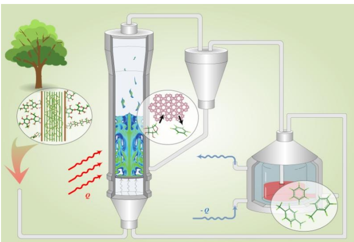


Catalytic Processes for the Production of Fuels and Chemicals from Lignocellulosic Biomass

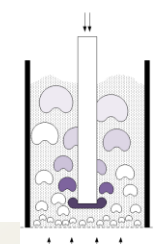
Prof. George W. Huber

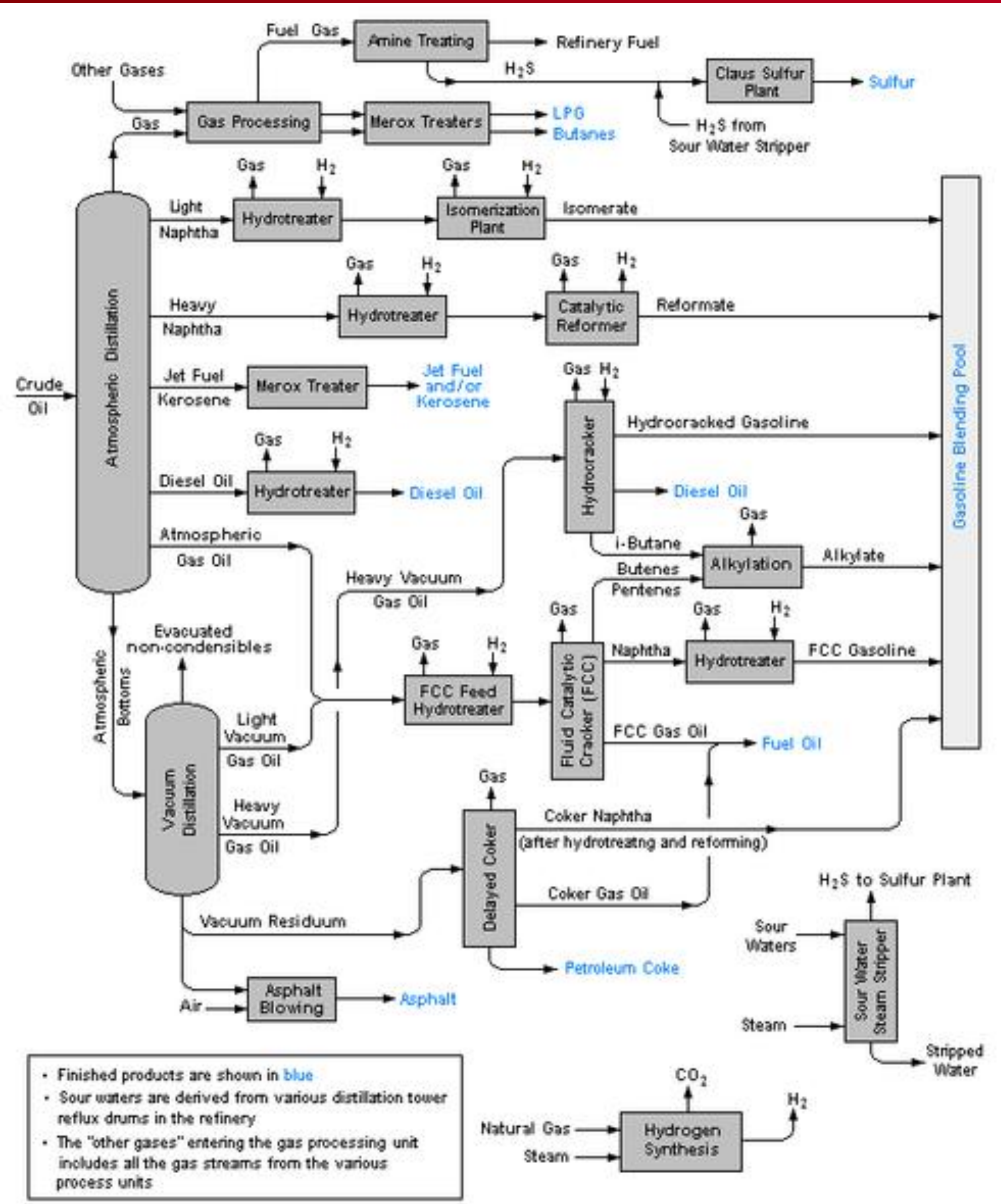
University of Wisconsin-Madison

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

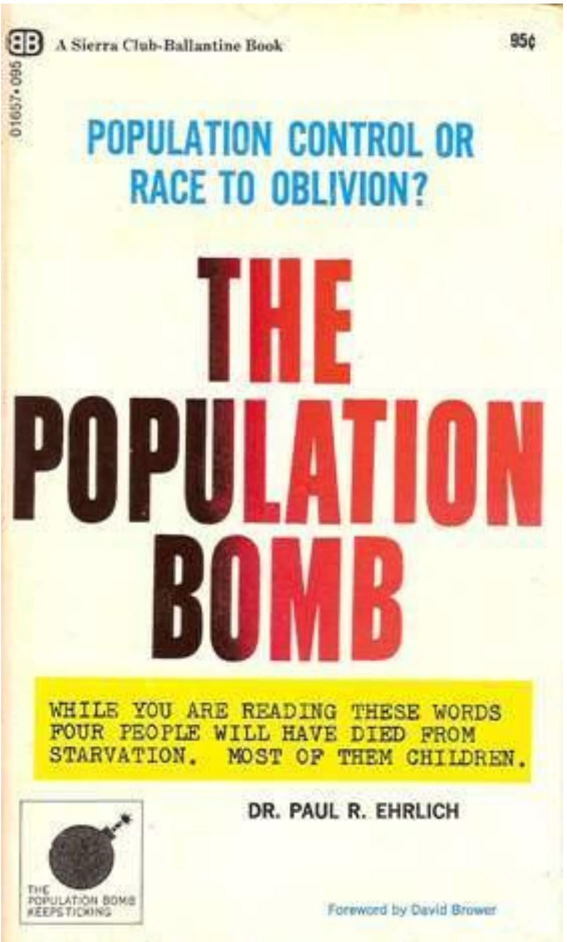
The Petroleum Refinery of Today (Source: Wikipedia)

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).

