDS = 0 or 1 1 for solids

Every year Plant Performance increases by 20%  
Year 1 40%; Year 2 48%.... Year 6 100%

If Plant Performance fails to reach 40% capacity after year 1 it is unlikely to achieve nameplate capacity without a significant capital investment.

Correct Way to Estimate Economics for Pioneer Process Plants

Impossible to predict economics without a working prototype.

<table>
<thead>
<tr>
<th></th>
<th>n&lt;sup&gt;th&lt;/sup&gt; Plant</th>
<th>Optimistic</th>
<th>Base Case</th>
<th>Pessimistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital Cost (millions $)</td>
<td>$287</td>
<td>$479.8</td>
<td>$911.6</td>
<td>$1,236.3</td>
</tr>
<tr>
<td>Product Value ($/GGE)</td>
<td>$3.09</td>
<td>$4.32</td>
<td>$6.55</td>
<td>$8.23</td>
</tr>
</tbody>
</table>

MM Wright, JA Satrio, RC Brown, DE Daugaard, DD Hsu; Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels; NREL/TP-6A20-46586, November 2010
New Technologies in the Petrochemical Area do Make Money

The time required for commercialization can vary substantially.

<table>
<thead>
<tr>
<th>Degree of market familiarity</th>
<th>Low</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product-line extensions into new markets</td>
<td>Success rate: 30–40%</td>
<td>Time to commercialization: 2–7 years (average 5)</td>
</tr>
<tr>
<td>New-product launches in new markets</td>
<td>Success rate: 15–20%</td>
<td>Time to commercialization: 8–19 years (average 14)</td>
</tr>
<tr>
<td>Product-line extensions into existing markets</td>
<td>Success rate: 40–50%</td>
<td>Time to commercialization: 2–5 years (average 4)</td>
</tr>
<tr>
<td>New-product launches in existing markets</td>
<td>Success rate: 30–40%</td>
<td>Time to commercialization: 6–15 years (average 11)</td>
</tr>
</tbody>
</table>

McKinsey on Chemicals; Chemical innovation: An investment for the ages; M. Miremadi, C. Musso, J. Oxgaard.
Pyrolysis is the cheapest technology to convert biomass into a liquid fuel. Several companies are producing pyrolysis oils on commercial scale today. Iowa State (Robert Brown), Conoco Phillips, and National Renewable Energy Laboratory concluded minimum cost of biofuel:

- Hydrolysis $5-6/GGE > Gasification $4-5/GGE > Pyrolysis $2-3/GGE (GGE = gallons of gasoline energy equivalence.)
- (Study assumption: nth plant economics; 10% IRR; 2000 tons/day feedstock; Feedstock cost $75/ton; 100% equity financing.)

Challenges with pyrolysis technology:

- Controlling the chemistry
- Low quality fuel
- Upgrading of pyrolysis vapors
- Catalysts and reaction engineering
- Hydrogen requirements for upgrading (Hydrogen is more expensive than actual pyrolysis oil)

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

**Oak Wood Bio-oil**

- **Elemental Composition**
  - C: 47.0%
  - H: 8.2%
  - O: 44.8%

- **Viscosity**:
  - Viscosity: ~150 cP

- **Non-Combustibles**
  - Ash: 0.03 wt%

- **Acidity**
  - pH: 2.75

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

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# Bio-oil Composition

## Oxygenates / Sugars

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>C #</th>
<th>MW</th>
<th>Carbon %</th>
<th>Overall wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 sugars (xylose)</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>5</td>
<td>150</td>
<td>11.65</td>
<td>11.51%</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2</td>
<td>60</td>
<td>9.73</td>
<td>9.61%</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>6</td>
<td>162</td>
<td>7.17</td>
<td>6.37%</td>
</tr>
<tr>
<td>Hydroxyacetaldehyde</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2</td>
<td>60</td>
<td>6.17</td>
<td>6.10%</td>
</tr>
<tr>
<td>2,5-dimethyl tetrahydrofuran</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O</td>
<td>6</td>
<td>100</td>
<td>2.49</td>
<td>1.37%</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;</td>
<td>6</td>
<td>182</td>
<td>1.97</td>
<td>1.97%</td>
</tr>
<tr>
<td>2-methyl tetrahydrofuran</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O</td>
<td>5</td>
<td>86</td>
<td>1.71</td>
<td>0.97%</td>
</tr>
<tr>
<td>Hydroxyacetone</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3</td>
<td>74</td>
<td>1.68</td>
<td>1.36%</td>
</tr>
<tr>
<td>Catechol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6</td>
<td>110</td>
<td>1.07</td>
<td>0.65%</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6</td>
<td>116</td>
<td>1.02</td>
<td>0.65%</td>
</tr>
<tr>
<td>1-hydroxy-2-butanone</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>88</td>
<td>0.93</td>
<td>0.67%</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O</td>
<td>6</td>
<td>100</td>
<td>0.8</td>
<td>0.44%</td>
</tr>
<tr>
<td>5-hydroxymethylfurfural</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6</td>
<td>126</td>
<td>0.57</td>
<td>0.39%</td>
</tr>
<tr>
<td>Furfural</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5</td>
<td>96</td>
<td>0.54</td>
<td>0.34%</td>
</tr>
<tr>
<td>Other Light Oxygenates</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.94</td>
<td>2.24%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Carbon %</th>
<th>Overall wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolitic Lignin</td>
<td>51.00</td>
<td>30.00%</td>
</tr>
<tr>
<td>Sugars/sorbitol</td>
<td>20.79</td>
<td>19.85%</td>
</tr>
<tr>
<td>Oxygenates</td>
<td>28.21</td>
<td>25.15%</td>
</tr>
<tr>
<td>Water/ash</td>
<td>0</td>
<td>25.00%</td>
</tr>
</tbody>
</table>

