Fraunhofer

UNIVERSITY OF DELAWARE

Inaugural Fraunhofer – Delaware Technology Summit

Inaugural Fraunhofer – Delaware Technology Summit

Energy and Life Sciences – Solutions for Sustainability

University of Delaware
Clayton Hall
March 5/6, 2013

Fraunhofer

UNIVERSITY OF DELAWARE

Inaugural Fraunhofer – Delaware Technology Summit

SESSION B.3: SUSTAINABLE ENERGY CONCEPTS

Plenary Talk

"Infrastructure-Ready Biomass-Derived Oils: Incentives, Options and Process Models"

– Michael Klein
Dan Rich Chair of Energy,
Chemical and Biomolecular Engineering
UD Energy Institute (UDEI)
University of Delaware

Infrastructure-Ready Biomass-Derived Oils: Incentives, Options and Process Models

Zhen Hou, Craig Bennett, Scott Horton, Brian Moreno and Michael T. Klein

Energy Institute
University of Delaware
Newark, DE 19716

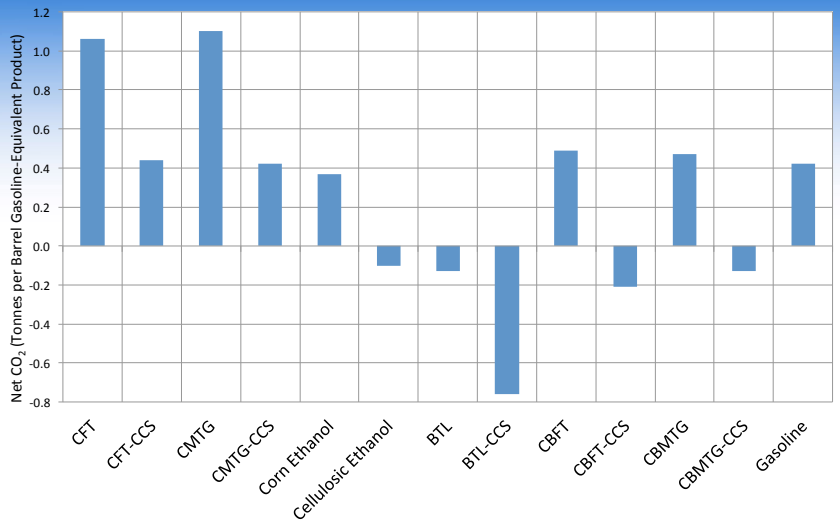
Inaugural Fraunhofer - Delaware Technology Summit
Energy and Life Sciences —Solutions for Sustainability
March 5, 2013
4:45-5:15 pm

Infrastructure-Ready Biomass-Derived Oils

Outline

- The appeal of Biomass
- The significance of the infrastructure
- Infrastructure-ready options
- Reaction Engineering modeling tools to "Organize, Evaluate and Improve" Infrastructure-ready options
- Some preliminary modeling results

The Appeal of Biomass



America's Energy Future: Technology and Transformation, The National Academies Press (adapted)

BIOMASS CONVERSION OPTIONS

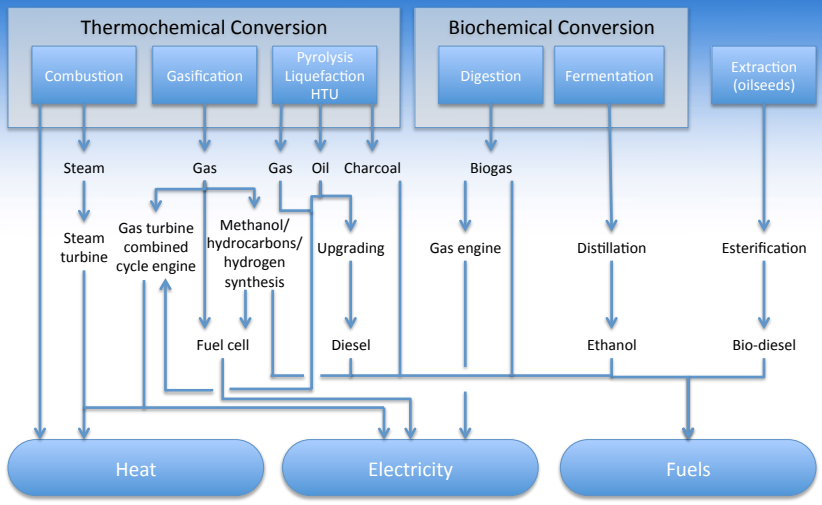


Figure 1. Main conversion options for biomass to secondary energy carriers, adapted (Turkenburg 2000). Some categories represent a wide range of technological concepts as well as capacity ranges at which they are deployed, which are dealt with further in the main text.