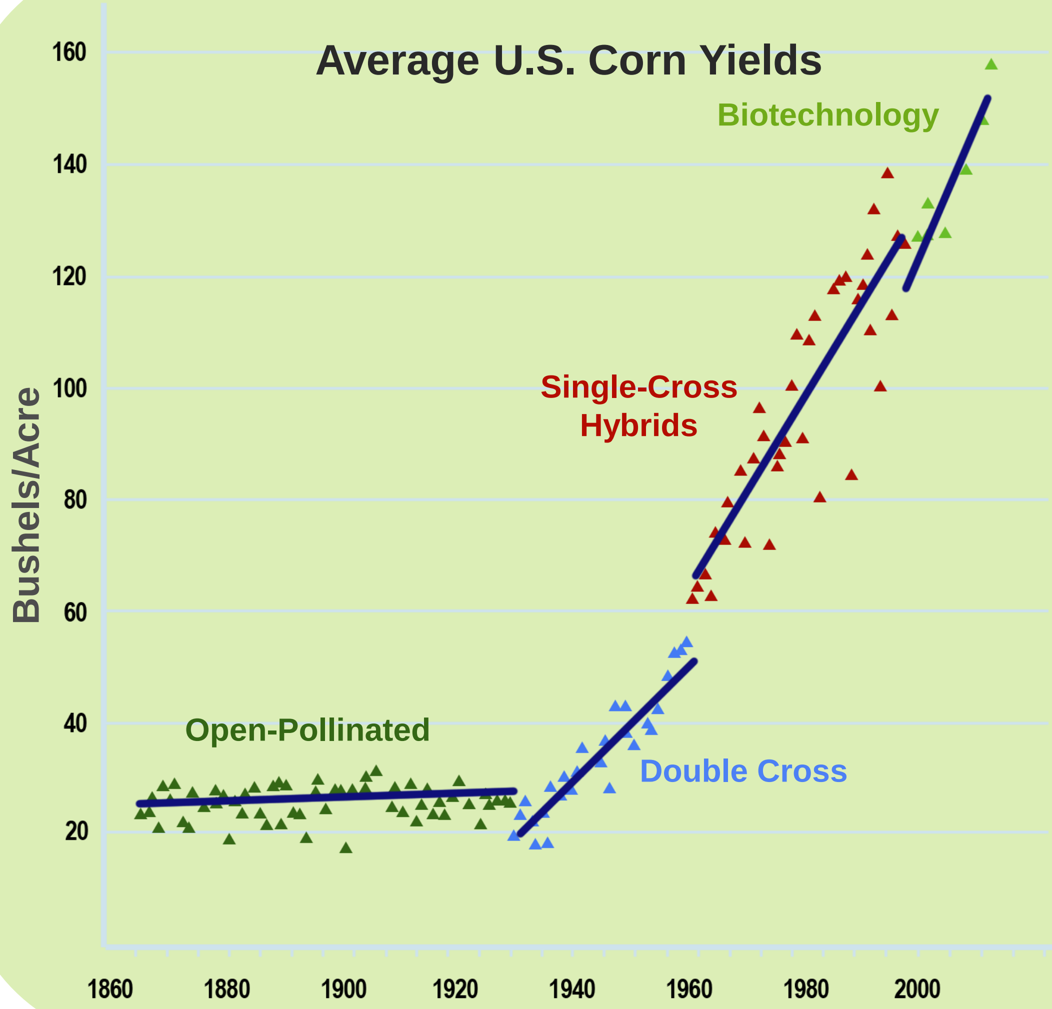
- Cost on an energy basis decreases: Vegetable Oils > Starches > Cellulosic biomass.
- Ease of conversion decreases: Vegetable oils < Starches < Cellulosic biomass.

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

090512-CER-Wall Street deck

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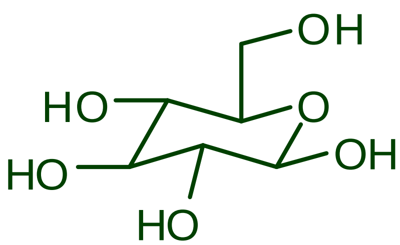
If we use our agricultural resources more efficiently we can feed the world's population and produce bioenergy.

Corn Yield Trends (Bushel Per Acre)			
	1990	2000	2005
World Average	59	70	75
USA	113	137	149
Argentina	60	93	109
China	74	78	80
Brazil	33	47	54
India	23	29	31
Sub-Saharan Africa	22	24	25

Source: Monsanto/Doane Forecast

Slide from Richard Hamilton, CEO Ceres

The biomass conversion challenge

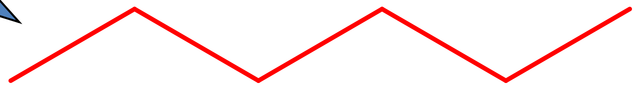


Selective conversion of a highly functionalized oxygenated molecule, into a flammable liquid product that fits into current infrastructure.

