

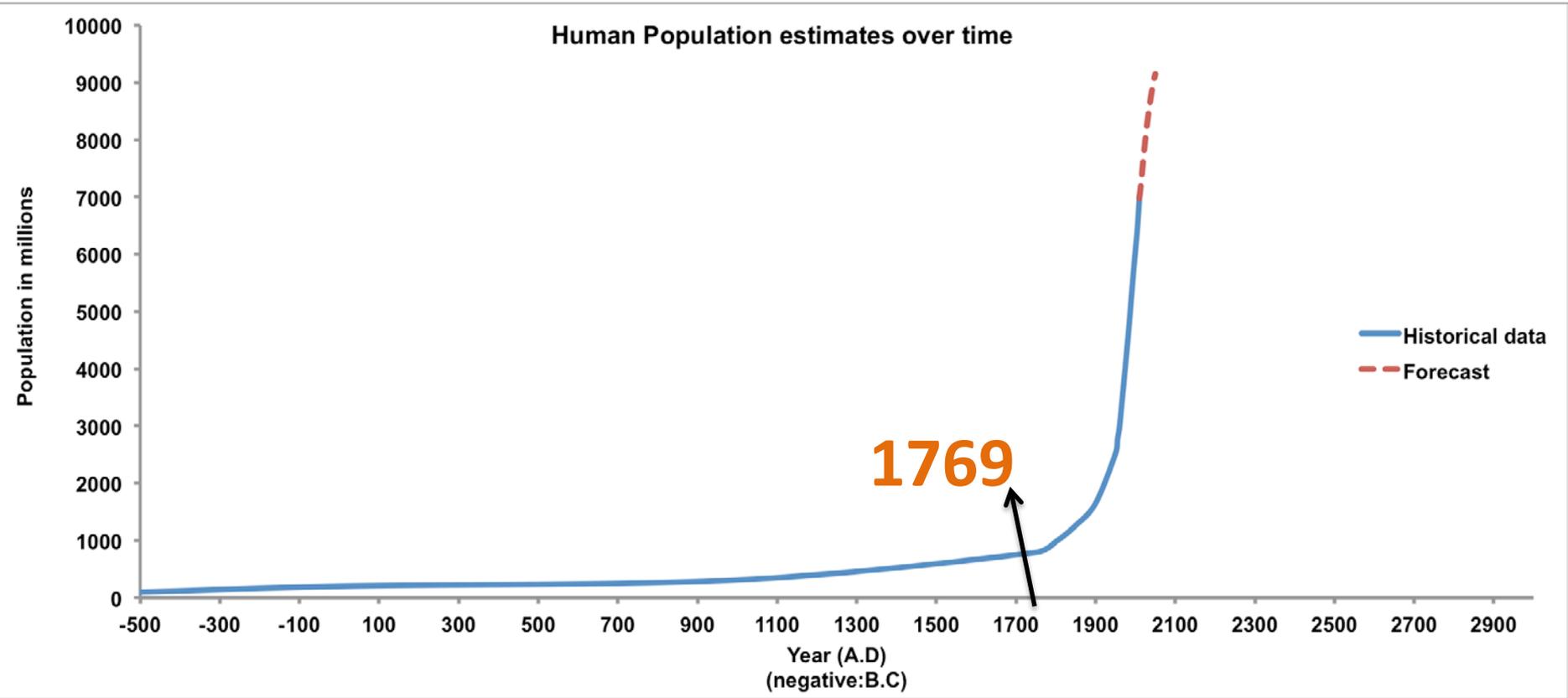
# Solar Economy-Is it Feasible?

**Rakesh Agrawal**

**School of Chemical Engineering  
and The Energy Center at Discovery park  
Purdue University  
West Lafayette, IN 47907**

# Why is Energy Important?

# World Population



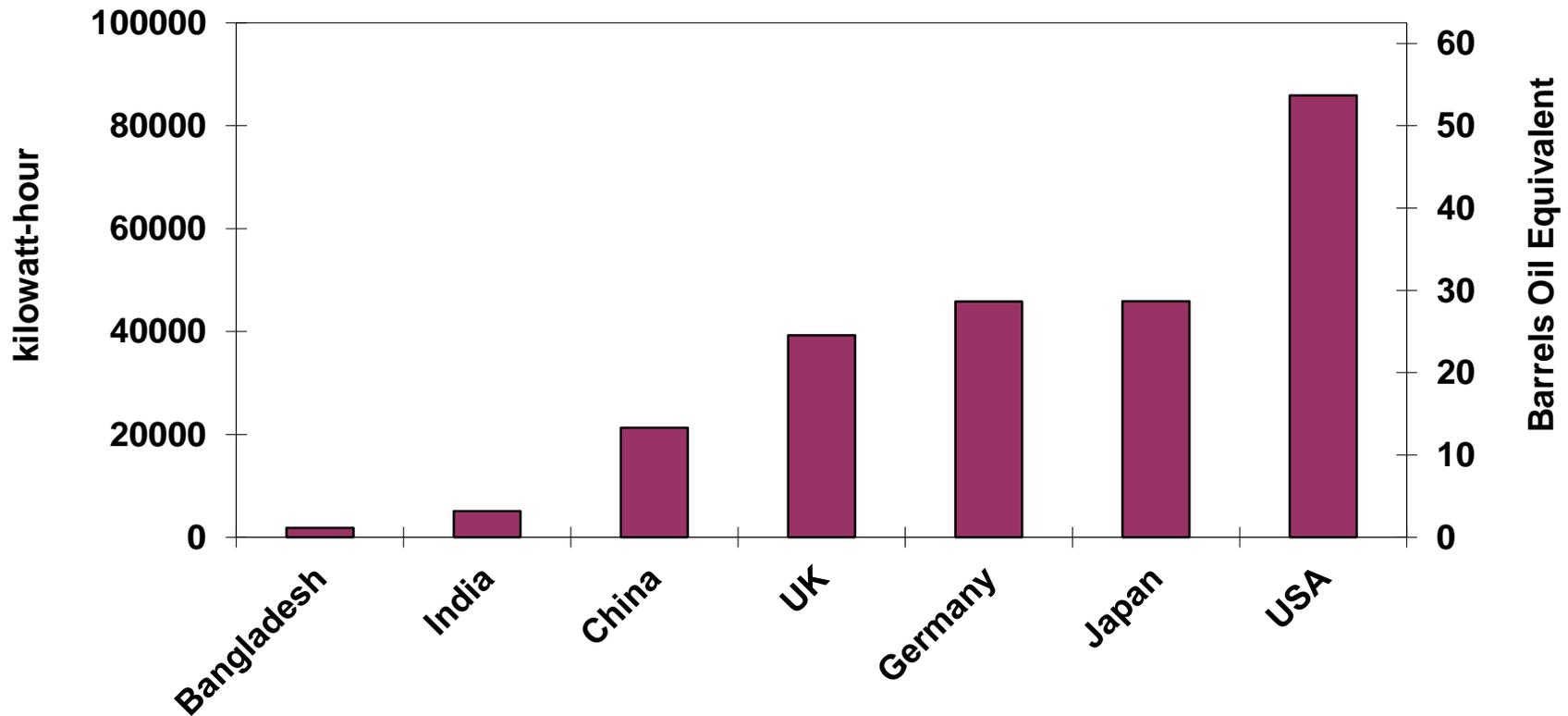


**James Watt and his 1769 steam engine**

Source: David J.C. Mackay 2009

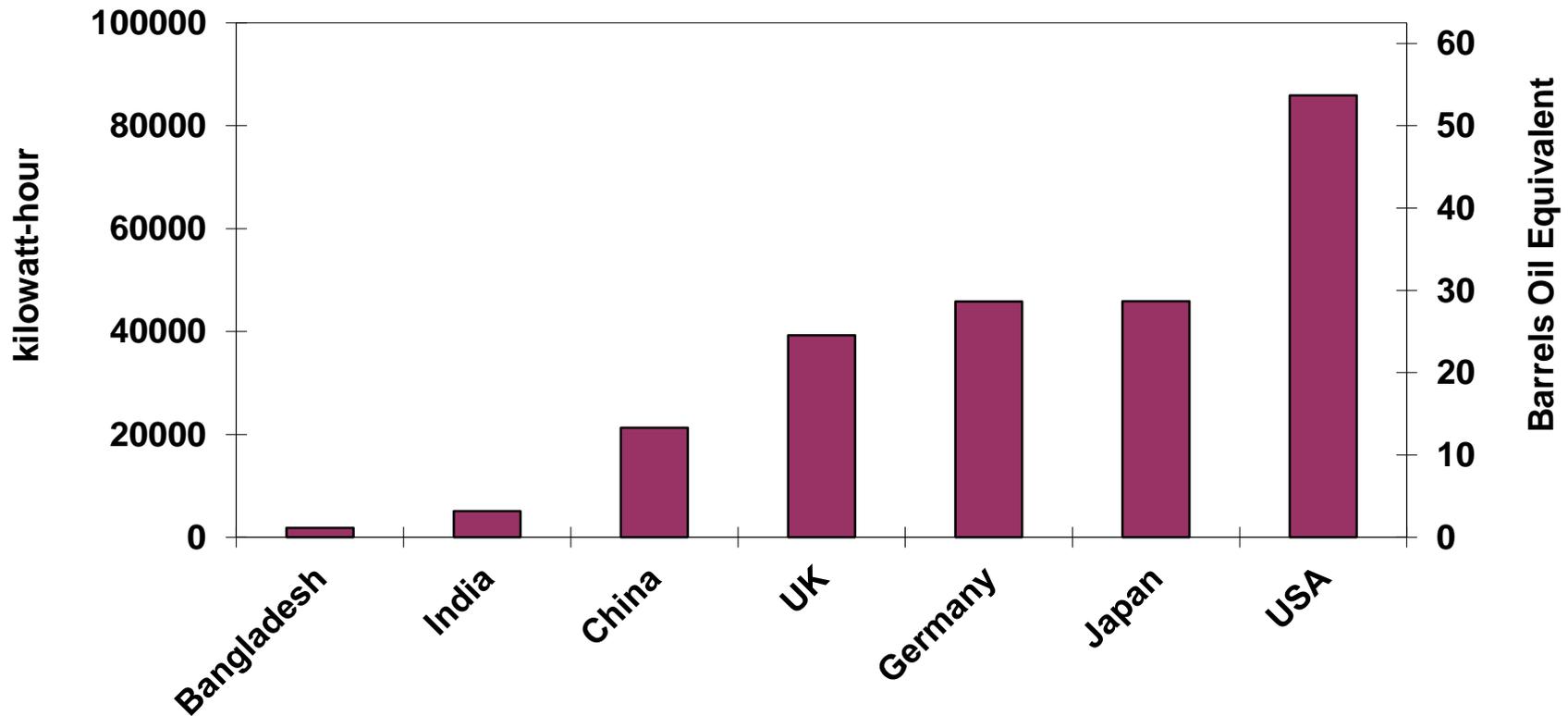
# Energy Consumption is Way of Life in Industrialized Countries