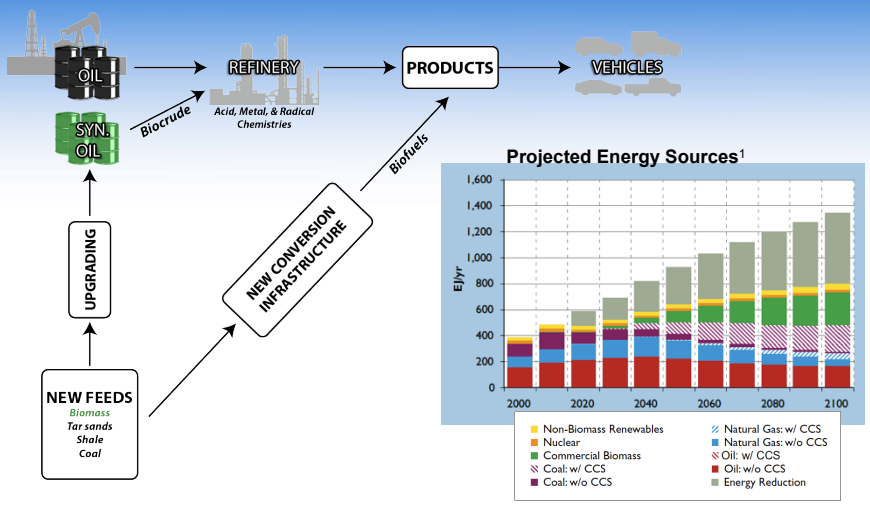
ANDRE FAAIJ, Mitigation and Adaptation Strategies for Global Change (2006) 11: 343–375 C Springer 2006, DOI: 10.1007/s11027-005-9004-7

5

The Significance of Existing Infrastructure

- Valued at ~ 3-6 Trillion USD
- Investment decisions "deliberate" in nature
- Geographically-Based (will not relocate)
- Units with characteristic time of decades
- High bar for alternative "shut down" technology

Integration with Existing Infrastructure



[1] Clarke LJ, Edmonds H, et. al. *Scenarios of Greenhouse Gas Emissions and Atmospheric Concentrations.* 2007. U.S. Department of Energy.

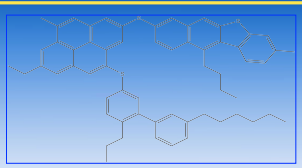
Organizing, Evaluating and Improving

*Integrated **modeling** of the reactions, process, economics and life-cycle analysis provides:*

- Quantitative ***organization*** of **current** science and engineering knowledge base
  - The "discipline" of modeling
  - Quantitative models identify science gaps and needs
  - New models can be assembled in ~ 5 years
- Quantitative ***evaluation*** of **current** science and engineering knowledge base
  - Identifies needed improvements in technology and science
  - Precise research targets for issues that need to be addressed
- Quantitative ***organization*** of **improved** science and engineering knowledge base
  - Provides scenarios for the adoption of technology platforms
  - Objective technical basis for decision making

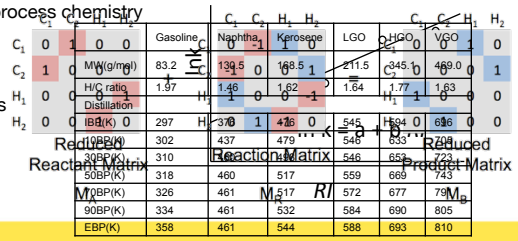
8

Molecular-level Modeling Approaches and Tools



CCCCc1c2ccc(Sc3cc4cc(C)c5cc(CC)cc6cc(Sc7ccc(CCC)c(c7)c7cccc(CCCCCC)c7)c(c3)c4c56)cc2cc2sc3cc(C)ccc3c12

1. Structural and Composition Models
   - Measurements (GS-MS, NMR, etc.)
   - Modeling: transforming measurements to molecules
     - MolGen and Monte Carlo simulation of structure
     - CompGen: A "Fixed Footprint" approach
2. Reaction Modeling
   - $N < N_C$: "Conventional" deterministic methods, e.g., INGen
   - $N > N_C$: Stochastic methods, e.g., Monte Carlo simulation of reaction
   - $N > N_C$: Hybrid methods, e. g., The Attribute Reaction Model
3. Reactivity Correlations
   - Fundamentals based kinetics correlations for homologous family of reactions
   - Order 10 [O(10)] LFERs for every process chemistry
4. Property Estimation
   - Molecules to commercial lumps
   - End-use vs. internal-use properties