Biomass-derived Feedstocks
High functionality
Low Thermal Stability

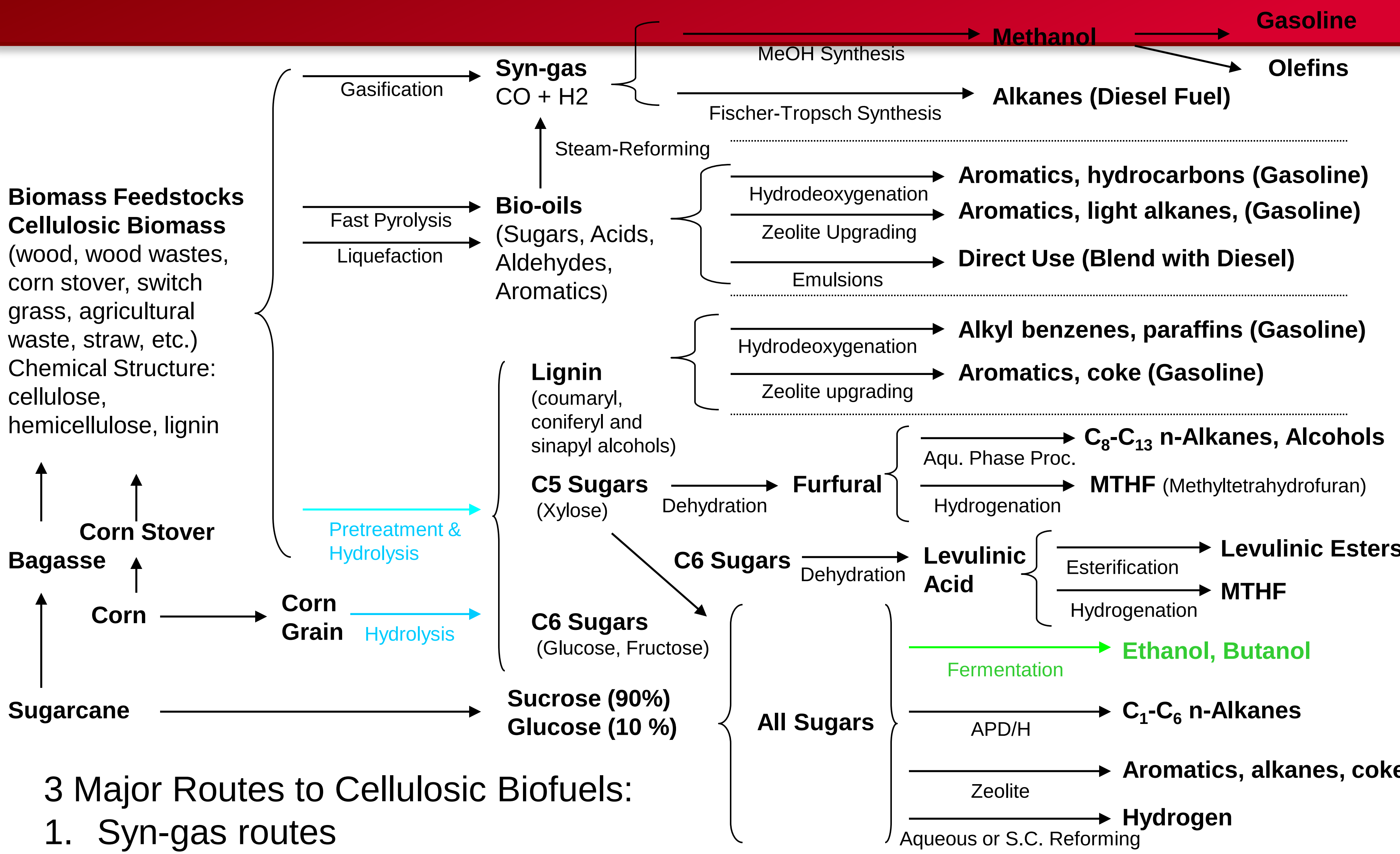
Biomass Reduction

Liquid Fuel
Low functionality
High Thermal Stability



Challenges

- Yields
- Economics
- Products that fit into existing infrastructure
- Capital Cost
- Decrease number of process steps



3 Major Routes to Cellulosic Biofuels:

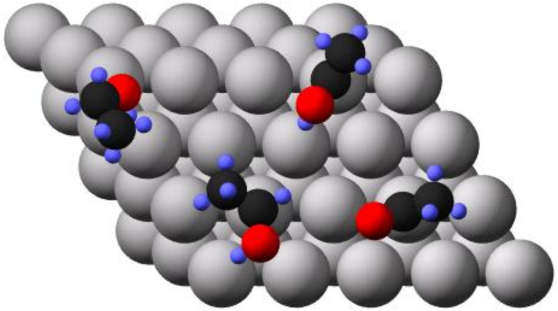
1. Syn-gas routes
2. Bio-oil routes
3. Depolymerization routes

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

G.W. Huber, S. Iborra, A. Corma; Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, Chemical Reviews 106, 4044 (2006).

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

Oak Wood Bio-oil

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

Elemental Composition

Viscometry

Viscosity: ~150 cP

Non-Combustibles

Ash: 0.03 wt%

Solubility

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

Acidity

pH: 2.75

S. Czernik, A. V. Bridgwater, Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **18,** 590-598 (2004).

Catalytic Fast Pyrolysis: Process Development Unit

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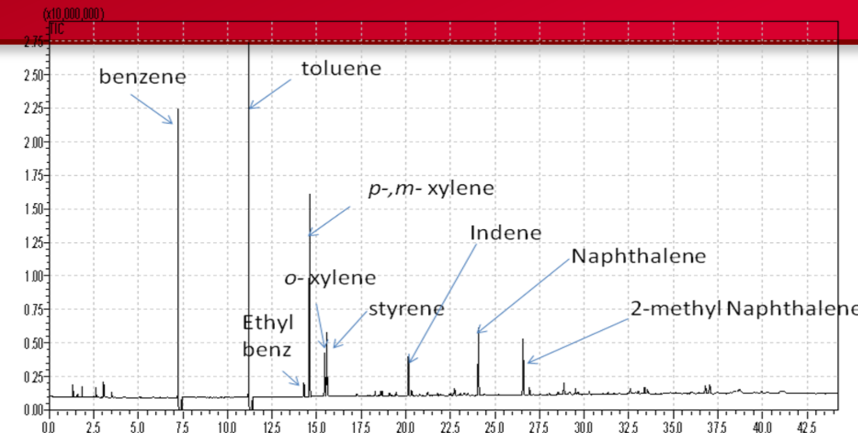