## 2010 Primary energy consumption per capita



# Energy Consumption is Way of Life in Industrialized Countries

## 2010 Primary energy consumption per capita



**Fossil Fuel Provides 85% Energy!**

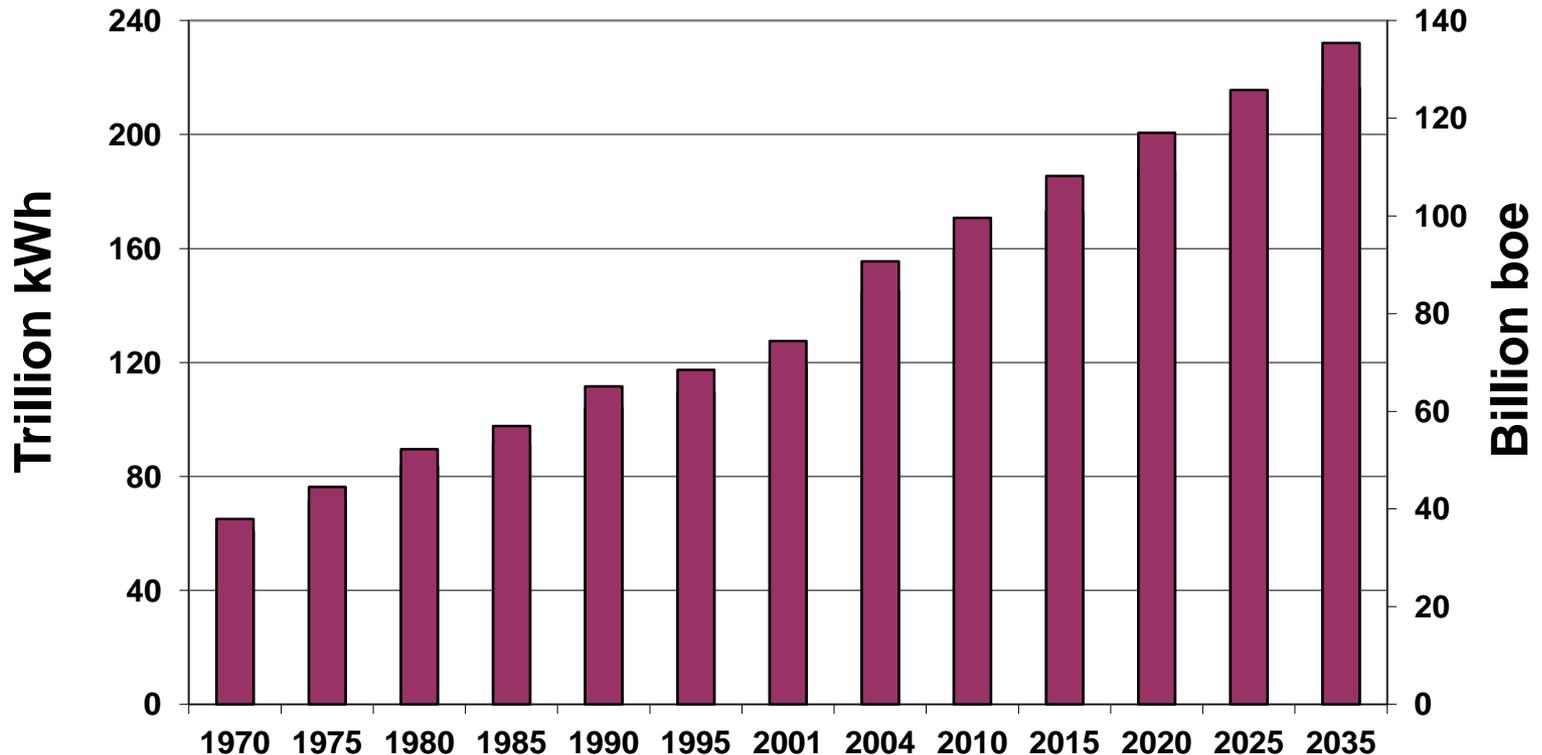
## However...

- **The world population is expected to rise**

# However...

- The world population is expected to rise
- **World energy consumption rate is expected to rise**

# World Market Energy Consumption



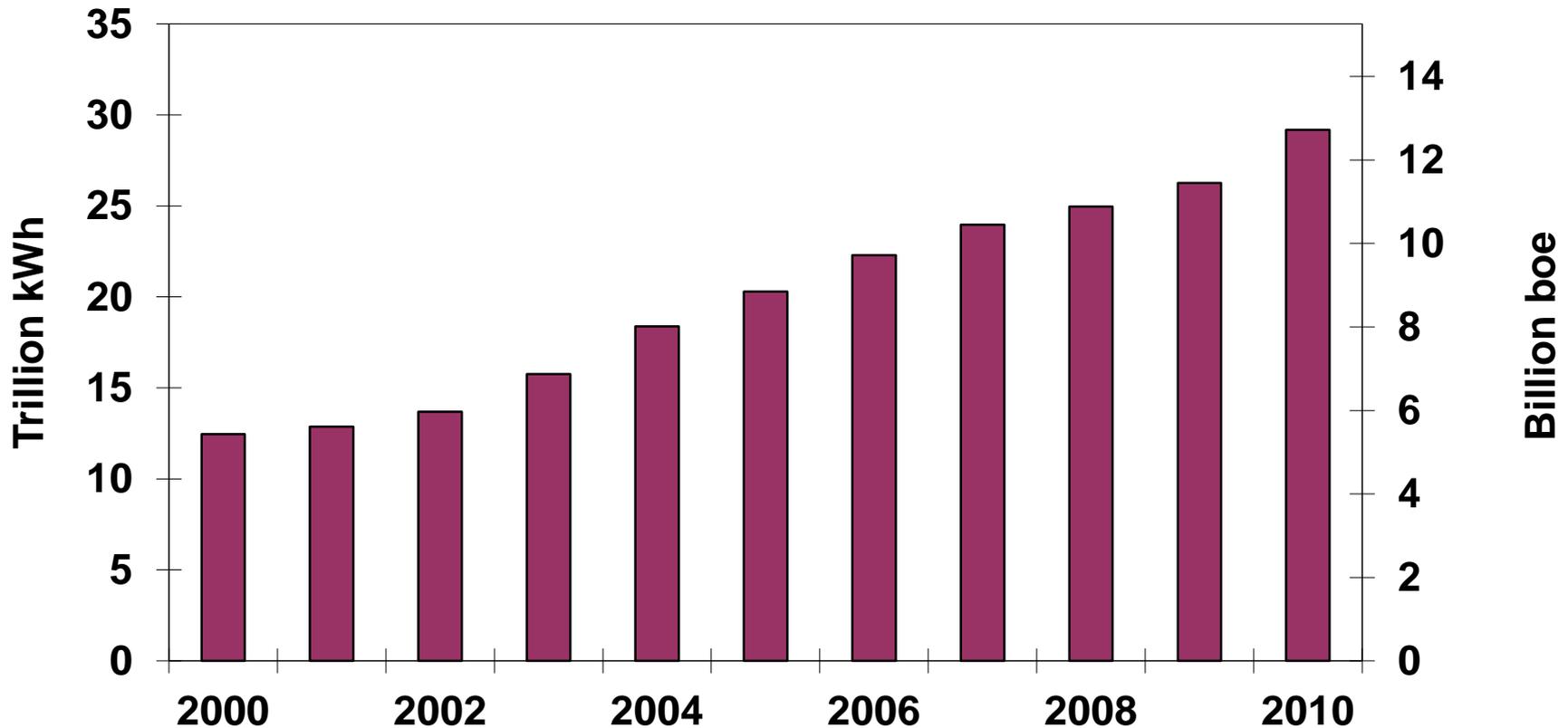
- World primary energy usage rate in 2007 was 14.8 TW
- By 2050, the usage rate could be 28 TW

**Consumption rate could double!**

# However...

- The world population is expected to rise
- World energy consumption rate is expected to rise
- **China's current economic growth is expected to accelerate energy consumption**

# China's Recent Energy Consumption



- Average growth rate over past quarter century > 10%!
- Current China's primary energy consumption = 17.8 billion boe
- Current USA's primary energy consumption = 16.7 billion boe

# China's Recent Energy Consumption

- Average growth rate > 10%!
- 2007 China's primary energy consumption = 13.7 billion boe
- Current China's primary energy consumption = 17.8 billion boe
- Current USA's primary energy consumption = 16.7 billion boe
- If primary energy @ per capita rate of Japan = 43.9 billion boe
- Current total world's energy consumption = 81.4 billion boe

# However...

- The world population is expected to rise
- World energy consumption rate is expected to rise
- China's current economic growth is expected to accelerate energy consumption
- **Oil production will peak during the lifetime of a child born today**

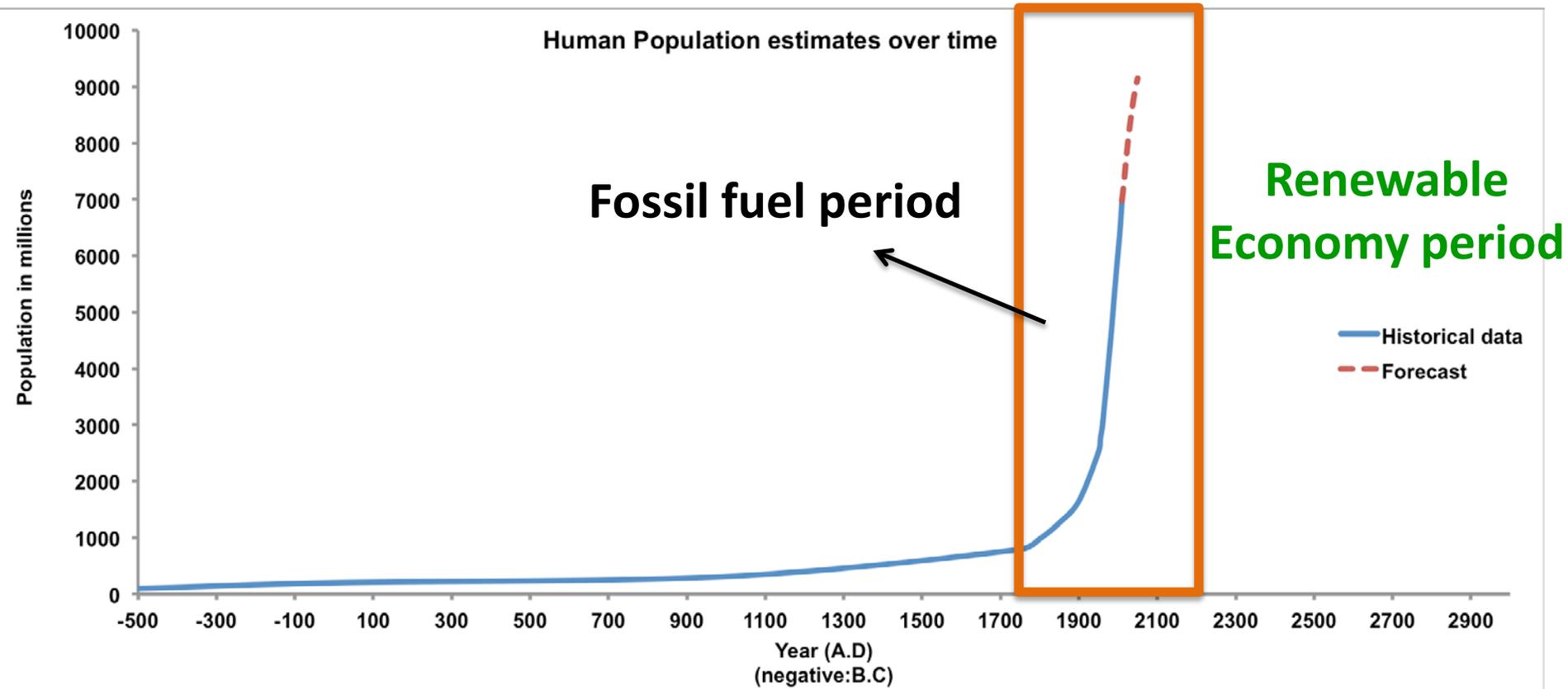
# However...