9

Equivalent Computational Representations

pentane

Bond Electron Matrix

	C_1	C_2	C_3	C_4	C_5	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}
C_1	0	1	0	0	0	1	1	1	0	0	0	0	0	0	0	0	0
C_2	1	0	1	0	0	0	0	0	1	1	0	0	0	0	0	0	0
C_3	0	1	0	1	0	0	0	0	0	0	1	1	0	0	0	0	0
C_4	0	0	1	0	1	0	0	0	0	0	0	0	1	1	0	0	0
C_5	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1	1	1
H_1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_3	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_4	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_5	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_6	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_7	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H_8	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
H_9	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
H_{10}	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
H_{11}	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
H_{12}	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0

Adjacency List

```
Pentane
0 0 C:   {1,1},   {5,1},   {6,1},   {7,1};
1 0 C:   {0,1},   {2,1},   {8,1},   {9,1};
2 0 C:   {1,1},   {3,1},   {10,1},   {11,1};
3 0 C:   {2,1},   {4,1},   {12,1},   {13,1};
4 0 C:   {3,1},   {14,1},   {15,1},   {16,1};
5 0 H:   {0,1};
6 0 H:   {0,1};
7 0 H:   {0,1};
8 0 H:   {1,1};
9 0 H:   {1,1};
10   0 H:   {2,1};
11   0 H:   {2,1};
12   0 H:   {3,1};
13   0 H:   {3,1};
14   0 H:   {4,1};
15   0 H:   {4,1};
16   0 H:   {4,1};
```

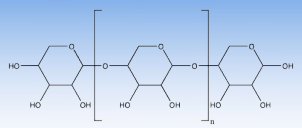
String Code

C(C(C(H3)H2)C(C(H3)H2)H2)

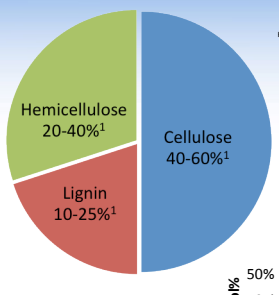
SMILES Code

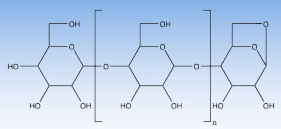
CCCCC

Lignocellulosic Biomass

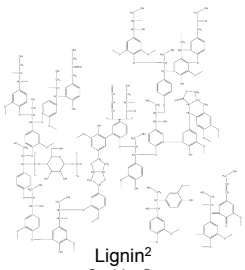


Hemicellulose
$C_5H_8O_4$

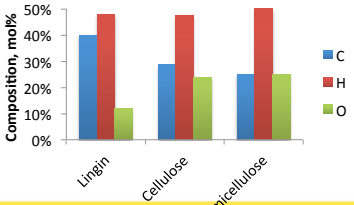




Cellulose
$C_6H_{10}O_5$

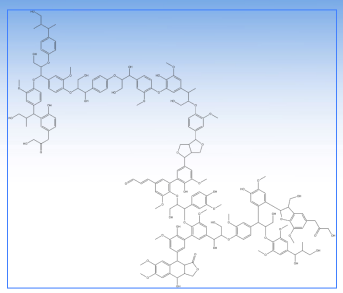


Lignin[2]
$C_{10}H_{12}O_3$



[1] Yang H, Yan R, *et al*. *Energy & Fuels*. 2006. 20 (1), 388-393.
[2] Freudenberg K, Neish AC. *Science*. 1969. 165 (3895), 784.

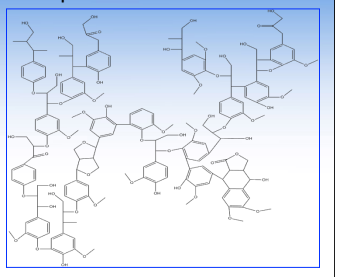
Freudenberg Lignin Model as a String



The computer "knows" Lignin as its SMILES code

O=CC=Cc1cc(OC)c(c(c1)c1cc(cc(c1O)OC)C1OCC2C1C
OC2c1ccc(c(c1)OC)OC(C(c1cc(OC)c(c(c1)Oc1ccc(cc1O
C)C(C(Oc1ccc(cc1)C(C(Oc1ccc(cc1OC)C(C(Oc1ccc(cc1
)C(C(CO)C)C)CO)Oc1ccc(cc1OC)C(c1cc(ccc1O)CC(=O)
CO)C(CO)C)CO)O)CO)O)O)C)CO)OC(C(c1ccc(c(c1)OC)
O)Oc1c(OC)cc(cc1c1cc(cc(c1O)OC)C1C2C(=O)OCC2C(
c2c1cc(OC)c(c2)OC)O)C(C(Oc1ccc(cc1OC)C(c1cc(O)c(
cc1C1Oc2c(C1CO)cc(cc2OC)CC(=O)CO)OC)C(Oc1c(OC
)cc(cc1OC)C(C(CO)C)O)CO)CO)O)CO