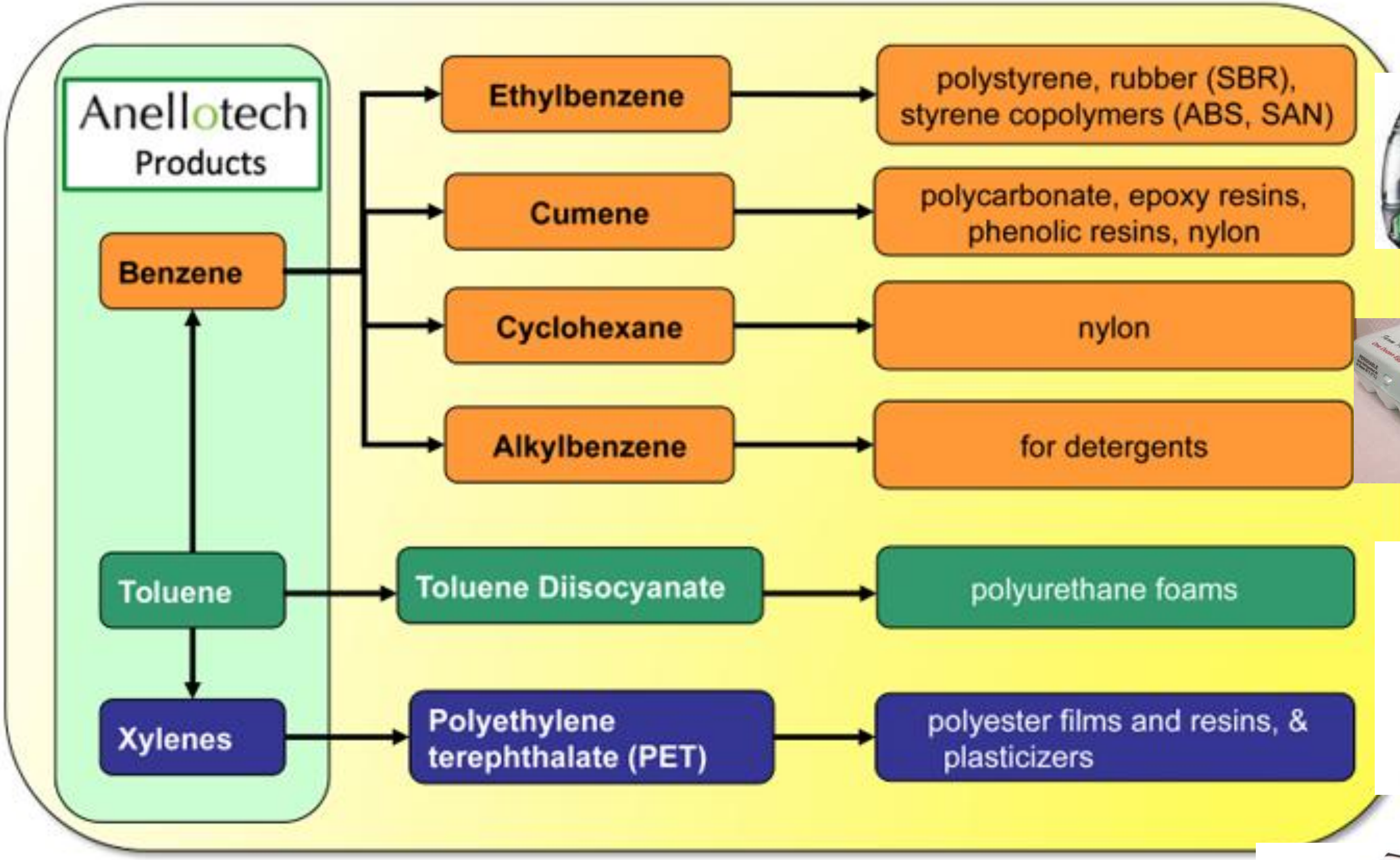
GCMS of raw liquid only observe aromatics

Feed: Pine Wood Sawdust

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

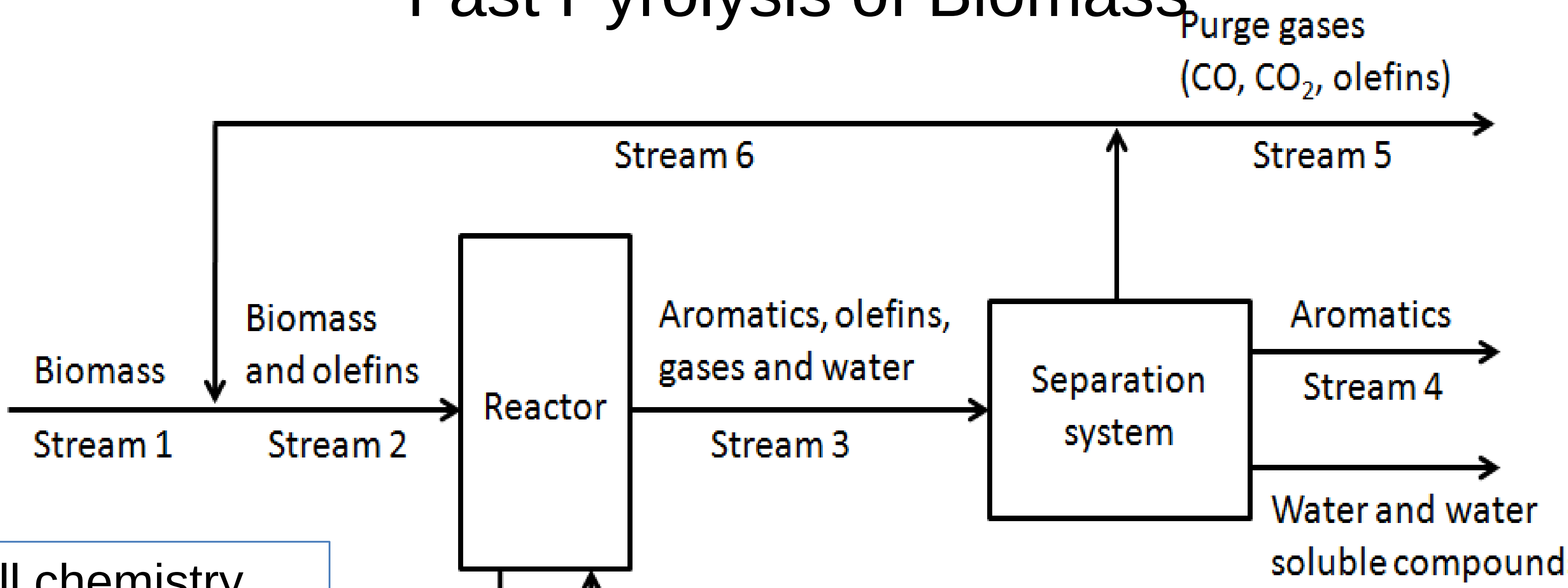
Raw Liquid Product (Contains aromatics and water)

