One Chemical Engineer’s Foray into Contemporary Energy Issues: 1) Developing Biofuels via Catalytic, Non-Fermentation Routes and 2) New Materials for Carbon Capture

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ERE and GCEP Seminar, Stanford University
Palo Alto, CA
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Jones Group: Materials Synthesis, Catalysis, Adsorption:

Current Group

Students:

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Research Support

NSF
DOE-BES
DOE-NETL
ACS-PRF
Dreyfus Foundation
Chevron
ExxonMobil
ConocoPhillips
Dow
Global Thermostat
IPST-GT
SEI-GT
Alternative Energy: The Georgia Tech Portfolio:

The Alternative Energy Portfolio: Non-Fossil Energy

- **Solar Energy and Photovoltaics** – ECE, Chem, ChBE, MSE, ME, Physics
  Center for Organic Photonics and Electronics – Marder, Director
  Center of Excellence in Photovoltaic Research and Education – Rohatgi, Director

- **Biofuels** - ChBE, Chem, ME, ISyE
  Chevron Biofuels Program – Strategic Energy Institute
  DOE Bioenergy Science Center (with ORNL, Tennessee, UGA, Dartmouth, others)

- **Nuclear Energy** – ME

- **Hydrogen Energy** – ChBE, MSE, GTRI, Chem, ME
  Center for Innovative Fuel Cell and Battery Technology

- **Wind Energy** – ME, Physics, AE, GTRI
  Coastal wind farms
Georgia Tech has a world-class program in CO₂ Separations Research.

The CO₂ Separations Portfolio: Near Term Options

- CO₂ Capture from Low Concentration Sources (e.g., Flue Gas)
  - New sorbent-based separation concepts (materials and contacting systems)
  - Fundamental materials design and modeling
  - Comprehensive systems analysis

- CO₂ Capture from High Concentration Sources (e.g., Natural Gas)
  - Hybrid membrane and sorbent materials
  - Inorganic membranes

- Current Partners
  - Siemens Energy (Power generation with CO₂ Capture /Sequestration)
  - Air Liquide (membrane/sorbent production for gas separations)
  - DOE-NETL, NSF, Dreyfus Foundation (CO₂ capture)
  - King Abdullah University of Science and Technology-Saudi Arabia (CO₂ Capture)
  - ExxonMobil, Chevron, Conoco Phillips, (CO₂ Capture/Separation)

Pls: Koros, Jones, Sholl, Chance, Nair, Fedorov
Georgia Tech has a world-class program in CO\textsubscript{2} Separations Research.

The CO\textsubscript{2} Separations Portfolio: Non-Fossil & Longer Term Options

- CO\textsubscript{2} Capture from the Atmosphere
  - Air capture, if economic, can be implemented anywhere and is not tied to point sources.
  - Global Thermostat

- On-Board CO\textsubscript{2} Capture from Vehicles
  - Fuel cell vehicle with on-board CO\textsubscript{2} capture.
  - Andrei Fedorov, ME
One Chemical Engineer’s Foray into Contemporary Energy Issues:

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and

2) New Materials for Carbon Capture
Energy Demand Growth Dominated by Developing Countries:

Global Economics and Energy

- Population Growth
- GDP Growth
- Energy Demand Growth

Source: ExxonMobil
How the Energy Demand Will be Met:

Message: Advances in wind and solar energy are desperately needed, but even with tremendous growth, society will continue to rely on fossil energy for electricity and fossil plus bio-energy for transportation for the next several decades.

Source: ExxonMobil
Biofuels:


• More than doubles annual biofuel volumes required in five years, increasing mandates from 7.5 to 15.2 billion gallons by 2012.

• Requires at least 36 billion gallons per year by 2022 (~20% of projected gasoline consumption in 2022).

• Ethanol from corn: projected maximum is < 50% of this 36 billion gallon figure!

• Need new sources of biofuels! Green gasoline. Green diesel.

http://www.ecs.umass.edu/biofuels/
Biofuels from a Reaction Engineering Perspective:

Current feedstock, crude oil:  
- liquid, fractionate  
- hydrocarbon, CH₂  
- 100+ years of refinery processing, capital equipment and know-how  
- add functionality with catalysis (N, O, P, S)

Future feedstock, biomass:  
- solid feedstock  
- high oxygenated, CH₂O  
- transportation costs huge  
- remove functionality (O)  
- need new scientific and engineering advances:
  1. pretreatment, liquefaction, gasification (make a fluid!)  
  2. deoxygenation and upgrading fluid to fuel.
Biofuels from Lignocellulosic Biomass:

Two core objectives in converting biomass into transportation fuels:

1. pretreatment, liquefaction, gasification (make a fluid!)
2. deoxygenation and upgrading fluid to fuel.