- The world population is expected to rise
- World energy consumption rate is expected to rise
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- Oil production will peak during the lifetime of a child born today
- **For most nations it is national energy independence and security issue**

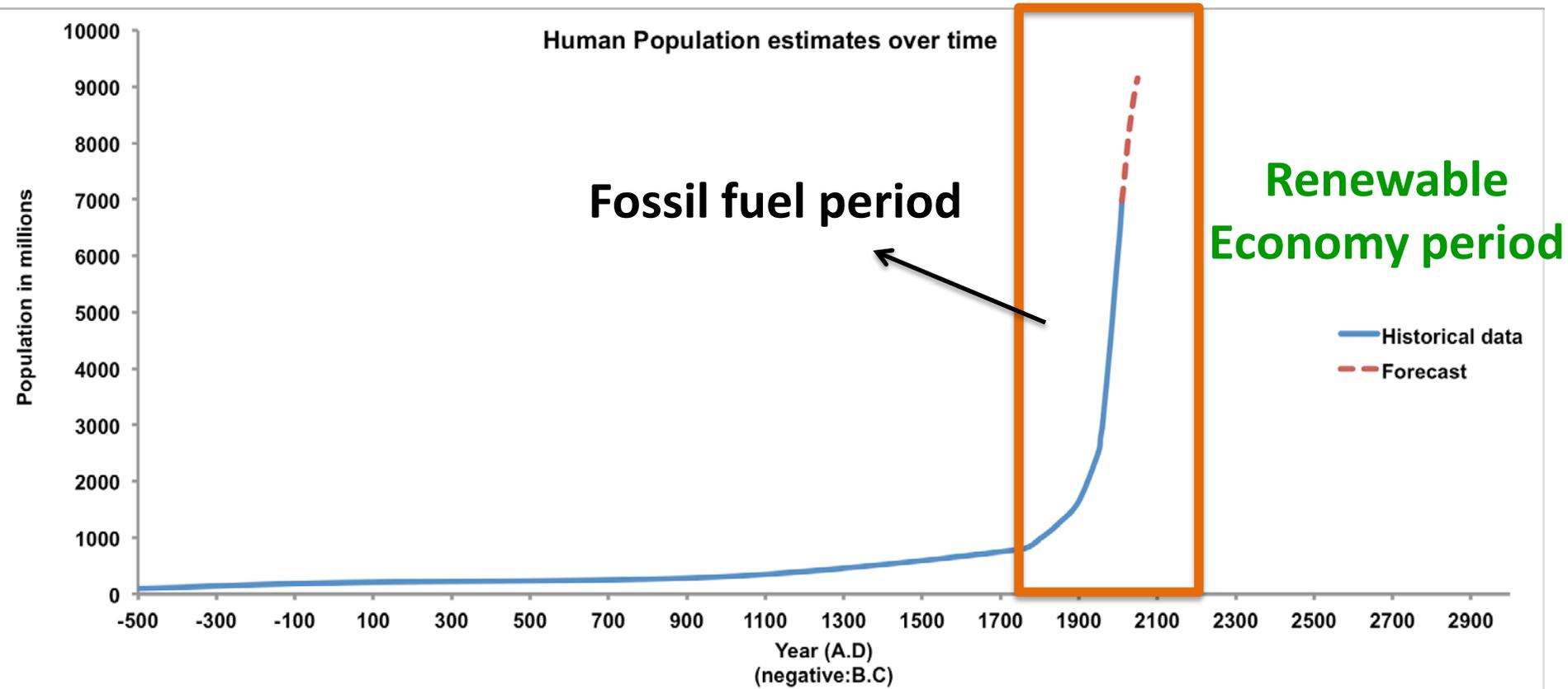
# However...

- The world population is expected to rise
- World energy consumption rate is expected to rise
- China's current economic growth is expected to accelerate energy consumption
- Oil production will peak during the lifetime of a child born today
- For most nations it is national energy independence and security issue
- **It takes a long time to develop a new energy source and its infrastructure**

# Fossil Energy: in context of human civilization



# Fossil Energy: in context of human civilization



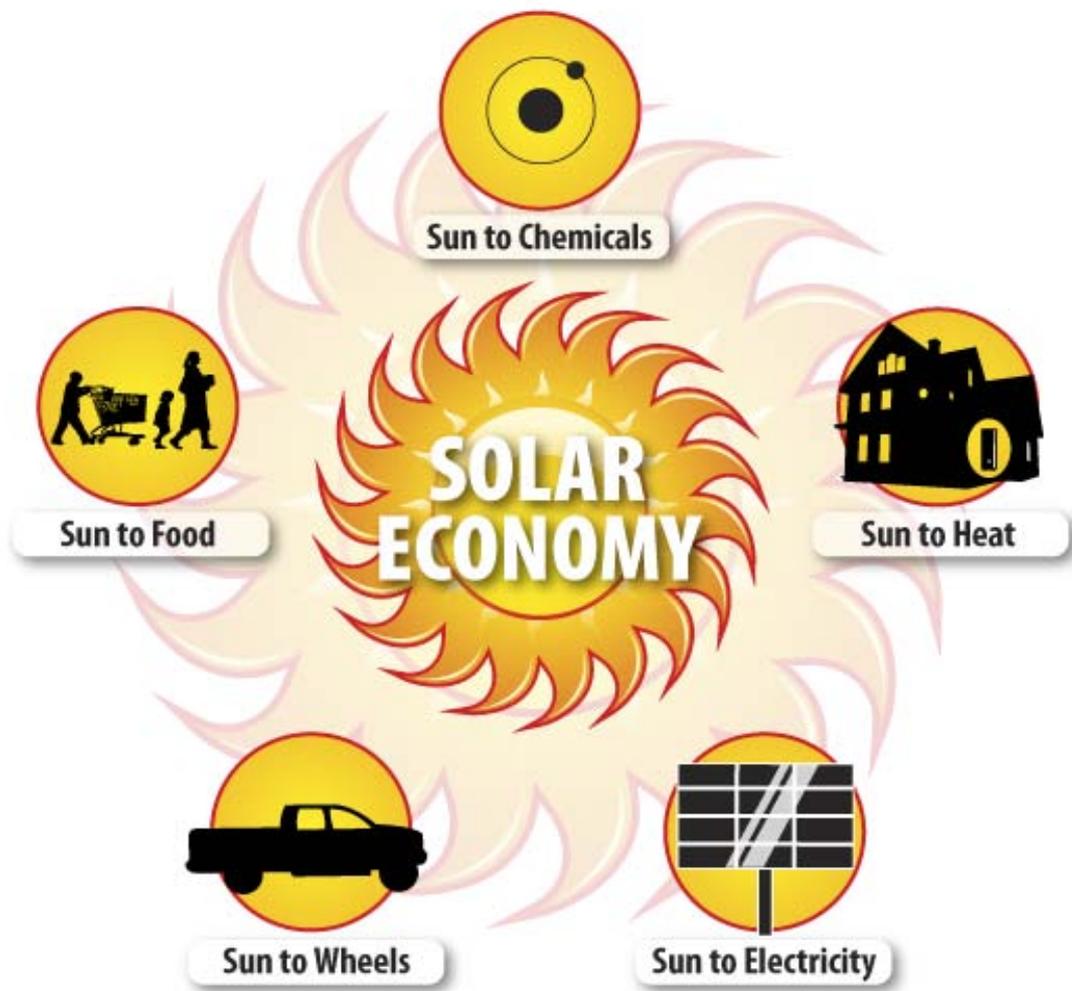
**Therefore, we must understand energy transformation and use issues to develop alternative energy strategies**