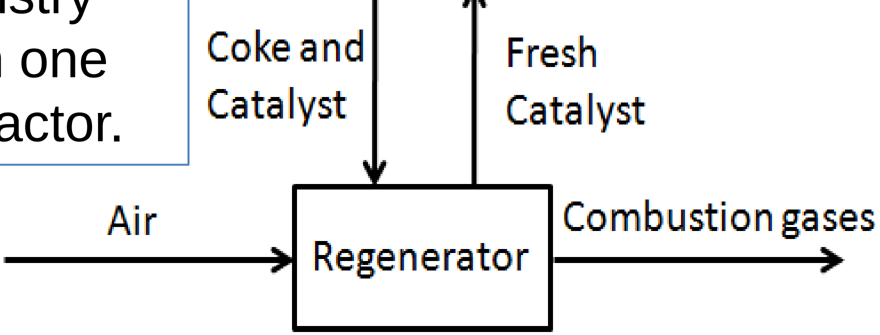
Aromatic Products



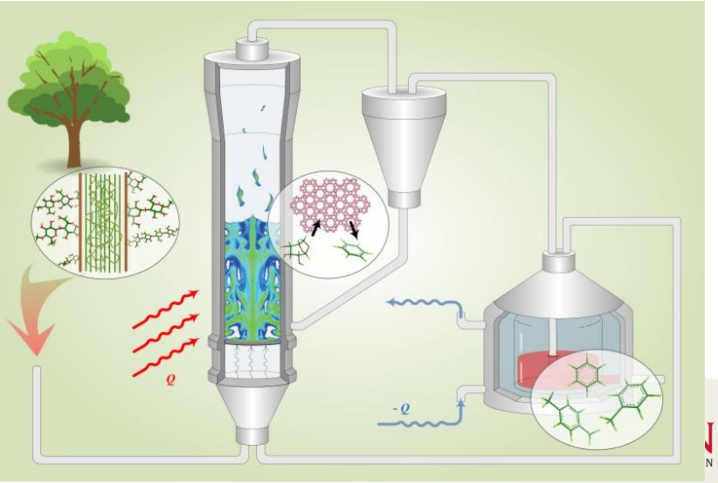
$120 billion aromatics market raw materials to make plastics.

Production of Renewable Aromatics by Catalytic Fast Pyrolysis of Biomass





All chemistry occurs in one single reactor.

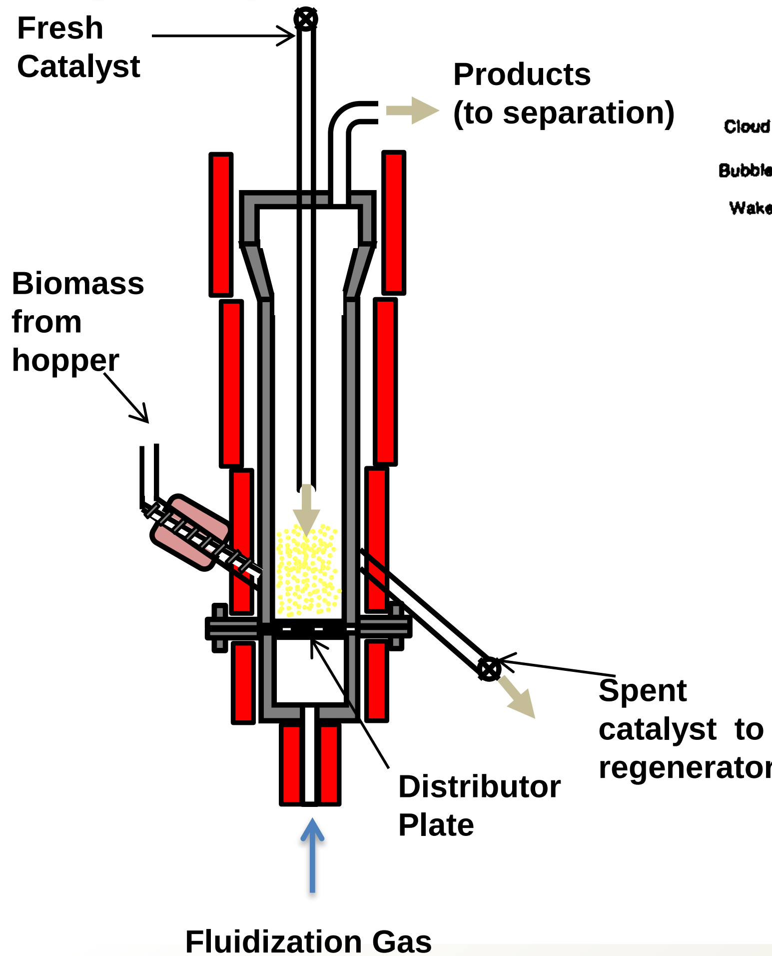


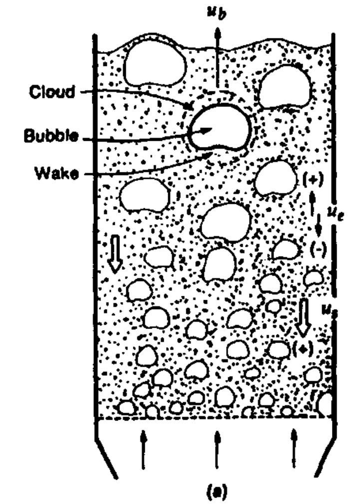
Torren R. Carlson, Yu-Ting Cheng, Jungho Jae and George W. Huber, Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust, Energy and Environmental Science (2011) 4 145-161.