- Carbon % values obtained from Kamala, Huber et. al (not yet published)
- Weight % normalized based on typical bio-oil feedstock
Bio-oil undergoes phase separation when heated

1 day

5 day

7 day

• Bio-oil phase separates on accelerated aging (heated to 90°C)
• A thick tarry phase is formed at the bottom and a less viscous top phase
Hydrodeoxygenation (HDO) of Biomass

- Selective removal of oxygen (as H₂O or CO₂) 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% H₂O)
- Minimize hydrogen consumption
- Design of Catalyst is crucial
Liquid Products produced from HDO of pyrolysis oils

- Pyrolysis oil produced from pine wood
- HDO in two stage reactor
- Reactor plugs after 66 hr
- Make C10-C24 cycloalkane
- 73 % carbon yield at 66 hr
- 41 % carbon overall (low yield)
Current Technology for Hydrotreating

<20h TOS

- Extensive coke formation early
- Gasoline and gas products favored over distillate-range fuels
- Low value of residual oil?

>80h TOS

- Catalyst deactivation
- Shift to high boiling residual oil products

Bio-oil 100 → Hydrotreating → Deoxygenated Oil 55.0 → Distillation → Light Gases 20.8

- Gasoline 18.1
- Jet Fuel 17.9
- Diesel 17.0
- Residual Oil 2.7

Bio-oil 100 → Hydrotreating → Deoxygenated Oil 64.8 → Distillation → Light Gases 25.9

- Gasoline 17.5
- Jet Fuel 15.9
- Diesel 15.9
- Residual Oil 15.6

Coke 24.2
Coke 9.3
Biochemical startup announces para-xylene breakthrough

December 5, 2012 | Rebecca Coons

Anellotech, a New York City-based start-up developing biobased routes to aromatics, says it has licensed technology from the University of Massachusetts-Amherst that will triple the para-xylene yields of its catalytic fast pyrolysis (CFP) technology.

www.anellotech.com
Block Flow Diagram for Catalytic Fast Pyrolysis

All chemistry occurs in one single reactor.

Reactors for 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
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
CFP involves reactions in solid biomass, gas phase and inside catalyst

Desired Chemistry:
Pyrolysis (homogeneous)
Dehydration (heterogeneous & homogeneous)
Oligomerization & decarbonylation (heterogeneous)

Undesired Chemistry:
Homogeneous and Heterogeneous coke formation
Aromatic Yield Increases with Heating Rate

Reaction Conditions: Temperature 600°C; ZSM-5;
Feed: Glucose; Catalyst to Feed Ratio 19
C₆O₆H₁₂ → 12/22 C₇H₈ (63 % Yield) + 48/22 CO (36 % Yield) + 84/22 H₂O

P-xylene selectivity can be enhanced by modifying the catalyst

- Modification of ZSM5 catalyst increases p-xylene distribution from 33% to 95%.
- Aromatic selectivity can be tuned to produce targeted aromatics.
- Ratio of p-xylene, m-xylene, and o-xylene can be adjusted.

Overall p-Xylene carbon selectivity (left axis) and xylenes distribution (right axis) obtained from the conversion of 2MF + propylene over various ZSM-5 catalysts (*modified catalyst)

Pilot Plant being built for CFP Technology

Anellotech, Inc.

ifp Energies nouvelles

Axens IFP Group Technologies

Johnson Matthey Process Technologies

SUNTORY

www.anellotech.com

Anellotech’s TCat-8 development and testing unit for converting biomass to BTX. Photo courtesy of Zeton Inc.
INTEGRATED CATALYTIC PROCESS TO PRODUCE RENEWABLE DISTILLATE FUELS FROM BIOMASS
Project Goal and Key Technical Challenges

Convert 80% carbon present in the biomass to C_8+ alkanes using stable, catalytic processes with residence times below 1 hour.

Project Goal

Gasification

Fischer-Tropsch Synthesis

Syn-gas

Project Goal

Cellulose + Lignin

Hemicellulose

Hydrolysis

Catalytic Conversion

Breakdown of Biomass Polymers

C-C Bond Formation

Chevron, Typical carbon number distribution- No. 2-D Diesel Fuel
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).

Sankey Diagram for Carbon Yields and Capital Costs

Conclusions

- We can convert biomass into all the same fuels and chemicals that are produced from petroleum.
- We do a poor job of predicting the economics of pioneer process technologies.
- Pyrolysis can produce a low quality liquid fuel called a bio-oil or pyrolysis oil.
- Pyrolysis oil can undergo hydrotreating.
- Catalytic Fast Pyrolysis can produce aromatics directly from biomass.
- Distillate Range Fuels can be produced from biomass.
- Methane conversion can be understood with theoretical model.