# Some Alternate Resources

- Biomass
- Hydroelectricity
- Wind
- Geothermal
- Nuclear
- Solar

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

# Solar economy vision



# **Development of a Solar Economy Provides Unprecedented opportunity for Innovations**

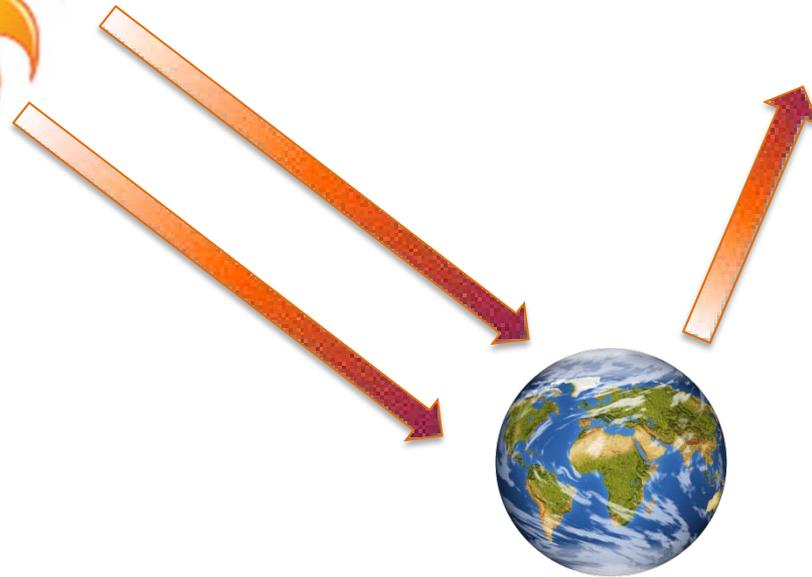
# The Journey of Solar Photons

Looking through the lens of time

# Absorption & Radiation from Earth's surface

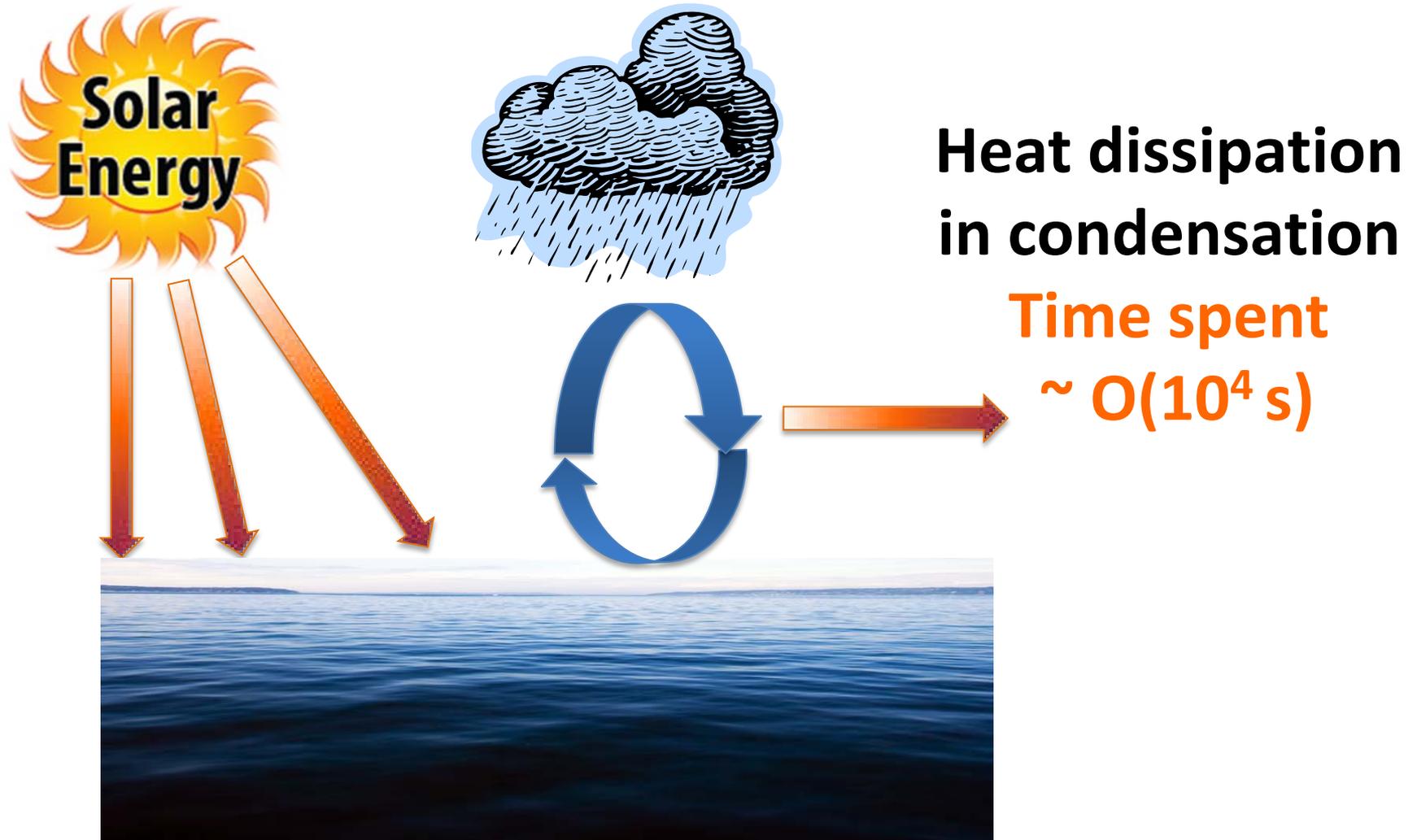


Time spent  $\sim O(10^0 \text{ s})$

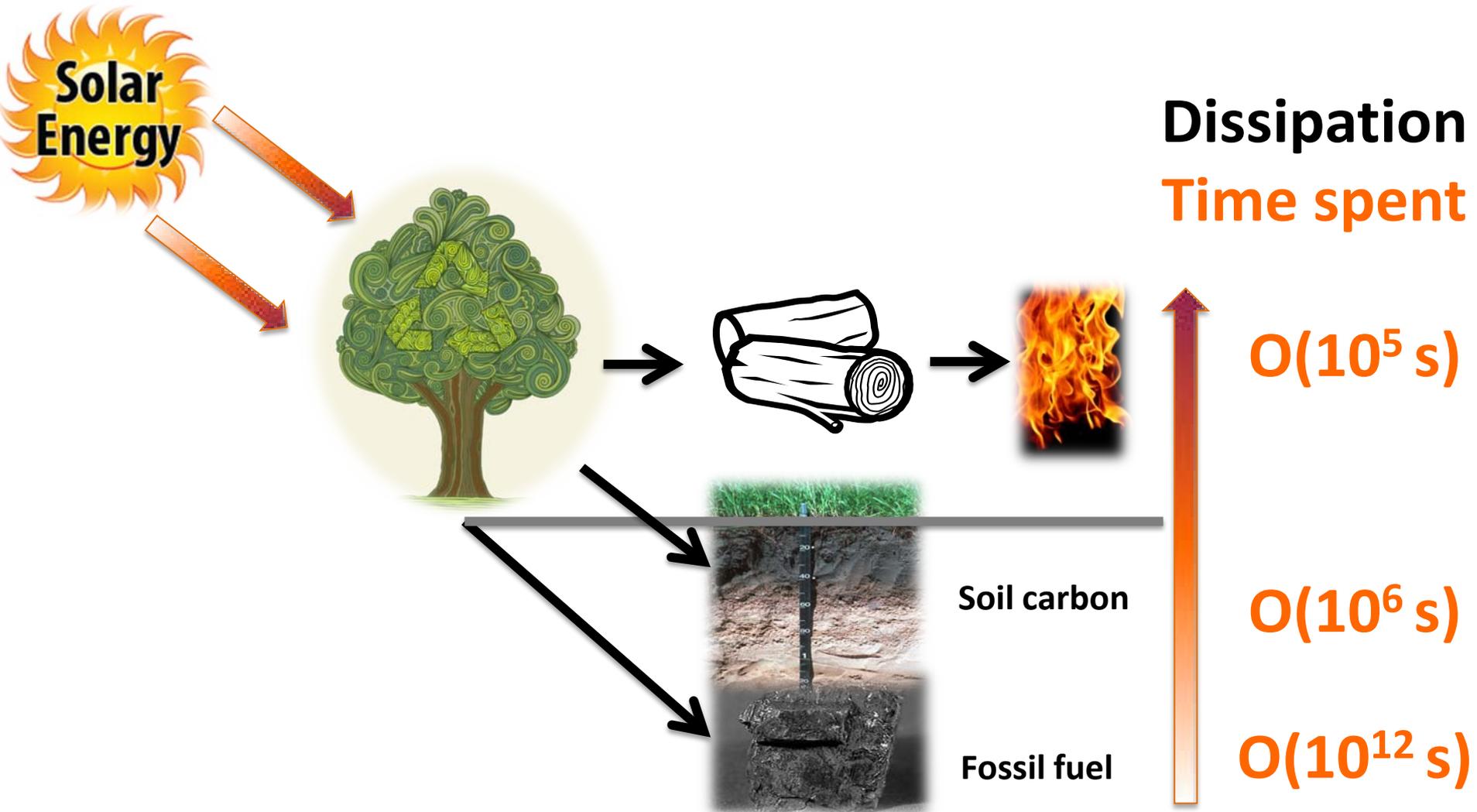


$\sim$  few seconds

# Dissipation during water cycle



# Dissipation during carbon cycle



**Harness solar energy**



**Transform solar Energy**



**Use it for human activities**



**Dissipate to outer space**

# Challenge for solar economy

**Harness, Transform, Store and Use  
solar photons on a time scale of  
human activities ~  $O(10^3-10^5 \text{ s})!$**

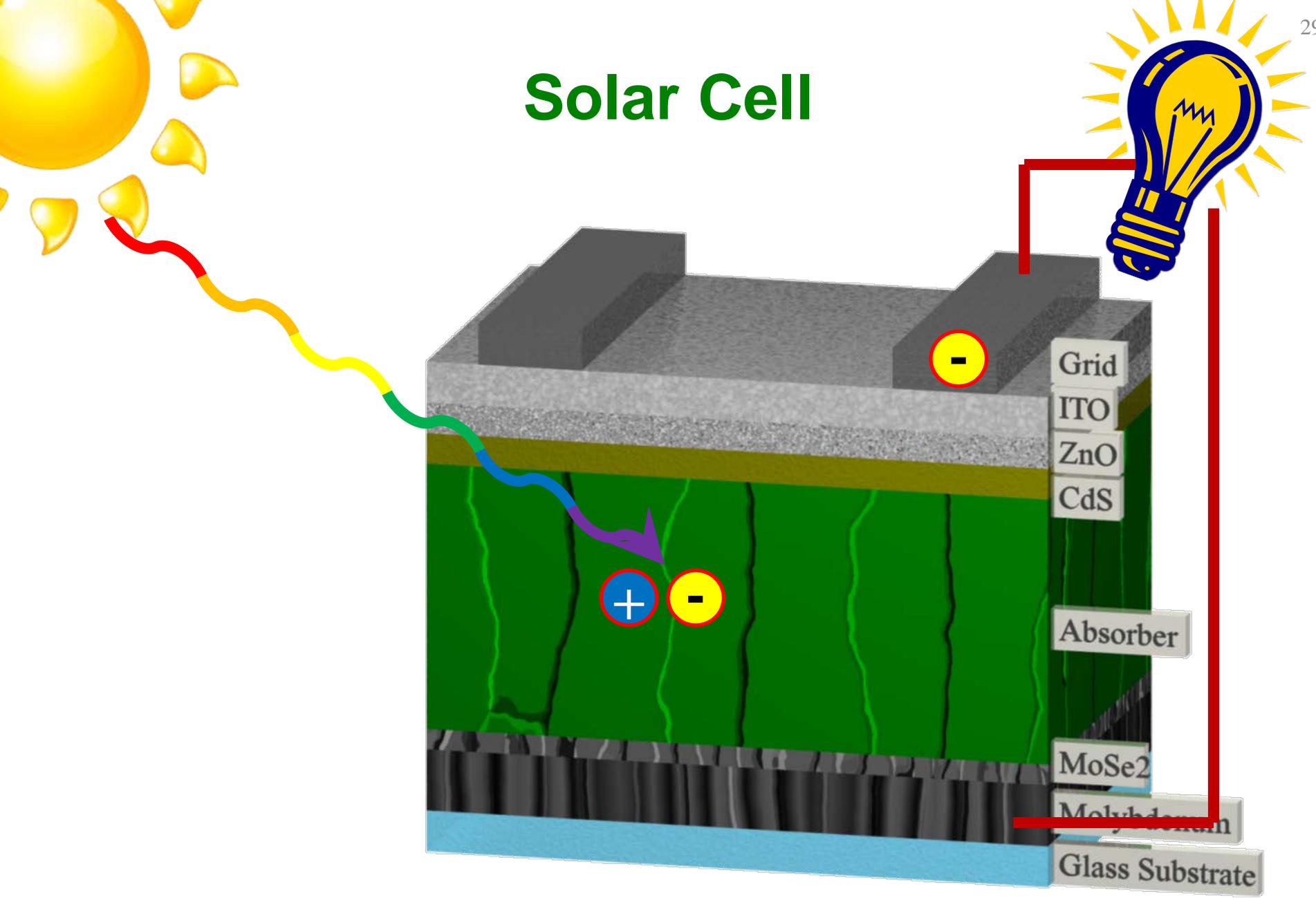
# A Three Part Presentation .....

- 1. Harnessing** of Solar Energy -- Solar Cells from Nanocrystal Inks
- 2. Transformation** of Solar Energy -- Energy System Analysis with Emphasis on Transportation Sector
- 3. Storage** of Solar Energy -- A Chemical Storage Cycle

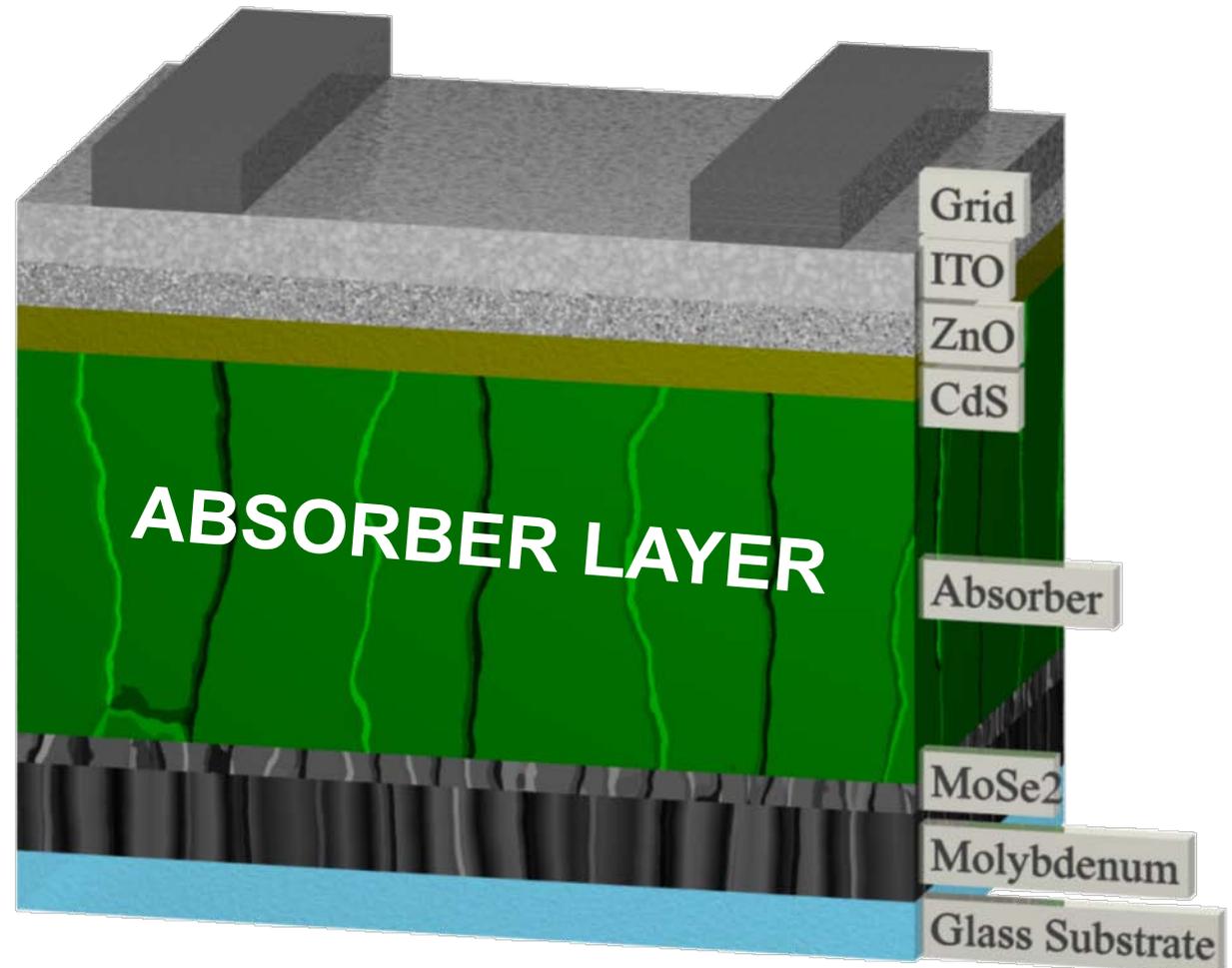
# A Three Part Presentation .....