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

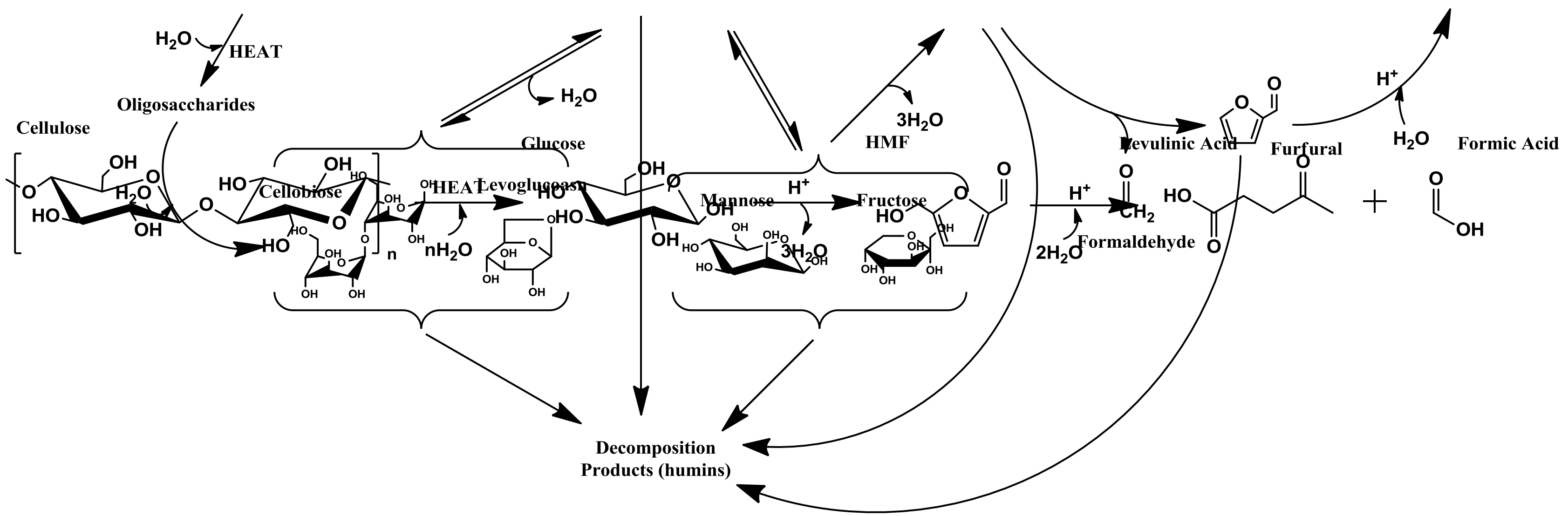




Hydrolysis based Technologies for Biomass Conversion

Biomass can undergo hydrolysis reaction to make carbohydrates and other products

- Challenge: Complex reaction scheme



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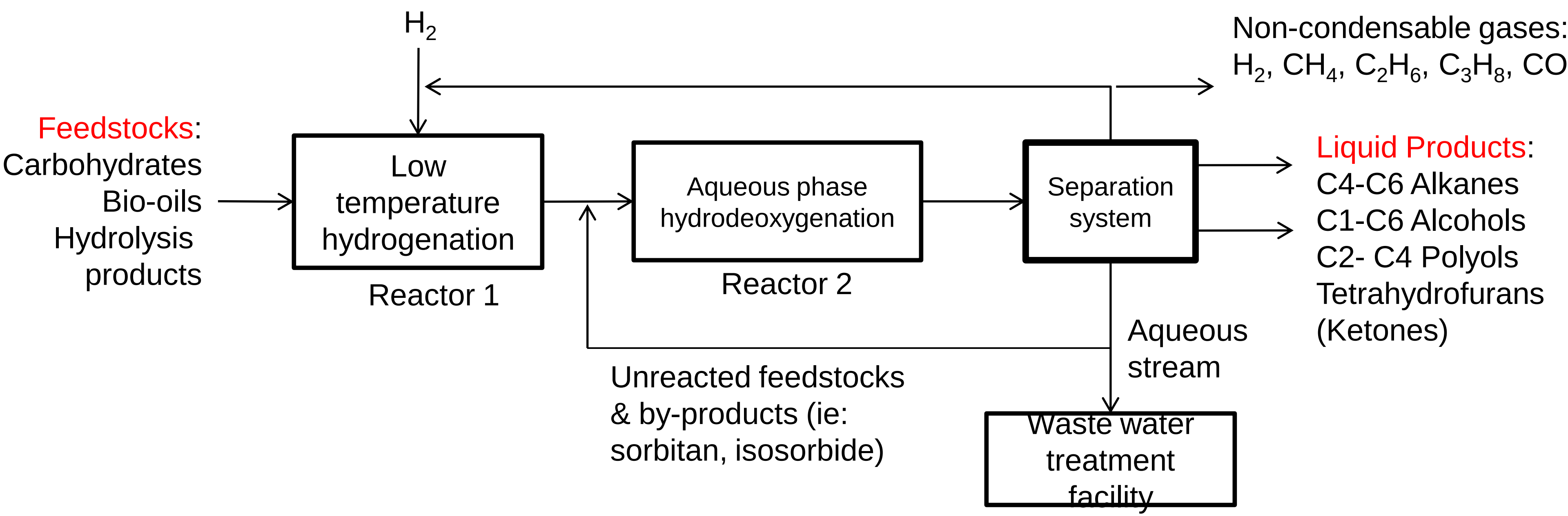
Conceptual Process Design of Aqueous Phase Hydrodeoxygenation Technology