Our Feedstocks:
--lignocellulosic biomass:
  - loblolly pine
  - switchgrass
Loblolly Pine and Switchgrass:

Proposed structural segment of lignin

Cellulose

Hemicellulose
galactoglucomannan

\[
m_{\text{Mono-Hemi}} = \frac{4}{3} \times \text{Mannose + Arabinose} + \text{Galactose} + \text{xylose}; \text{eq. 1}
\]

\[
m_{\text{Mono-cell}} = \text{Glucose} - \frac{1}{3} \times \text{Mannose}; \text{eq. 2}
\]

\[^{1}\text{Roberts, J. C., Paper Chemistry. 2nd ed. Blackie Academic: London; 1996.}\]
Conversion to Liquids:

Acid hydrolysis dissolve carbohydrate part of lignocellulosic material leaving modified-lignin as solid residue.

Furans, commonly referred to as degradation products when making ethanol, are actually our target compounds from biomass.
High conversion of fructose (90%) and yield to HMF (80%)
Using protic acids in mixed aqueous/organic media.

Dumesic et al., Science, 2006, 312, 1933
Zhang – Conversion of Glucose to HMF:

High yield of HMF from glucose (~70%) using metal chloride catalysts in ionic liquids.

Zhang et al., *Science*, 2007, 316, 1597
Loblolly Pine and Switchgrass:

Lignin

Cellulose

Hemicellulose

Proposed structural segment of lignin

Galactoglucomannan

C9

C6

C5-C6

Gasoline: C5-C12, ideally branched ~C8

Diesel: C12+ linear alkanes
Can we develop a simple route to **green gasoline or green diesel** using entirely biomass derived feedstocks?

Goals and constraints:
1) Decrease oxygen content.
2) Enhance molecular weight.
3) Only biomass-derived compounds.

Suggested paths:

1. (a) Hydrogenation or (b) dehydration
   (a) need renewable hydrogen source, $\$\$\$\$
   (b) can lead to coking and product loss.

2. Work with reactive compounds.
Molecular Weight Enhancement:

Carbon-carbon bond forming reactions:
-- aldol condensation (Dumesic 2005)
  -- adv: versatile, many coupling partners
  -- dis: no easy biomass derived partners
-- Kneovenagel condensation (Jones 2007)
  -- adv: easy, high-yielding reactions
  -- dis: limited array of coupling partners

Kneovenagel (KN) reaction requires a ketone or aldehyde and an “activated methylene compound.”

Malonic acid is an activated methylene compound that can be derived from biomass:\(^1\):

\[
\text{sugars} \rightarrow 3\text{-hydroxypropionic acid} \rightarrow \text{malonic acid}
\]

Molecular Weight Enhancement:

KN reactions of HMF or furfural and malonic acid:

99+% conversion
99+ % yield of product

THF solvent
Ethylenediamine catalyst
80 °C. 5 hours.

-- very efficient process.
-- 3 oxygen atoms removed from sugar via water during furan formation, 1 during KN reaction.
Hydrogen from Biomass:

Aqueous phase reforming (APR) Dumesic, 2002

-- biomass-derived model compounds (glucose, sorbitol, etc.) converted to hydrogen in high yield.

First application of APR to real biomass, Jones, 2007

-- pine simultaneously hydrolyzed and converted to hydrogen in comparatively poor yields.

Many labs now working on improving practical application of APR with biomass.

Renewable hydrogen gives us, in principle, a complete, all biomass route to green gasoline!