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# Solar Cell

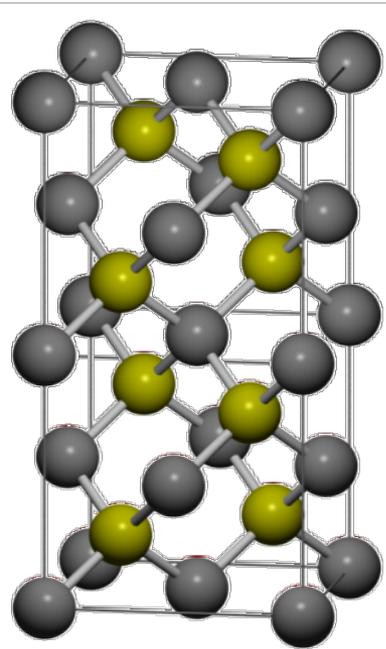


# Solar Cell

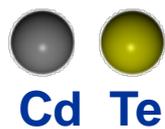
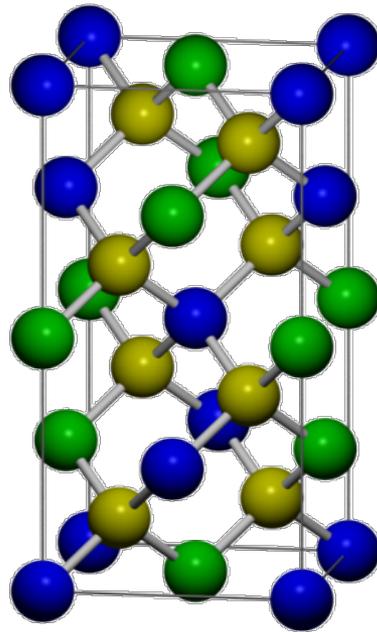


# Solar Material Structure

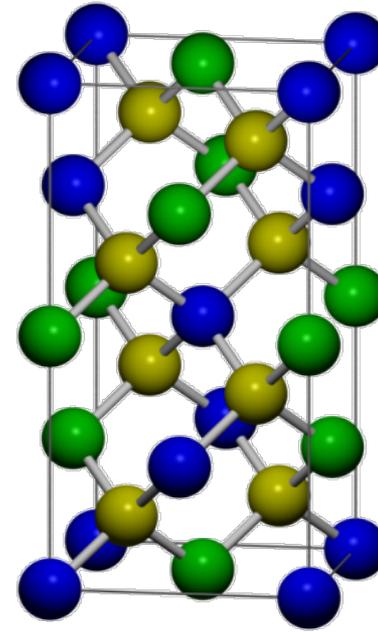
**Diamond Cubic**  
IV Silicon



**Zincblende**  
II-VI CdTe  
III-V GaAs

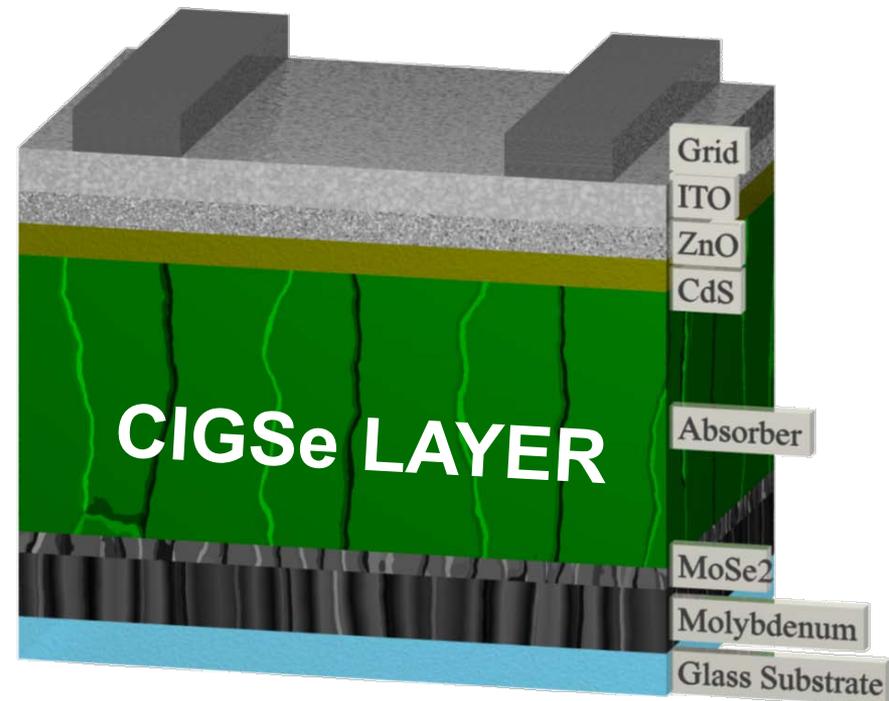


**Chalcopyrite**  
I-III-VI<sub>2</sub> CIGSe

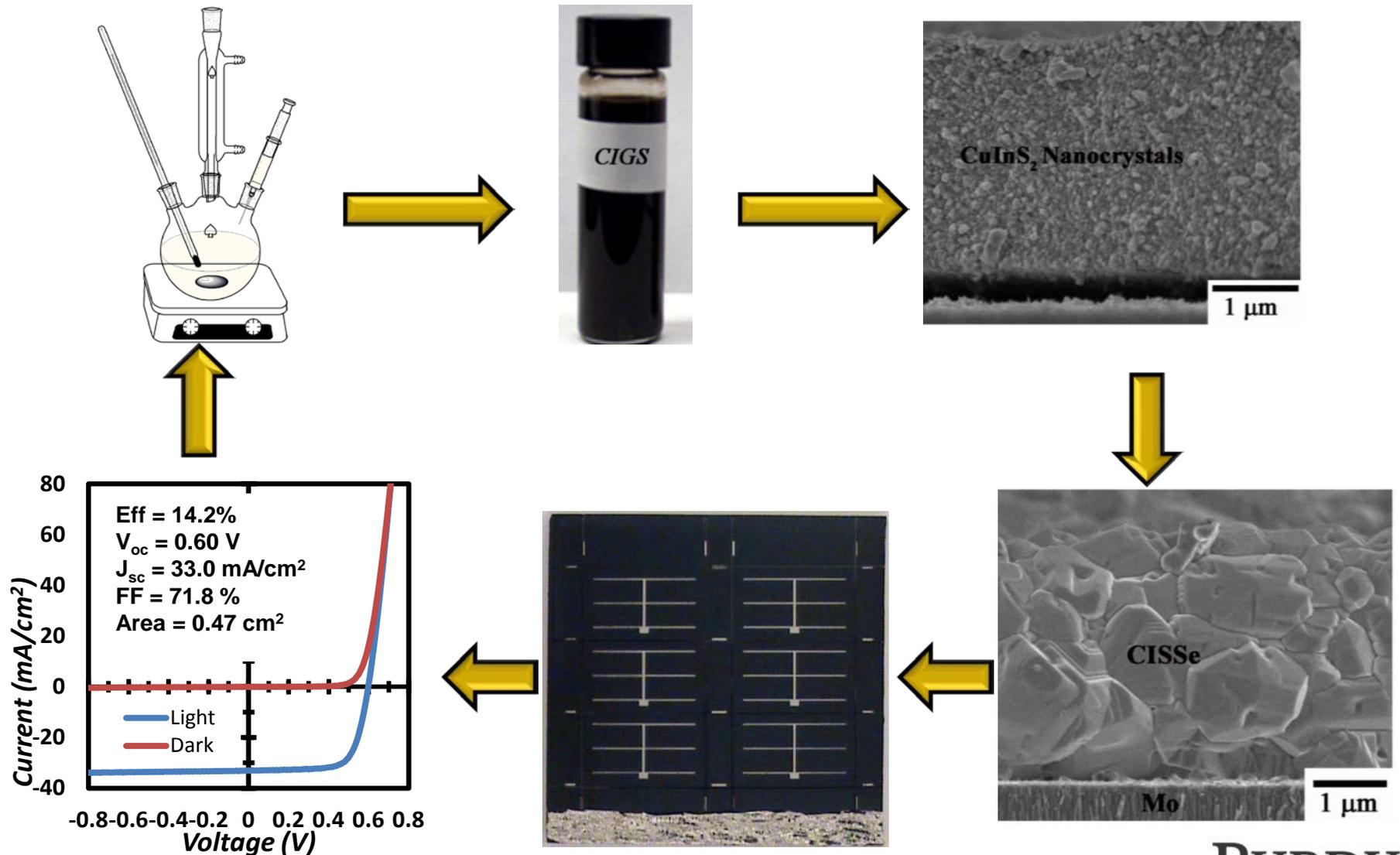


# Cu(In,Ga)Se<sub>2</sub> (CIGSe) Solar Cell

- High photon absorption coefficient
- Low material consumption
- Optimal bandgap by adjusting In/Ga ratio – higher voltage achievable
- Most efficient (~20%) amongst thin-film solar cells at lab scale



