Human Population Growth

Human Population estimates over time

© Agrawal, 2012

Data source: Wikipedia & UN
James Watt and his 1769 steam engine

Source: David J.C. Mackay 2009
Energy: Fundamental to Our Lives!

Human Population estimates over time

Fossil fuel period

1769

Data source: Wikipedia & UN
Energy: Fundamental to Our Lives!

Therefore, we must understand energy transformation and use issues to develop alternative energy strategies.

Data source: Wikipedia & UN
Beyond Fossil Fuels: Solar Economy

Fossil fuel period

Solar Economy period

Human Population estimates over time

Population in millions

Year (A.D.) (negative: B.C.)

Historical data
Forecast

©2013 R. Agrawal

Data source: Wikipedia & UN
Why Solar Energy?

- Solar energy incident on earth in 1 hour\(^1\)
  \[ \sim 4.3 \times 10^{20} \text{ J} \]

- 2012 World primary energy consumption\(^2\)
  \[ \sim 5.1 \times 10^{20} \text{ J} \]

**Solar** is the only easily available energy source that can **alone** meet all the energy needs.

---

1. Lewis and Nocera, PNAS, 2006
Essence of Solar Economy

Transform and use solar photons on a much smaller time scale $\sim O(10^3-10^6 \text{ s})$!
1. How Dense is Solar Energy?

~10 gallons per minute

Or

~20 MW of power supply

©2013 R. Agrawal

Source: epa.gov, Wikipedia
Observation 1

Low density of solar energy is a challenge for use
2. Availability of Sunlight

Intermittency

Geographic Variability

Source: nrel.gov, NASA
Observation 2:
Energy storage needed at all levels

~$10^2$ W  ~$10^3$ W  ~$10^6$ W  ~$10^8$ W
3. Large Scale Energy Requirement

- World primary energy usage rate in 2007 was 14.8 TW
- By 2050, the usage rate could be 28 TW

**Consumption rate could double!**
Observation 3
Large-scale only possible if cost-effective
Observation 4
Harnessing solar energy efficiently is vital
Fuels and Chemicals

...possibly need renewable carbon sources...

...as well as Hydrogen...
Renewable Carbon Sources

CO\textsubscript{2} @ 398 ppm\textsuperscript{1}

- Direct CO\textsubscript{2}?
- Aquatic autotroph (Algae)
- Regulated fuel crops
- Dedicated fuel crops
- SAW biomass

Competing for land use

Sustainably Available (SA) Biomass

Observation 5

SA biomass = primary energy + carbon source
Biomass-to-Fuel: Carbon Recovery

~26-47% biomass carbon recovered as fuel

SA Biomass = sustainably available biomass

SA Biomass → Fuel

Standalone processes
- Gasification/Fischer-Tropsch
- Fermentation
- Hydrothermal gasification
- Pyrolysis-hydrotreating

©2013 R. Agrawal

Singh, Delgass, Ribeiro and Agrawal, Environ. Sci. Tech., 2010
Standalone Processes+ SA Biomass for US Transportation

- Sustainably available biomass potential = 498 Million tons/yr\(^1\)

- Transportation fuels use in the USA, 2011 = 12.68 Mbbl/day\(^2\)

12-20% (1.6-2.6 Mbbl/day) of current US transportation demand produced using SA biomass with standalone processes

©2013 R. Agrawal

1. Liquid transportation fuels NRC report, 2010
2. Davis et al., Transportation energy data book, 2012
Solar conversion efficiencies

- **H₂**: 5-50%
- **Biomass**: 0.3-2%
- **Liquid Fuel**: 0.15-1%
- **Electricity**: 10-44%
- **Heat**: Upto 70%

~ 50% efficient

©2013 R. Agrawal
Observation 6
Biomass is primarily a carbon source

Avoid using biomass for non-carbon needs (heat/electricity/H₂)
Augmented Biomass Conversion

Up to 100% biomass carbon recovery possible


©2013 R. Agrawal
Systematic Augmented Process Synthesis

How to Find the optimum process?