CML Input from ChemDraw



Substituents: 39 Attributes

Cores : 19 Attributes

63 Connections:

Chemical Reaction as a Matrix Operation

	C_1	C_2	H_1	H_2
C_1	0	1	0	0
C_2	1	0	0	0
H_1	0	0	0	1
H_2	0	0	1	0

Reduced Reactant Matrix

M_A

+

	C_1	C_2	H_1	H_2
C_1	0	-1	1	0
C_2	-1	0	0	1
H_1	1	0	0	-1
H_2	0	1	-1	0

Reaction Matrix

M_R

=

	C_1	C_2	H_1	H_2
C_1	0	0	1	0
C_2	0	0	0	1
H_1	1	0	0	0
H_2	0	1	0	0

Reduced Product Matrix

M_B

[1] Bennett CA. PhD Dissertation. Chemical and Biochemical Engineering, Rutgers University. 2009. (Adapted)

Reaction Families

Mechanism Level

Radical

- Bond fission
- Hydrogen abstraction
- β-scission
- Addition
- Termination

Ionic

- Isomerization
- Hydride shift
- Methyl shift
- Hydrogen abstraction
- β-scission
- Protonation
- Deprotonation
- Ring closure
- Ring expansion
- Addition

Pathways Level

Ring

- Ring saturation
- Dealkylation
- Side chain cracking
- Ring closure
- Ring opening
- Ring isomerization
- Aromatization

Oxygenate

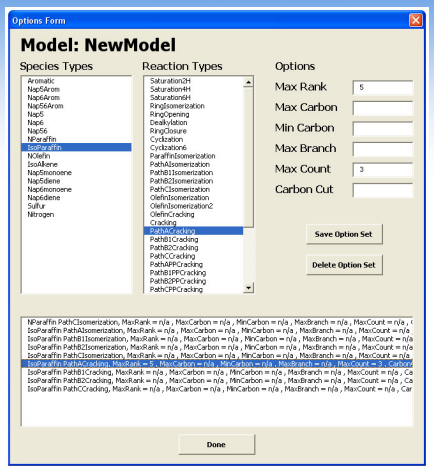
- Hydration
- Dehydration
- Tautomerization
- Decarboxylation
- Decarbonylation
- Hydroxyl shift

Paraffin/Olefin

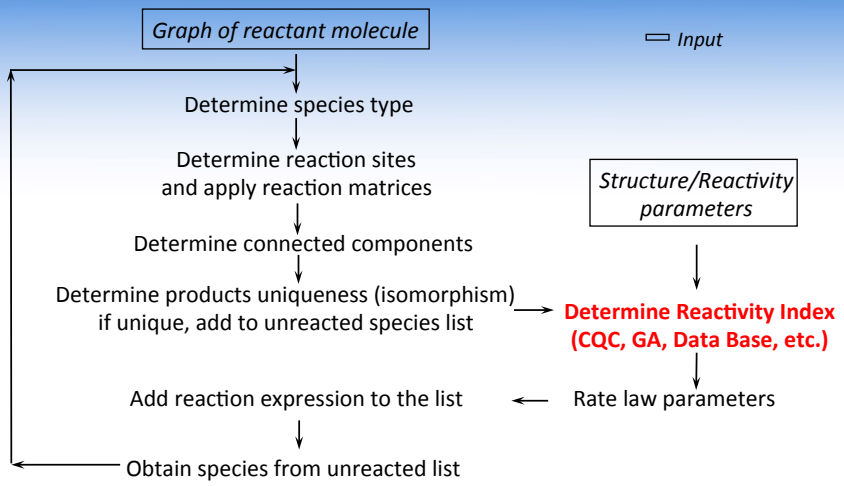
- Isomerization
- Cyclization
- Hydrogenolysis
- Cracking
- Double bond shift
- Methyl shift
- Hydrogenation
- Dehydrogenation
- Hydrodesulfurization
- Denitrogenation
- Diels Alder

Reactions Sent to Control File Via Front End

- Process models defined by species/reaction combinations
- Large library of species and preprogrammed reaction types
- Combination of mechanistic and pathways level chemistries