Catalytic Hydrogenation:

Hydrogenation: - catalyst (Pt, Pd, Ru on alumina, silica, carbon) - temperature (100-300 °C) - pressure (1-100 atm)

Products identified by NMR, LC-MS, GC-MS

Partially reduced products:

- 

![Chemical structures](image1)

- 

![Chemical structures](image2)

- 

![Chemical structures](image3)

Fully reduced product:

- 2-methyl-nonane
Glucose to Green Gasoline:

-- only reaction processes shown.
-- yields assigned based on best literature reports.
-- glucose derived from APR
Biomass Conversion to Fuels Summary:

1. Lignocellulosic biomass is commonly fragmented to C6 and smaller monomeric units (sugars, furans, etc.).

2. For gasoline applications, we ideally desire C8 or C9 products.

3. We introduced a conceptual process for synthesis of green gasoline from entirely biomass feedstocks:

   -- HMF or Furfural from sugars
   -- Malonic acid from 3-HPA (from sugars)
   -- Hydrogen from APR

   -- Knoevenagel condensation catalyzed by basic catalysts followed by catalytic hydrogenation.
One Chemical Engineer’s Foray into Contemporary Energy Issues:

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and

2) New Materials for Carbon Capture
Motivation:

- The earth is warming (about 0.6 °C in last 100 years).
- Intergovernmental Panel on Climate Change (IPCC): 90% probability that increase in CO₂ concentration in the air is main culprit.
- Major source of CO₂ concentration increase is fossil fuel combustion.
- Future increases could have catastrophic consequences… or not.
- Need carbon mitigation options.

-Fossil fuels will continue to supply the bulk of electricity production for decades!

Temperature data from Hadley Centre, UK
CO₂ data from Earth Policy Institute
Post-Combustion CO$_2$ Capture:

Current, “mature” technology:

- aqueous amine absorption processes
  - massive amounts of recirculating amine and water needed.
  - large energy loss in heating the water in the stripping (regeneration) step.

Numerous emerging technologies:

- liquid ammonia capture
- solid sorbents
Targets:

- Low cost CO$_2$ capture technology based on adsorption processes.

- National Energy Technology Laboratory has estimated an 65-81% increase in the cost of electricity for capture with aqueous amines via absorption.

- Majority of the cost for CO$_2$ capture and sequestration is believed to be in capture step.

- Our work targets, simple, low cost amine adsorbents for post-combustion CO$_2$ capture at low temperatures.
Surprisingly little literature in this growing field. Less than 50 papers (for low temperature sorbents). Literature analysis shows:

Two categories of solid amine adsorbents:

1. Oxides or polymer supports with alkyl amine groups **covalently bound** to the support.
   
   _Advantage:_ can be robust to multiple temperature swing cycles.  
   _Disadvantage:_ tend to have low capacities.

2. Oxides or polymer supports with alkyl amine groups **impregnated or physisorbed** onto the support.
   
   _Advantage:_ tend to have high capacities.  
   _Disadvantage:_ tend NOT to be robust to multiple temperature swing cycles. Loss of amines.
Comparisons of multiple literature studies to identify “the best” sorbents is very difficult:

For example, the most common adsorbent, aminopropyl-coated mesoporous silica, has literature capacities ranging from 0.2 – 2.2 mmol CO$_2$ / g sorbent.

Why such variability?

Different materials, but this only plays a small part +/- 10-20%.

Different conditions: wet vs. dry; CO$_2$ partial pressure; temperature.

Different experimental methods: fixed bed vs. TGA.

Fixed bed processes:
Advantage: can give good sorbent – gas contacting.
Disadvantage: can be affected by T changes due to $\Delta$$H_{ads}$. 
Our Approach: A New Material for CO$_2$ Capture

**Must be low cost:** simple amine adsorbents via an easily scalable synthesis.

Characterization must simulate key points of **real flue gas conditions** and a real process:
- temperature swing process.
- ~10% CO$_2$ in inert, saturated with water vapor.

Must compare to best literature sorbents under exactly the same conditions.
Ordered Mesoporous Silica: SBA-15

Figure 2. Transmission electron micrographs of several MCM-41 materials having Ar pore sizes of (a) 20, (b) 40, (c) 65, and (d) 100 Å.
Literature Sorbents:

1. Aminopropyl-functionalized mesoporous SBA-15 silica.

2. Diamine-functionalized mesoporous SBA-15 silica.

3. Poly(ethyleneimine)-impregnated SBA-15 silica. akin to Song’s “molecular basket adsorbents.”


4. Tetraethylpentamine-impregnated *as-synthesized* SBA-15 silica.

Our New Material:

**Must be low cost:** simple amine adsorbents via an easily scalable synthesis.

--previously reported on silicon wafers: Kim, H. J. et al., *J. Colloid Interface Sci.* **2000** 227, 247.

-- hyperbranching polymerization of aziridine on/in mesoporous SBA-15 silica.