# Our CIGSe Liquid Deposition Method



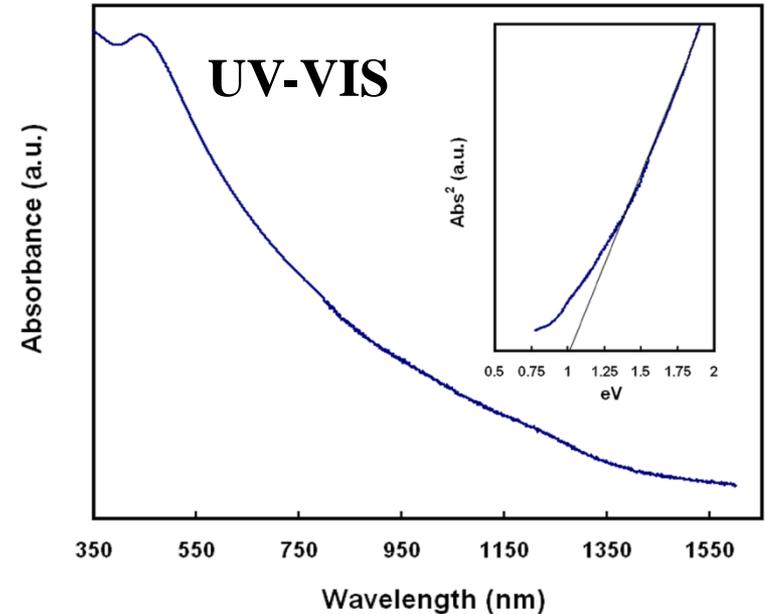
# Synthesis of ClSe Nanocrystal Ink

## Solution Phase Batch Reaction

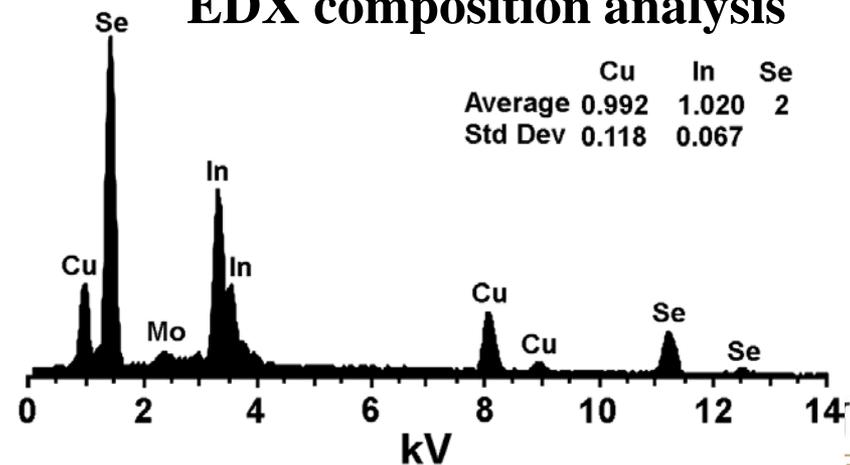


**Precursors:** CuCl, InCl<sub>3</sub>, Se  
**Solvent:** Oleylamine  
**Conditions:** P = 1 atm  
T = 225 – 285 C

Observed band gap = 1.04eV

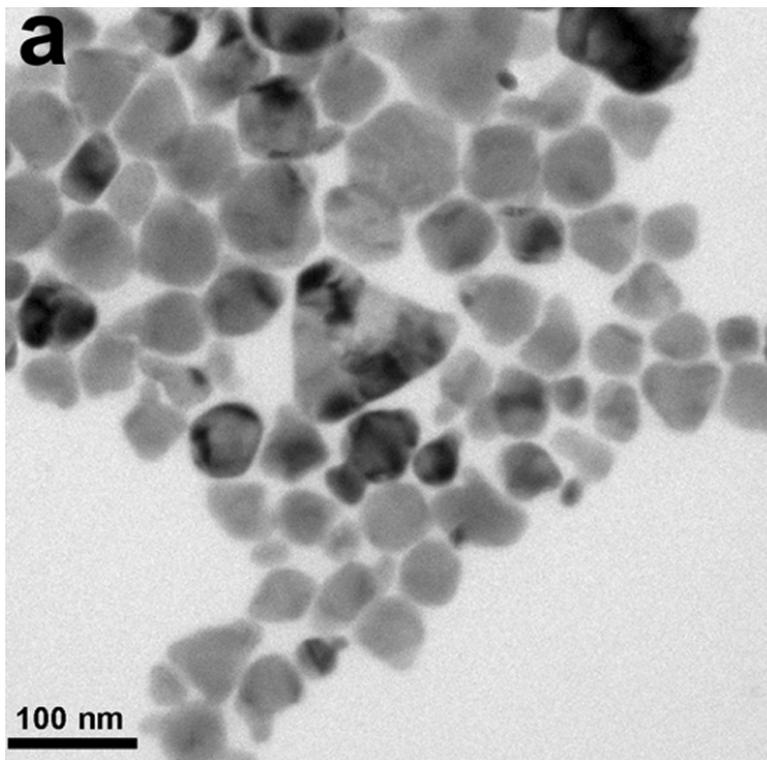


## EDX composition analysis

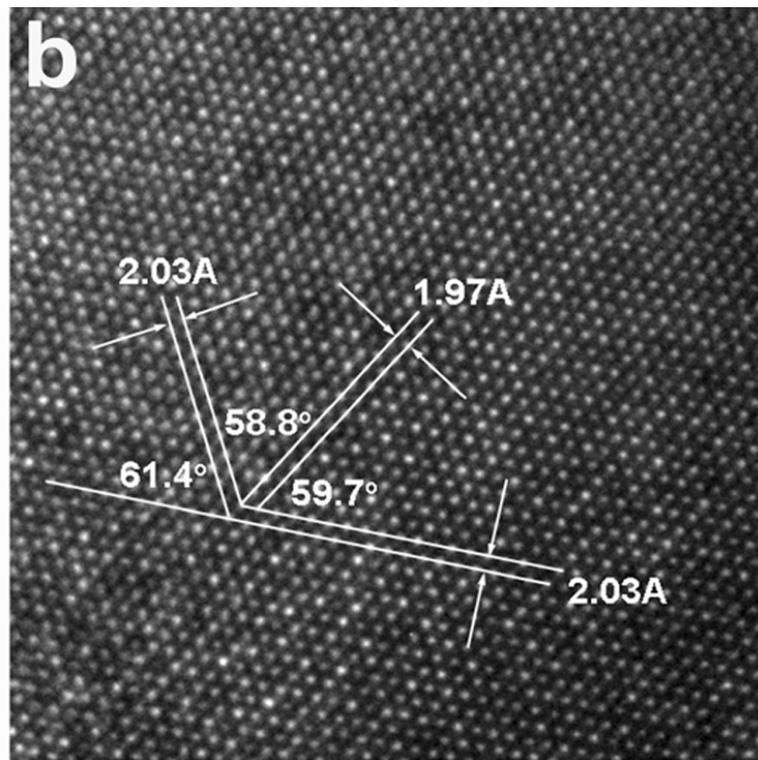


# HR-TEM of the Chalcopyrite Nanocrystals

[221] Zone Axis



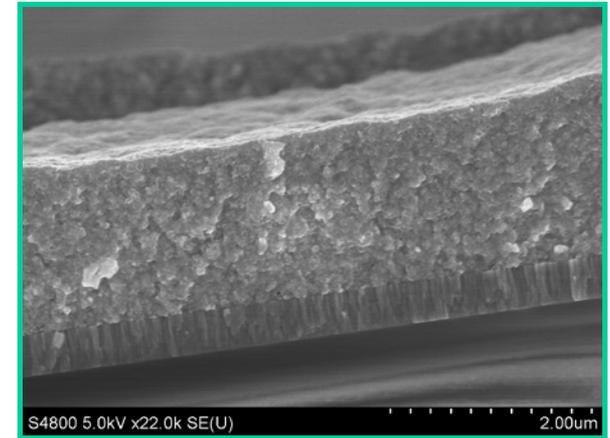
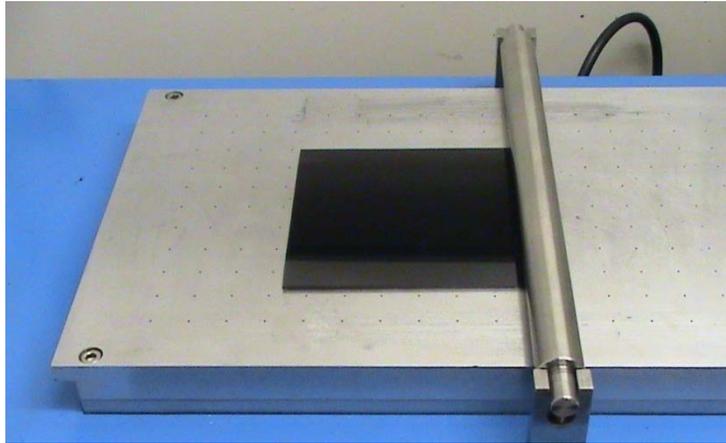
Large area TEM image



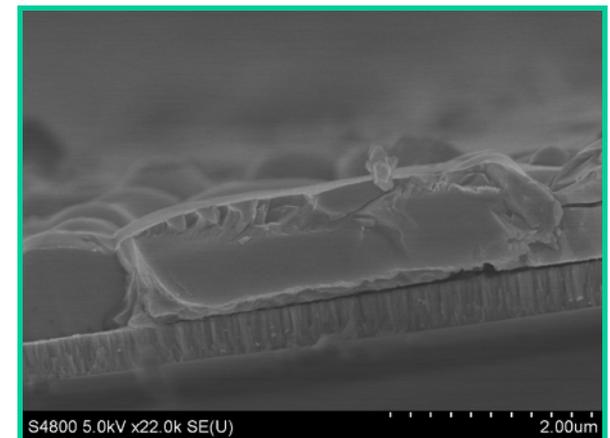
HR-TEM of a nanocrystal

# Scalable Coating Process and Dense Thin Film Formation

## Slot, Knife, or Roll Coating

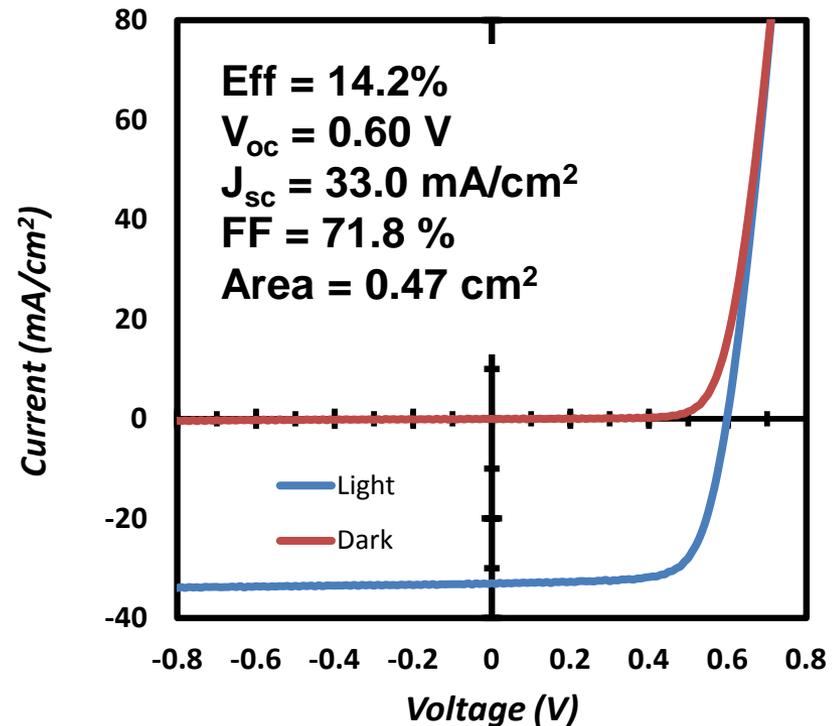
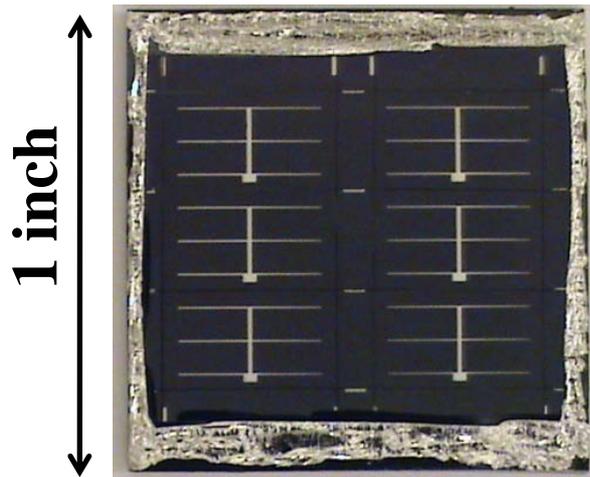


↓  
**Rapid Thermal Processing (RTP)  
with Se at 500 °C to form a  
dense highly crystalline layer**