FT=Fischer-Tropsch; HDO= hydrodeoxygenation
Augmented process synthesis: MINLP model

\[
\text{Min } Q_{\text{solar}} = \frac{Q_H}{\eta_{\text{STH}_2}} + \frac{Q_{\text{Heat}}}{\eta_{\text{STHe}}} + \frac{W_{\text{elec}}}{\eta_{\text{STE}}} \quad \text{.... Objective function}
\]

subject to,

\[
f(x, y) = 0 \quad \text{.... Mass, Energy balance, thermodynamic models}
\]

\[
h(x, y) \leq 0 \quad \text{.... Inequalities (split fractions, conversion etc.)}
\]

\[
carbon_{\text{eff}} \geq carbon_{\text{target}} \quad \text{.... Target carbon recovery level}
\]

\[
x^L \leq x \leq x^U \quad \text{.... Variable bounds}
\]

\[
y = \{0, 1\}
\]

- Branch and Bound based global optimization algorithm (BARON\textsuperscript{1})

\[\text{MINLP=} \text{ Mixed Integer Nonlinear Programming}\]

1. Tawarmalani and Sahinidis, \textit{Math Program.}, 2005
Benefit of Simultaneous Heat, Mass & Power integration

Consistently lower solar energy input than single pathway solution

Sun-to-H₂ = 6.2%, Sun-to-heat= 37.5%, Sun-to- electricity =10%
Observation 7
Systems analysis critical for biomass utilization

©2013 R. Agrawal
Observation 8
Efficient supply of solar hydrogen needed
What is the Most Efficient Process for Solar Hydrogen?

\[ Q_{\text{solar}} \]

\[ \text{H}_2\text{O}(l), \quad 1 \text{ atm}, \quad T_a \] → Water-splitting (endothermic) → \[ \text{O}_2(g) \quad \text{1 atm, } T_a \] → \[ \text{H}_2(g) \quad \text{1 atm, } T_a \]

Sun-to-\( \text{H}_2 \) efficiency (\%) = \[ \frac{\text{LHV of } \text{H}_2 \text{ produced from land}}{\text{Incident annual solar energy on the land}} \] \times 100

- Light \( \rightarrow \) Photochemical
- Heat \( \rightarrow \) Thermochemical
- Heat or light \( \rightarrow \) Electricity \( \rightarrow \) Electrolysis
Solar Energy Input as Light: Spectrum

Photochemical processes are limited by the fraction of the solar spectrum absorbed.

Theoretical Sun-to-H₂ efficiency: 31 - 46% (single or double band-gap photosystems)

Sun-to-$\text{H}_2$ thermochemical process

Use solar energy as heat to utilize the entire solar spectrum
Using Solar Energy as Heat

Direct (Thermal)
- Sun
- Concentrator
- $Q_{\text{solar}} = I_{\text{sun}} C$
- $Q_{\text{loss}}$
- Absorber at $T$
- $Q_{\text{heat,1}} (T)$

Indirect (Electrolytic)
- Sun
- Concentrator
- $Q_{\text{solar}} = I_{\text{sun}} C$
- $Q_{\text{loss}}$
- Absorber at $T$
- Heat engine
- $Q_{\text{heat}}$
- $Q_{\text{ambient}}$
- Work

©2013 R. Agrawal
Practical Thermal Water-splitting heat exchange ($\Delta T_{\text{min}}$) + high pressure ($P_{\text{op}}$)
Thermal vs Electrolytic Water-splitting

- **Electrolysis (950°C) with spectral resolution**
  - Multijunction PV
    - $\eta_{PV} = 44\%$
    - 38-45%
  - Single junction PV
    - $\eta_{PV} = 29\%$
    - 25-32%

**Graphical Representation**

- **Carnot**: 50%
- **Compensation**: 70%
- **Optical**: 80%
- **Ratio**: 5
- **HTC, Loss**: 0.49 - 0.17
- **dp, Loss**: 10%
- **$\Delta T_{min}$**: 0 K

©2013 R. Agrawal
Observation 9
Achievable $\text{STH}_2$ efficiency of 35-50% possible!
But Storing Energy as H₂ is Inefficient…

Need- high energy density and storage efficiency solutions!

Reference: EPRI report on Storage Technologies, 2010

Hydro= pumped hydroelectric power, CAES= compressed air energy storage
Storing Energy at the Grid-level
For Baseload renewable power supply
What is Grid-level Storage?

Sunlight available $\sim \frac{1}{5}$ of the day in US

Average $100 \text{ MW}_{\text{elec}}$ supply.....

.... $\sim 2 \text{ GWh}$ of electrical energy storage

High density critical for Grid-level storage
Hydrocarbons for Energy Storage

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{HC} + \text{H}_2\text{O} \]

- Store as liquid to minimize volumes
- Avoid handling large volume of pressurized gas

Reference: EPRI report on Storage Technologies, 2010

©2013 R. Agrawal

Hydro= pumped hydroelectric power, CAES= compressed air energy storage
Closed Carbon Energy Storage Cycle
Liquid CO₂ ↔ Liquid HC

Very little external carbon required as make up!
Is there a Preferred HC for Energy Storage?