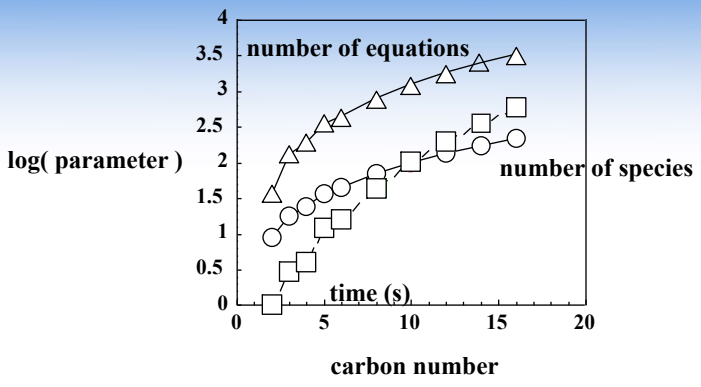


Network Building Algorithm

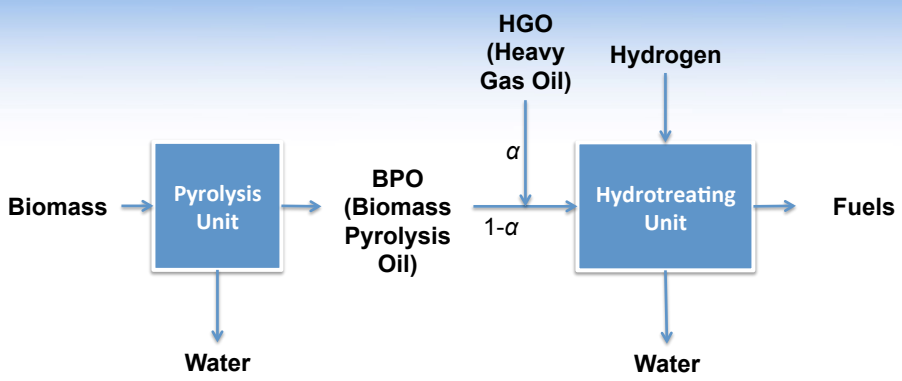


16

Fast and Efficient Model Building

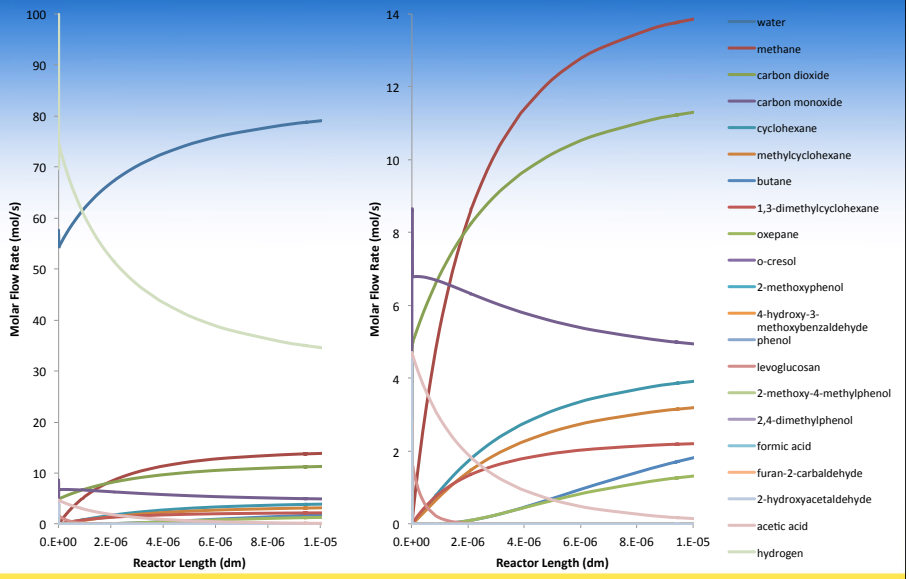


Co-Processing of BPO & HGO



18

Reactor Profile for Major Species



19

Organize, Evaluate and Improve

Preliminary Status

- Quantitative organization of science and engineering knowledge base
- Identified some key technology gaps, science needs
  - Petroleum was inherently profitable, which allowed for 100+ years of technology development
  - Biomass not inherently competitive, issues need to be addressed
    - H_2 consumption: expensive
    - H_2 consumption: CO_2 footprint
    - H_2O release
      - O rejection as H_20 or CO_2?
    - Energy density

Modeling Conclusions

- Irreducible complexity, as measured by model parameters:
  - Structure: O(10) 5-10 PDFs × 2-3 parameters each
  - Reactivity: O(10) 10 LFERs × 2 parameters each
  - Reaction Families: O(10) Reaction Matrices
- Rigorous kinetics can model interactions and competitions
- Net reduction of complexity: $O(10^5 \times 10^5)$ parameters reduced to O(30)

21