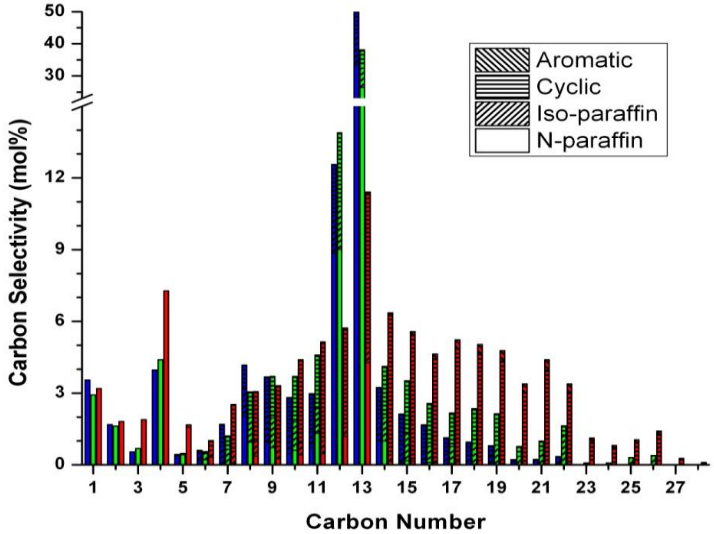


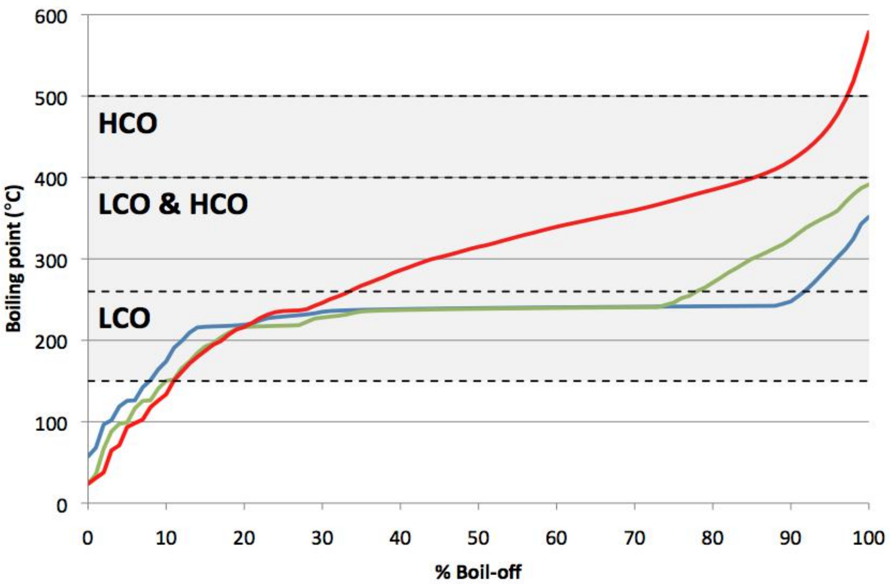
Reactor 1 catalysts: High rate of C=O Hydrogenation

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)

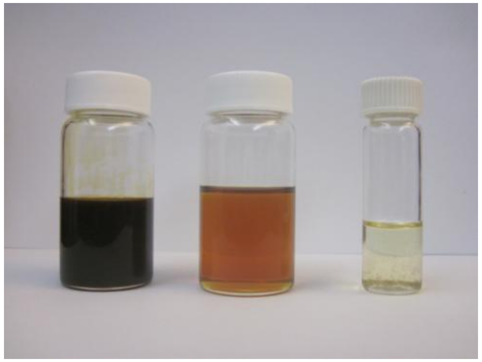
Li, N.; Tompsett, G. A.; Huber, G. W. *ChemSusChem* (2010) 3 1154-1157
D. C. Elliott, *Energy Fuels* **21,** 1792-1815 (2007)

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).