Consider the HC synthesis via
\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{HC} + \text{H}_2\text{O} \]
Metrics for HC Synthesis

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{HC} + \text{H}_2\text{O} \]

- Exergy stored per mole carbon (kJ/mol C)
- Fraction of H\textsubscript{2} exergy recovered in the fuel (%)
- Exergy density as a liquid (GJ/m\textsuperscript{3})
Metric #1: Exergy Stored per mole Carbon

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Exergy per carbon (kJ/mol C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>806</td>
</tr>
<tr>
<td>Ethane</td>
<td>723</td>
</tr>
<tr>
<td>Propane</td>
<td>692</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>652</td>
</tr>
<tr>
<td>Cetane</td>
<td>640</td>
</tr>
<tr>
<td>Methanol</td>
<td>693</td>
</tr>
<tr>
<td>Ethanol</td>
<td>654</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>684</td>
</tr>
</tbody>
</table>
Metric #1: Exergy Stored per mole Carbon

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Exergy per carbon (kJ/mol C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>806</td>
</tr>
<tr>
<td>Ethane</td>
<td>723</td>
</tr>
<tr>
<td>Propane</td>
<td>692</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>652</td>
</tr>
<tr>
<td>Cetane</td>
<td>640</td>
</tr>
<tr>
<td>Methanol</td>
<td>693</td>
</tr>
<tr>
<td>Ethanol</td>
<td>654</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>684</td>
</tr>
</tbody>
</table>

- Methane stores the highest energy per carbon atom → least carbon supply
### Metric #2: Fraction of H₂ Exergy Stored

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fraction of H₂ exergy in fuel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>85.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>88.0</td>
</tr>
<tr>
<td>Propane</td>
<td>88.4</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>88.9</td>
</tr>
<tr>
<td>Cetane</td>
<td>89.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>98.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>92.8</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>97.1</td>
</tr>
</tbody>
</table>

©2013 R. Agrawal
## Metric #2: Fraction of H₂ Exergy Stored

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fraction of H₂ exergy in fuel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>85.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>88.0</td>
</tr>
<tr>
<td>Propane</td>
<td>88.4</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>88.9</td>
</tr>
<tr>
<td>Cetane</td>
<td>89.0</td>
</tr>
<tr>
<td><strong>Methanol</strong></td>
<td><strong>98.3</strong></td>
</tr>
<tr>
<td>Ethanol</td>
<td>92.8</td>
</tr>
<tr>
<td><strong>Dimethyl Ether (DME)</strong></td>
<td><strong>97.1</strong></td>
</tr>
</tbody>
</table>

- Methanol and DME top candidate for H₂ efficiency
### Metric #3: Exergy Density as Liquid

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Exergy density as liquid (GJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>21.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>25.2</td>
</tr>
<tr>
<td>Propane</td>
<td>25.9</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>27.4</td>
</tr>
<tr>
<td>Cetane</td>
<td>25.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>12.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>18.6</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>20.2</td>
</tr>
</tbody>
</table>
### Metric #3: Exergy Density as Liquid

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Exergy density as liquid (GJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>21.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>25.2</td>
</tr>
<tr>
<td>Propane</td>
<td>25.9</td>
</tr>
<tr>
<td><strong>Iso-octane</strong></td>
<td><strong>27.4</strong></td>
</tr>
<tr>
<td>Cetane</td>
<td>25.5</td>
</tr>
<tr>
<td>Methanol</td>
<td>12.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>18.6</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>20.2</td>
</tr>
</tbody>
</table>

- Octane has the highest density
No single fuel favored in all three metrics.

Trade-off between metrics needs to be optimized for different end uses.
Among HC molecules...

... Consider the Use of Methane

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Exergy per carbon (kJ/mol C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>806</td>
</tr>
<tr>
<td>Ethane</td>
<td>723</td>
</tr>
<tr>
<td>Propane</td>
<td>692</td>
</tr>
<tr>
<td>Iso-octane</td>
<td>652</td>
</tr>
<tr>
<td>Cetane</td>
<td>640</td>
</tr>
<tr>
<td>Methanol</td>
<td>693</td>
</tr>
<tr>
<td>Ethanol</td>
<td>654</td>
</tr>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>684</td>
</tr>
</tbody>
</table>

- \( \text{CH}_4 \rightarrow \) **highest energy content per carbon**
- Liquefaction energy penalty (-162 °C)
Methane-cycle (Storage mode)

Minimize solar energy penalty of CH₄ liquefaction

SOEC=Solid Oxide Electrolysis
Methane-cycle (Delivery mode)

- Solid Oxide Fuel Cell for H₂

No power consumed for CO₂ capture and liquefaction!
Methane Storage Simulation Results

- **Efficiency**: Methane superior to H$_2$
- **Volume**: Methane superior to other options

Simulations carried out using Aspen Plus
Similar efficiencies possible with Methanol (52-54%)
Improve Efficiency of Energy Use
Improve Efficiency of Energy Use

An Example: Multicomponent nonazeotropic distillation
Why is Separations Research Important?