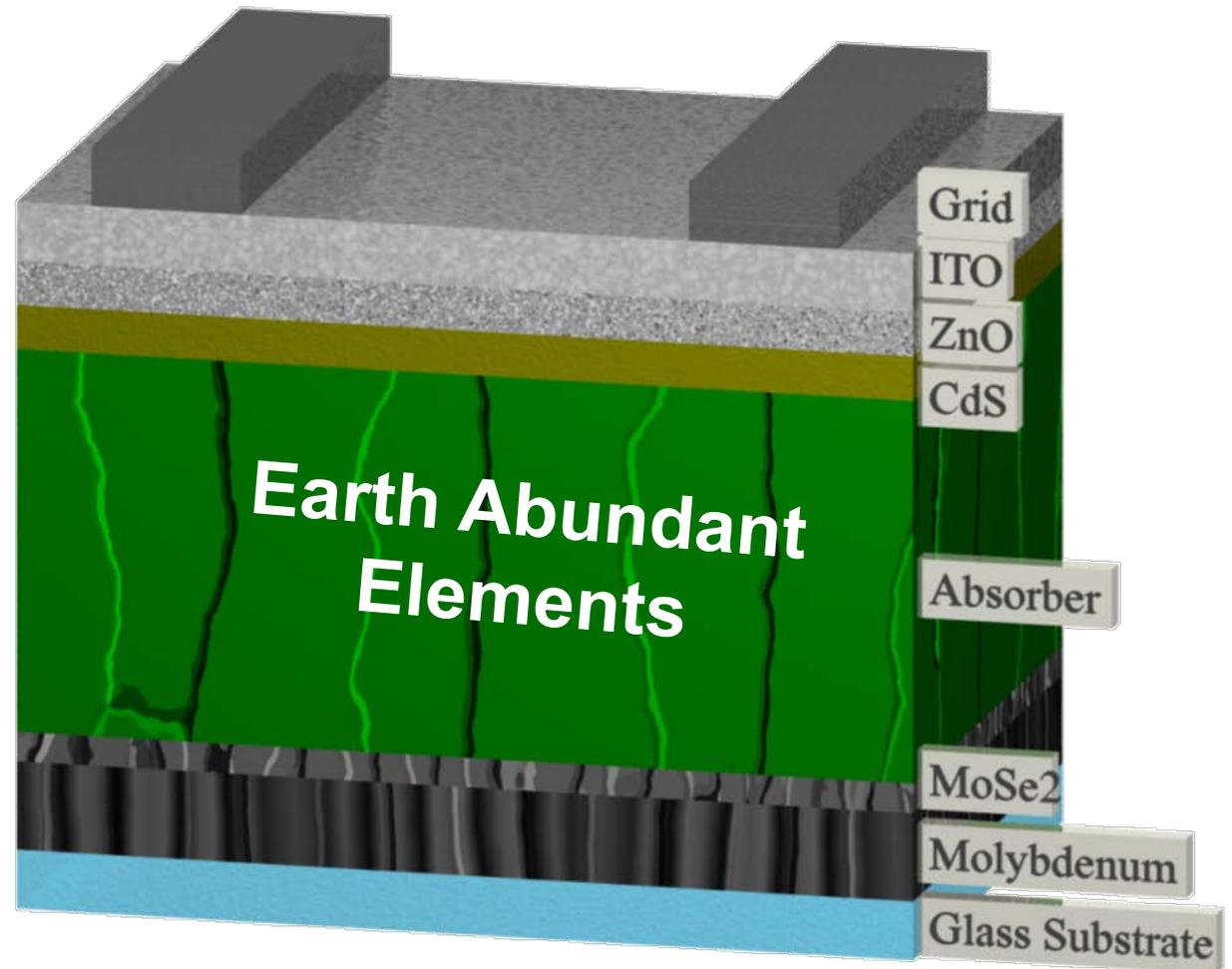
# Photovoltaic Device Performance

## Cu(In,Ga)(S,Se)<sub>2</sub> Solar Cell

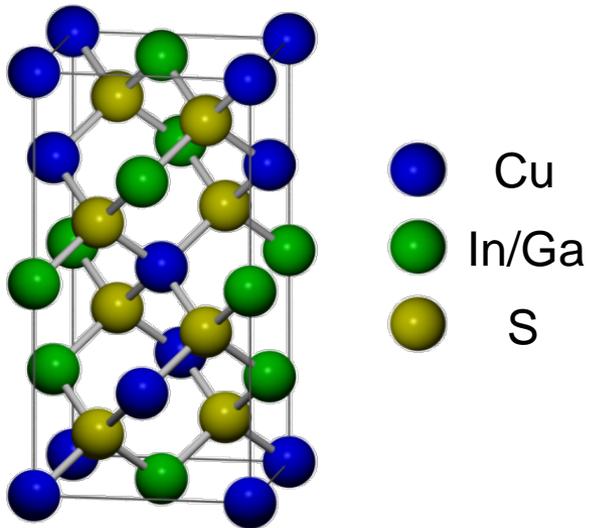


**However, a need to make thin film solar cells from earth abundant elements....**

# Thin Film Solar Cells From Earth Abundant



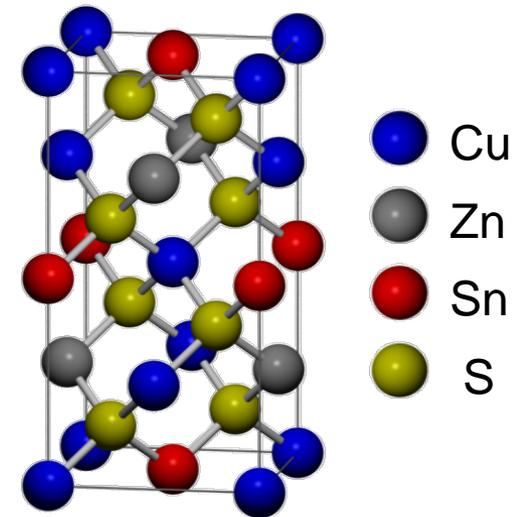
# CIGS



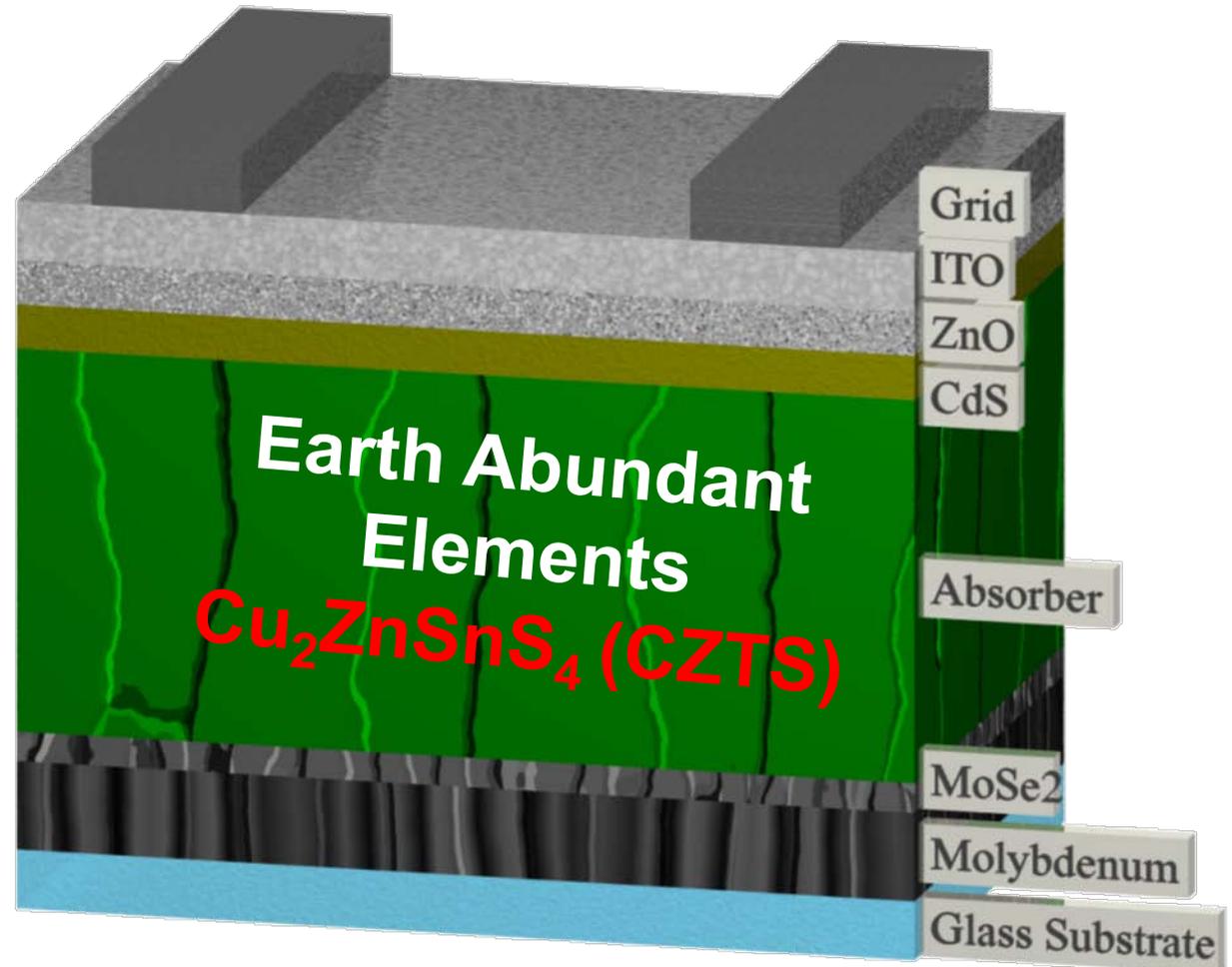
# CZTS



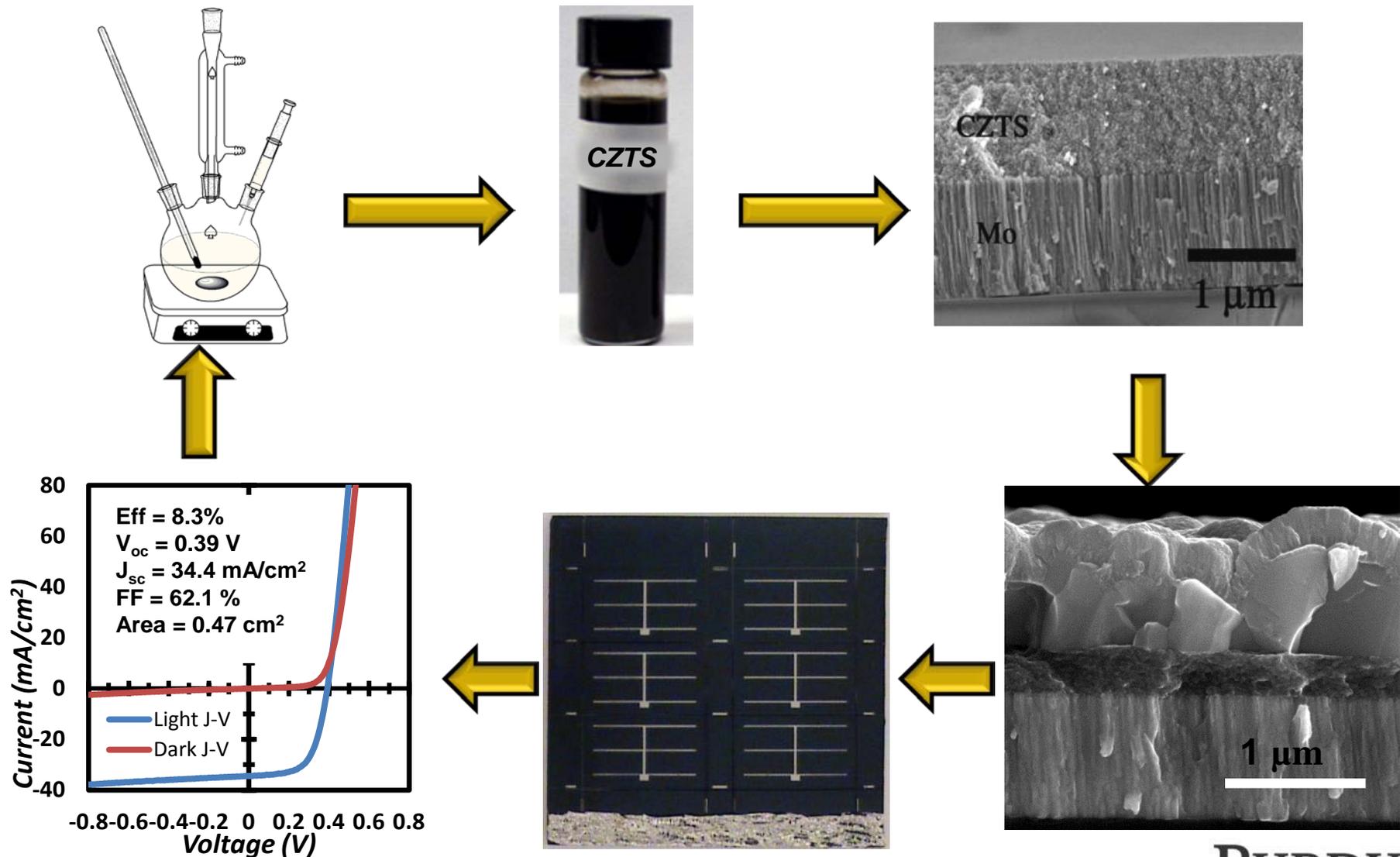
- Earth-Abundant Materials
- Similar (Kesterite) Crystal System



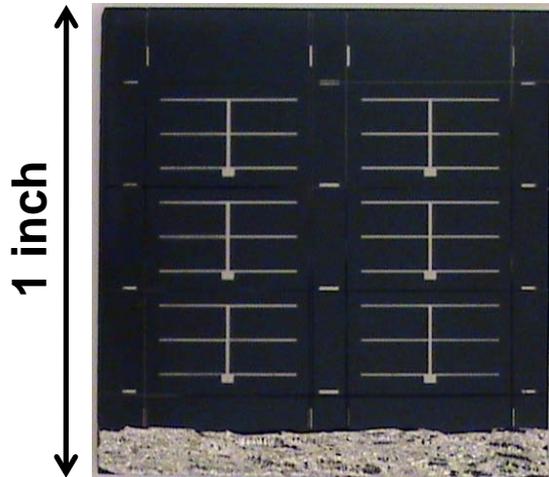
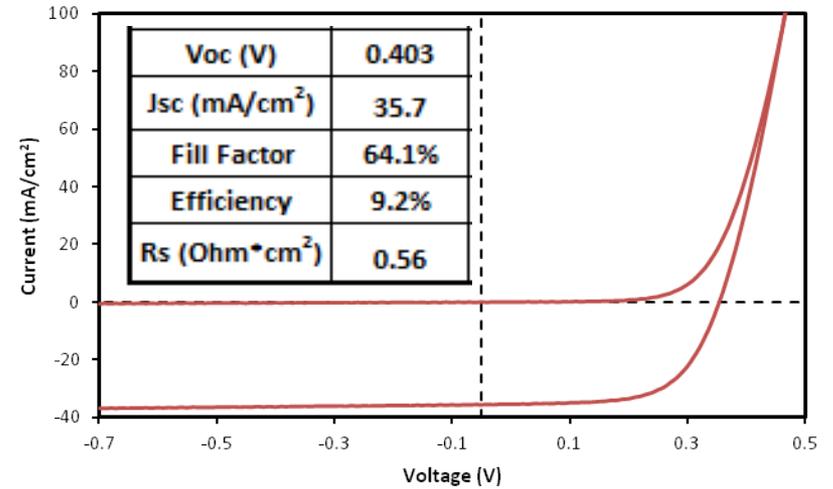
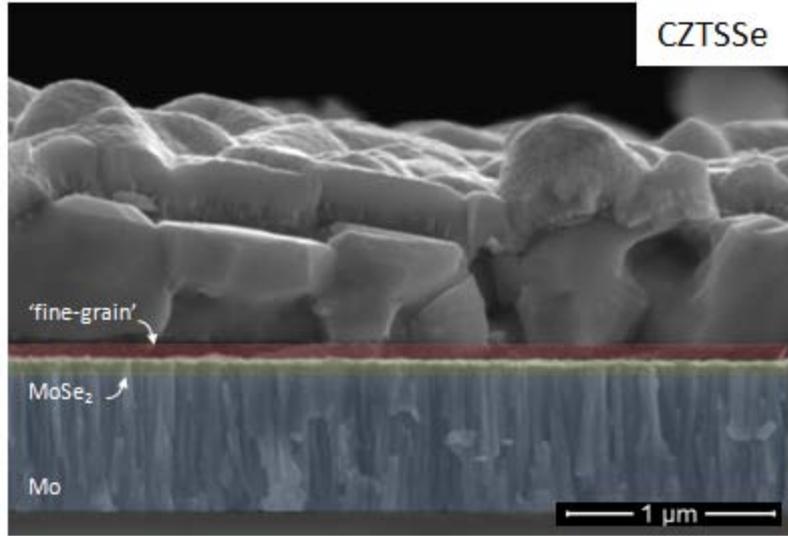
# Thin Film Solar Cells From Earth Abundant