-- single step, simple reagent, low temperature synthesis.

Caution: aziridine is toxic and reactive.
Our New Material - Characterization:

Raman spectroscopy:

- C-H stretches
- \(-\text{CH}_2\) - group

13C CPMAS spectroscopy:

- Broad peak consistent with indistinguishable CH2 groups.
- Consistent with a hyperbranching structure, but does not prove this.

Contains ~ 7 mmol N/ g sorbent silica based on elemental analysis.
Baseline Material - Characterization:

1. \( \text{N-CH}_2\text{-CH}_2\text{-NH}_2 \)
2. \( \text{N-CH}_2\text{-CH}_2\text{-NH}^- \)
3. \( \text{N-CH}_2\text{-CH}_2\text{-N}^- \)
4. \( \text{-NH-CH}_2\text{-CH}_2\text{-NH}_2 \)
5. \( \text{-NH-CH}_2\text{-CH}_2\text{-NH}^- \)
6. \( \text{-NH-CH}_2\text{-CH}_2\text{-N}^- \)
7. \( \text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}^- \)
8. \( \text{NH}_2\text{-CH}_2\text{-CH}_2\text{-N}^- \)

Quantitative, inversely-gated \( ^{13}\text{C} \) NMR spectroscopy

Commercial PEI, 800 Da, \( M_w \)

44 : 33 : 23

\( 1^\circ \) \( 2^\circ \) \( 3^\circ \)
Our New Material - Characterization:

1. $\text{N-CH}_2\text{-CH}_2\text{-NH}_2$
2. $\text{N-CH}_2\text{-CH}_2\text{-NH}$
3. $\text{N-CH}_2\text{-CH}_2\text{-N}$
4. $\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$
5. $\text{-NH-CH}_2\text{-CH}_2\text{-NH}$
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7. $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}$
8. $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-N}$

HAS organic materials, 840 Da, $M_w$

Quantitative, inversely-gated $^{13}\text{C}$ NMR spectroscopy

$28 : 47 : 25$
$1^\circ \ 2^\circ \ 3^\circ$
Our New Material - Characterization:

<table>
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<td>802</td>
<td>65</td>
<td>0.71</td>
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<td>57</td>
<td>0.41</td>
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<td>252</td>
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<tr>
<td>SBA-15 PEI (750k MW)</td>
<td>27</td>
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</table>

Uncalcined, template-containing SBA-15 has marginal porosity and surface area.

Impregnating uncalcined SBA-15 with TEPA gives a very low surface area material.

[SBA channel is completely filled.]

[H2N—N—N—N—NH2]
Our New Material - Characterization:

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Grafting of simple silanes on calcined SBA-15 gives large pore volumes does not effectively use the pore space in the solid support.

SBA channel is at best lined with amine-containing organic groups.
Open porosity should help transport rates.
Hurts overall capacity.
Our New Material - Characterization:

Nitrogen Physisorption Results

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Impregnating calcined SBA-15 with PEI gives a very low surface area material.

SBA channel is completely filled.
Our New Material - Characterization:

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<tr>
<td>SBA-15 GT-HAS</td>
<td>169</td>
<td>44</td>
<td>0.25</td>
</tr>
</tbody>
</table>

GT SBA-15-HAS:

retains much of its porosity and surface area while having a high amine loading.

SBA channel may be more effectively used.
Adsorption Rig:

Sorbent dispersed in inert sand to facilitate heat transfer and alleviate pressure drop.

Use of flow meters in every run insures adjustability of flow to mitigate $\Delta P$ through the bed.
Adsorption Rig:

Pretreat sorbent to desorb CO₂ from sorbent.

Sorbent dispersed in inert sand to facilitate heat transfer and alleviate pressure drop.

Use of flow meters in every run insures adjustability of flow to mitigate ΔP through the bed.
Adsorption Rig:

Pretreat sorbent or desorb CO$_2$ from sorbent.
Store sorbent under dry Ar, establish steady CO$_2$ flow through water saturator.
Pretreat sorbent or desorb CO₂ from sorbent.
Store sorbent under dry Ar, establish steady CO₂ flow through water saturator.
Switch to flow through the bed. CO₂ loss will be evident in the MS due to two factors:
1) CO₂ adsorption
2) CO₂ dilution/backmixing in Ar filled sorbent bed.
Pretreat sorbent or desorb CO₂ from sorbent. Store sorbent under dry Ar, establish steady CO₂ flow through water saturator. Switch to flow through the bed. CO₂ loss will be evident in the MS due to two factors: 1) CO₂ adsorption 2) CO₂ dilution/backmixing in Ar filled sorbent bed. Desorb CO₂ from sorbent.
Adsorption Rig:

Breakthrough curve running only sand – no specific adsorption, so these numbers give CO₂ “loss” due to dilution / backmixing.