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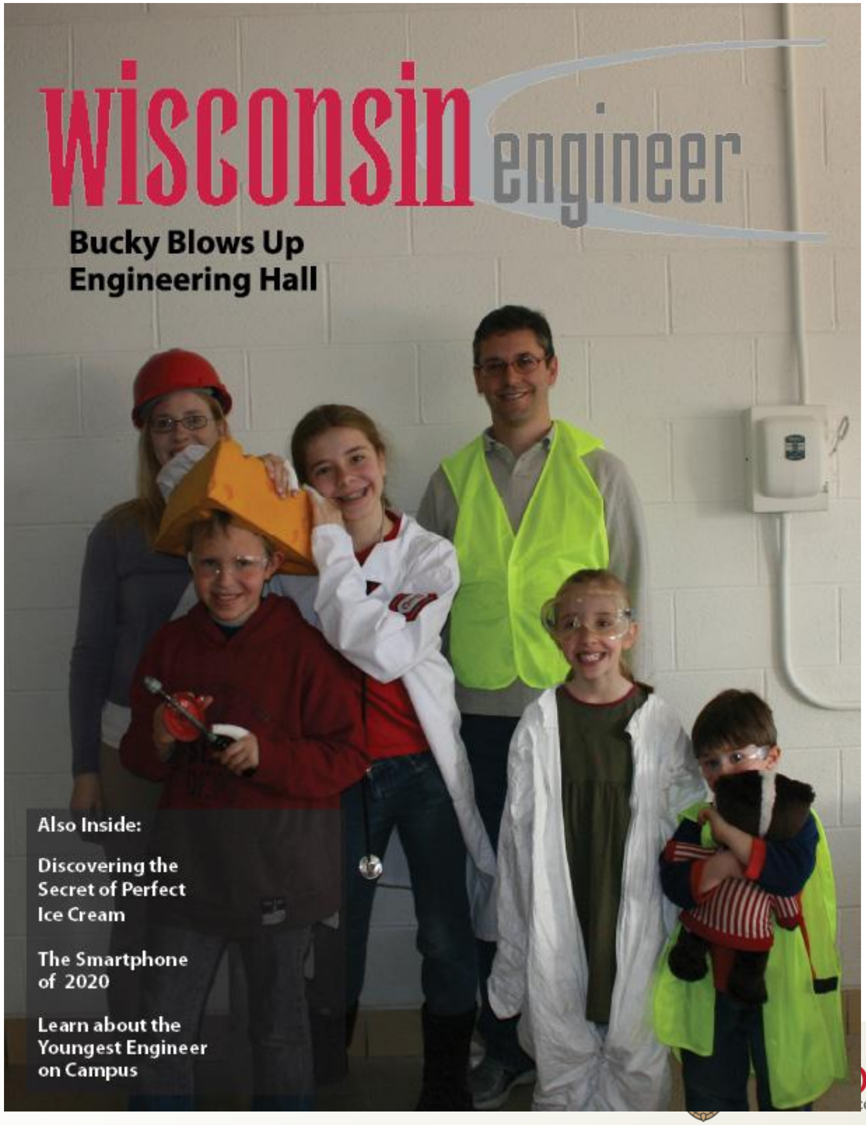
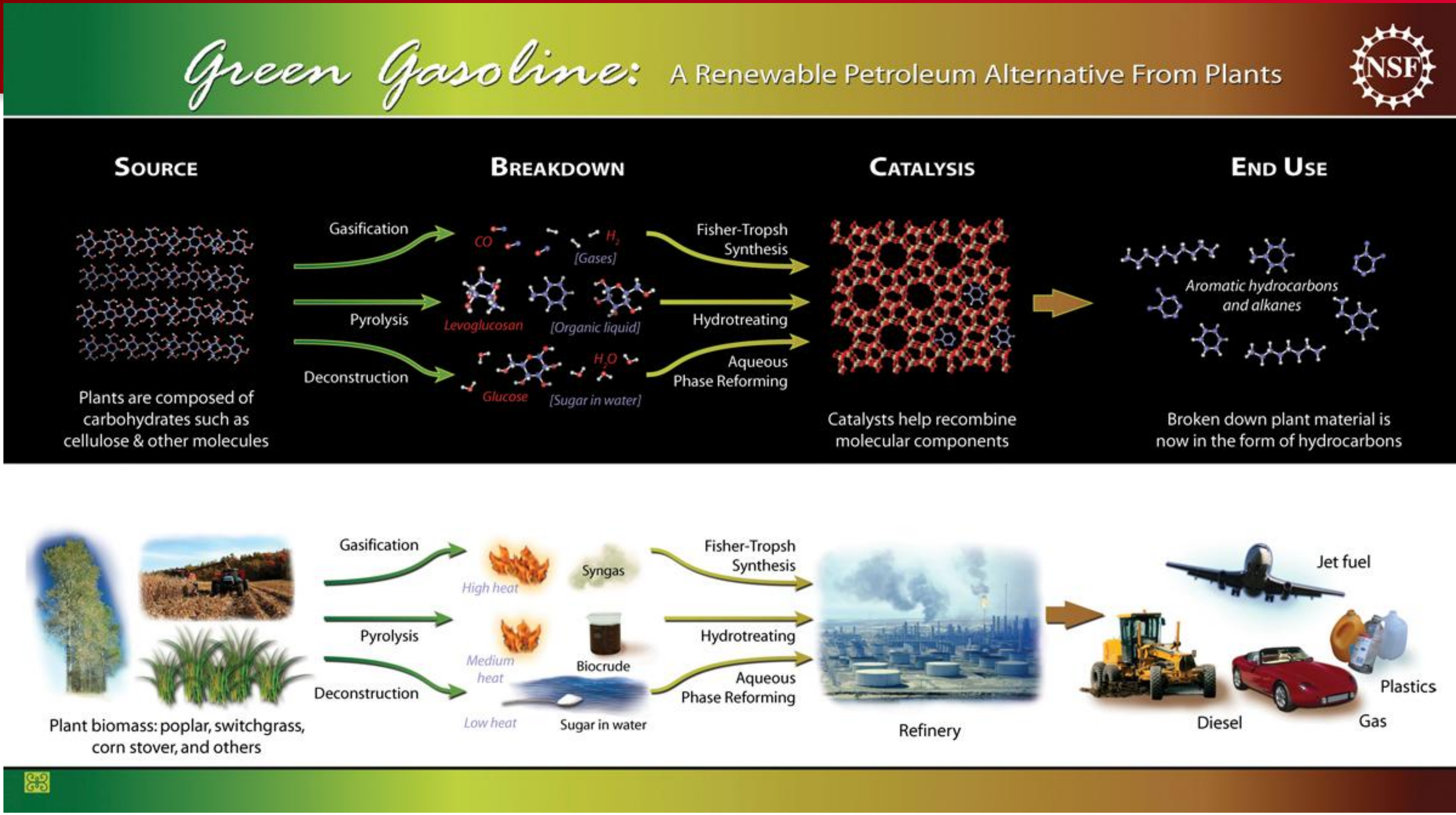
Engineers are critical to solve our energy challenges



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.



Breaking the Chemical and Engineering Barriers to Lignocellulosic Biofuels
www.ecs.umass.edu/biofuels

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Huber Research Group (http://biofuels.che.wisc.edu/)

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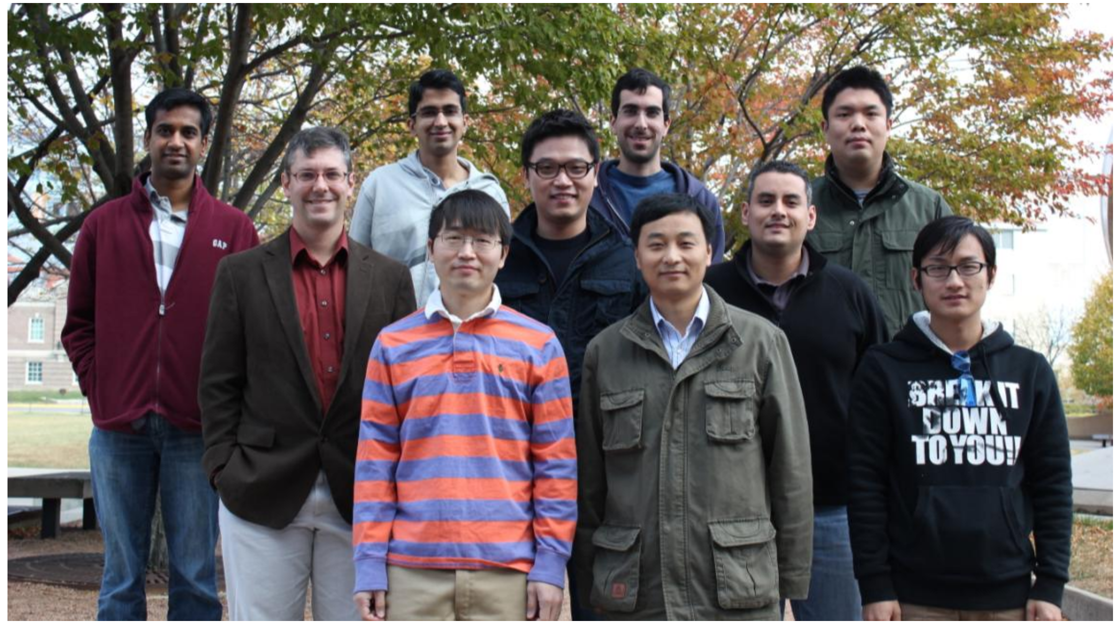
Delaware: Dr. Michael Klein, B. M. Moreno.

Wisconsin: J.A. Dumesic

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



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