- 40-70% of operating and capital cost of a typical chemical plant is due to separations
- 90-95% of all separations in chemical and petrochemical plants are by distillation
- 40,000 distillation columns in operation in US, and consume equivalent of ~ 1.2 million bbl of oil per day
- US refineries consume ~ 0.4 million bbl of oil per day for crude oil distillation alone

A saving of 20-50% in distillation energy could save 85-220 million bbl of oil equivalent per year ( ~ 8.5-22 billion dollars/year @ $100/bbl).

These energy savings are comparable to the discovery of a new giant oil field (100 million bbl) every year!
For a given application, our aim is to develop a method that allows a systematic search and identification of a separation system that is cost effective and energy efficient.
Developed a Method to Generate Search Space of Basic Configurations

A Four Component Example

But, the number of configurations increase rapidly with number of components

<table>
<thead>
<tr>
<th>Number of components in feed</th>
<th>Regular-column configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without Thermal Coupling</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>203</td>
</tr>
<tr>
<td>6</td>
<td>4,373</td>
</tr>
<tr>
<td>7</td>
<td>185,421</td>
</tr>
<tr>
<td>8</td>
<td>15,767,207</td>
</tr>
</tbody>
</table>

…. and we still have to identify the best one!

© R. Agrawal, 2013

NLP Formulation to Ranklist the Entire Search Space

\[ f_{i,AB} + f_{i,CD} = f_{i,ABCD} \]
\[ \sum_i \alpha_i \frac{f_{i,dist}}{\alpha_i - \theta_j} \leq V_s \]
\[ LTC_i + VTC_i = FTC_i \]
\[ \sum_{i=1:n-1} V_{col,i} \leq V_{transition} \]
\[ \min \sum_{i=1:n-1} V_{col,i} \]

- Succeeded in enumerating the useful distillation configurations for a given separation and rank them according to required vapor duty
- Solved the problem of developing a quick and reliable screening tool for multicomponent distillation
- Successfully applied our tool to proprietary separations at a major chemical company and identified several attractive configurations


© R. Agrawal, 2013  
*Branch-And-Reduce Optimization Navigator*
An Example

Petroleum crude distillation consumes huge amount of energy!

Different refineries process different crudes, yet they have generally used the same configuration for 75+ years.

Identified hundreds of configurations which are potentially 15-50% more energy efficient than the above configuration.

© R. Agrawal, 2013

Identified Novel Heat and Mass Integrated Configurations

Regular-Column Configuration

Heat and Mass Integrated Configuration

Multicomponent Distillation Research is Still Vibrant and Fun!

Also Relevant to the Solar Economy
In Summary…

• Solar economy requires energy and carbon efficient solutions

• Fuels and Chemicals
  • SA biomass analogous to primary energy/carbon source
  • Preserve carbon - augmented biomass conversion
  • Simultaneous heat, mass and power process integration

• Solar Hydrogen production
  • $\text{STH}_2$ efficiency of 35-50% using membrane reactors
  • Superior to known electrolytic and single bandgap methods

• Closed carbon cycles for grid-level energy storage
  • Storage efficiency of 55-58% and much reduced volume

• Use efficiency improvement in traditional areas will still be needed. Example: Multicomponent Distillation

• Energy modeling is multidimensional

©2013 R. Agrawal
Acknowledgments

Funding
Acknowledgments (Current Collaborators)

Energy Systems Analysis and Distillation:
Prof. Mohit Tawarmalani (Krannert School of Management)

Biomass To Liquid Fuel:
Prof. Nick Delgass, Prof. Fabio Ribeiro (Chemical Engineering)
Prof. Maureen McCann (Biological Sciences Molecular Biosciences)
Prof. Nick Carpita (Agriculture- Botany and Plant Pathology)
Prof. Hilkka Kenttämaa (Chemistry)
The Research Team
“A Great time to be a Chemical Engineer”
....Thank you