We see no evidence that such measurements are carried out routinely in most previous literature studies.
**Adsorption Capacity Results:**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Type</th>
<th>N loading mmol/g</th>
<th>Capacity mmol CO₂/g sorbent</th>
<th>Efficiency mmol CO₂/ mmol N</th>
<th>Multi-cycle Stability</th>
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<tbody>
<tr>
<td>SBA-AP</td>
<td>covalent</td>
<td>1.9</td>
<td>0.4</td>
<td>0.21</td>
<td>Yes</td>
</tr>
<tr>
<td>SBA-diamine</td>
<td>covalent</td>
<td>2.5</td>
<td>0.7</td>
<td>0.28</td>
<td>Yes</td>
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<tr>
<td>SBA-PEI (0.8k MW)</td>
<td>physisorbed</td>
<td>10.9</td>
<td></td>
<td></td>
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<td>SBA-PEI (750k MW)</td>
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<td>7.4</td>
<td>2.0</td>
<td>0.27</td>
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<tr>
<td>SBA-TEPA</td>
<td>physisorbed</td>
<td>10.9</td>
<td>2.74</td>
<td>0.26</td>
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<tr>
<td>GT-HAS</td>
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<td>7.0</td>
<td>3.11</td>
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25 ºC adsorption, 130 ºC desorption.
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<th>N loading mmol/g</th>
<th>Capacity mmol CO₂/g sorbent</th>
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<tr>
<td>SBA-AP covalent</td>
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<td>0.4</td>
<td>0.21</td>
<td>Yes</td>
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<tr>
<td>SBA-diamine covalent</td>
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<td>0.7</td>
<td>0.28</td>
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<tr>
<td>SBA-PEI (0.8k MW) physisorbed</td>
<td>10.9</td>
<td><strong>Non-reproducible</strong></td>
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<tr>
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<td>SBA-TEPA physisorbed</td>
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25 ºC adsorption, 130 ºC desorption.
## Adsorption Capacity Results:

Lack of multi-cycle stability!

Visible leaching of TEPA into sand.

### 25 ºC adsorption, 130 ºC desorption.

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Highest adsorption capacity.

Most efficient utilization of amine groups.

Multi-cycle stability.

25 ºC adsorption, 130 ºC desorption.
Regeneration and Reuse:

Multi-cycle stability.

Adsorption capacity is lower at 75 °C, but still highest among stable sorbents.

75 °C adsorption, 130 °C desorption.
Tailoring the Structure and Adsorption Properties:

- Synthesized HAS with varied amine loadings.

- Yield decreases as loading increases.

- BET surface area and pore volume decrease as loading increases.
Tailoring the Structure and Adsorption Properties:

- Capacity increases approximately linearly as a function of amine loading.

- Capacity at 25°C is on average 1.1 mmol CO$_2$/g higher than at 75°C.

- Higher amine efficiencies at lower loadings.

- Higher adsorption capacities now achieved after optimization of synthesis: >5.5 mmol/g
Adsorption Kinetics:

- Adsorption kinetics can be tailored.
- Sorption half-times are comparable to zeolites.
Conclusions:

New GT hyperbranched aminosilica sorbent has:

1. Very high capacity, the highest currently known.
3. Simple, low cost, scalable design.
4. Tailorable adsorption properties (kinetics, capacity)

Similar materials without an application were recently reported by Linden et al.:


Hicks, Drese, Fauth, Gray, Qi, Jones, J. Am. Chem. Soc. 2008, 130, 2902.

Current Work:

1. Fundamental thermodynamic characterization (isotherms)

2. Fundamental kinetic characterization (adsorption and desorption rates)

3. New process designs to minimize pressure drop and heat transfer issues.

4. Full economic systems analysis.
Financial support:

- Biofuels
- CO₂ Capture

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- NSF
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- Georgia Tech Institute of Paper Science and Technology
- Georgia Tech Research Institute
- Georgia Institute of Technology
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