# CZTSSe Liquid Deposition

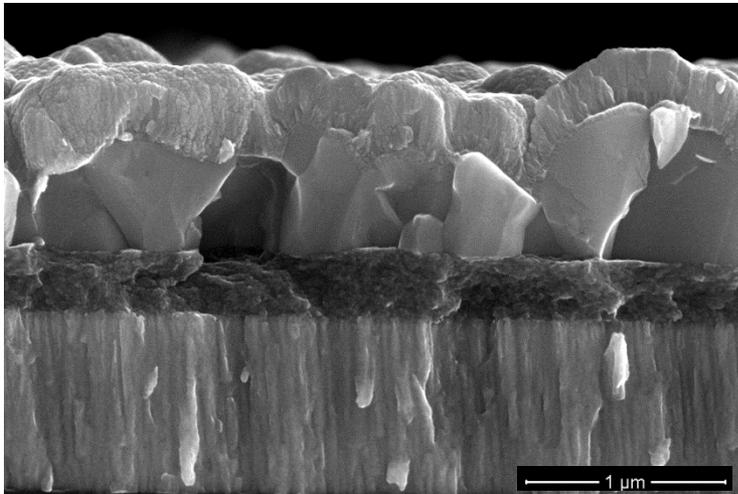


# CZTSSe from Nanocrystal Ink

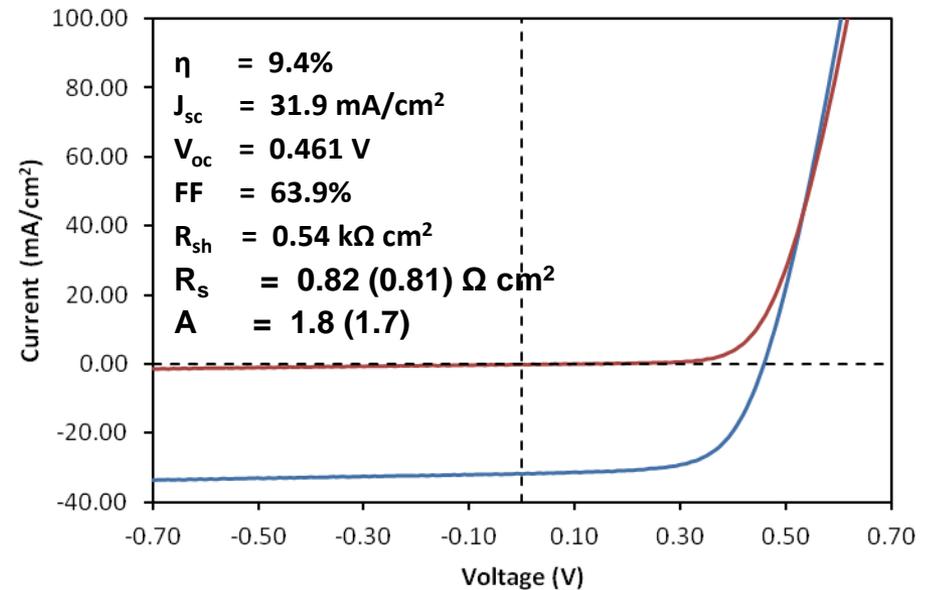


- Nanoparticle Optimization
- Sintering Optimization

# Band Gap Tailoring with partial Ge substitution for Sn



CZTGeSSe – 30% Ge



Reproducible results > 9% efficiency with 30% Ge-alloying

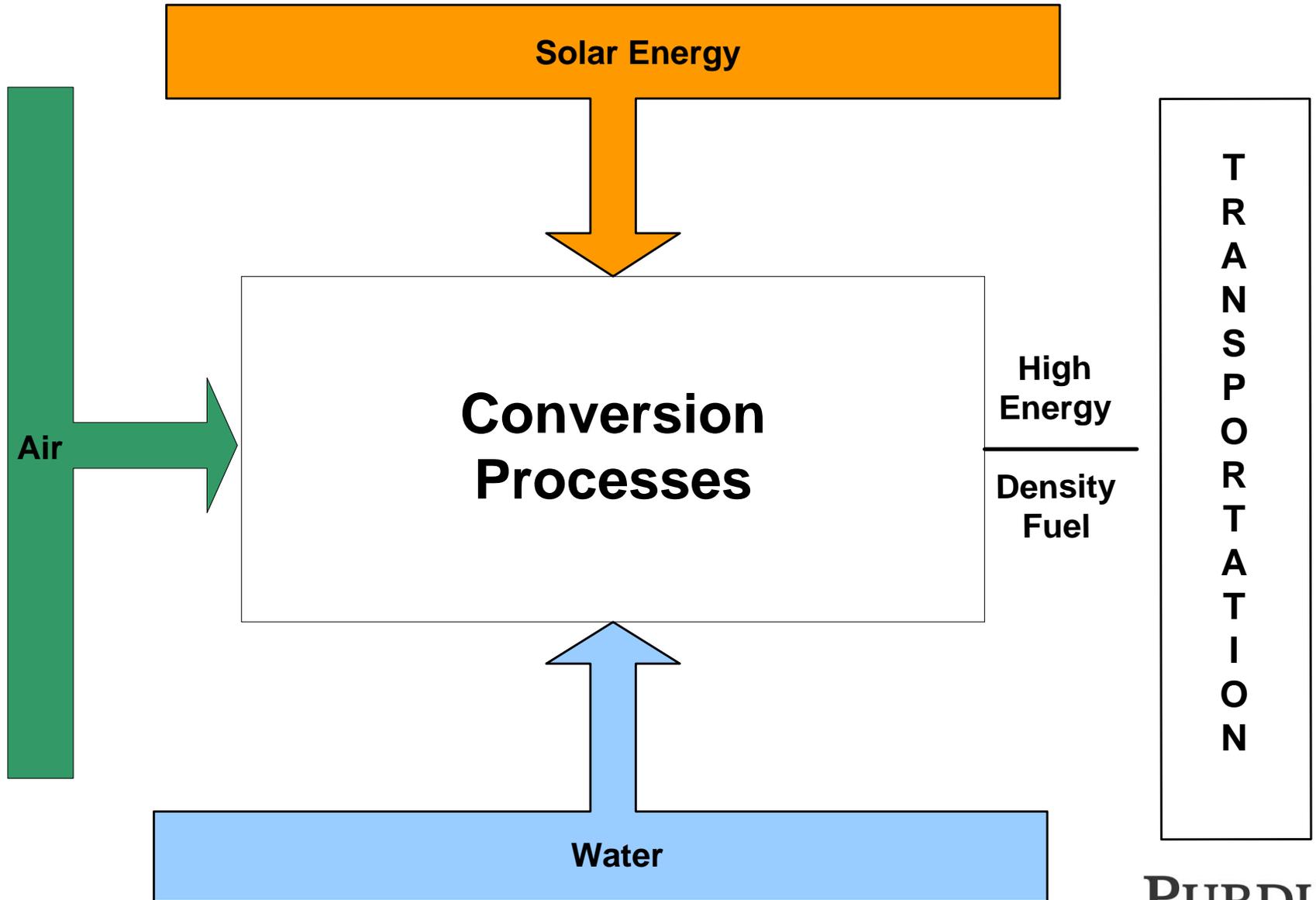
# Summary – Harnessing of Solar Energy: Nanocrystal Based Solar Cells

- Possible to make nanocrystal inks of the compound semiconductors.
- Proof-of-concept demonstrated for potentially low cost solar cells from nanocrystal inks.
- Kinetics of nanoparticle synthesis, insitu sintering of the absorber layer and optoelectronic characterization and modeling studies in progress to improve efficiency of these solar cells.

# A Three Part Presentation .....

1. Harnessing of Solar Energy -- Solar Cells from Nanocrystal Inks
- 2. Transformation of Solar Energy -- Energy System Analysis with Emphasis on Transportation Sector**
3. Storage of Solar Energy -- A Chemical Storage Cycle

... Of all the end uses most challenging is transportation

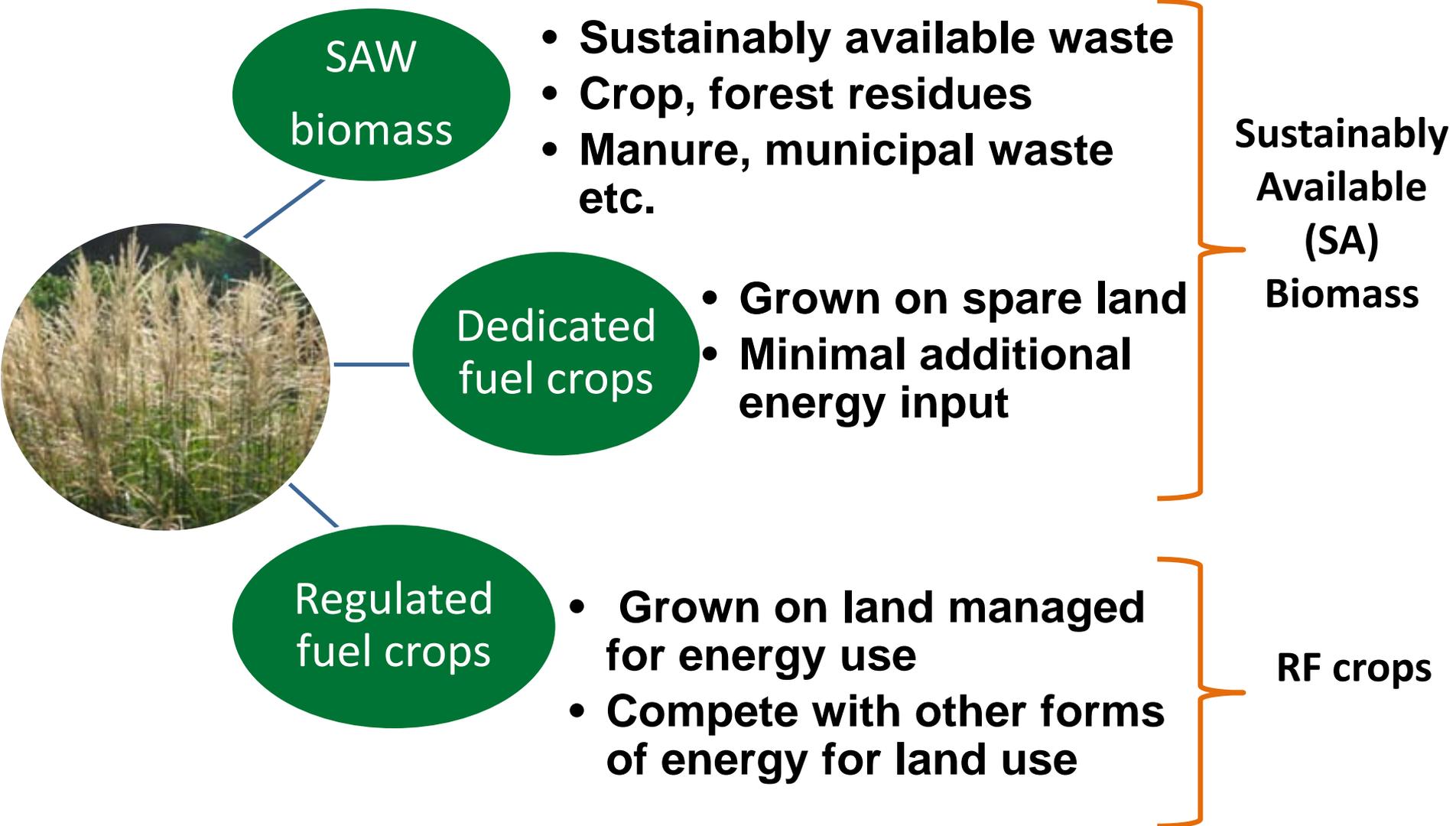


# High Energy Density Fuel from Renewable Resources

**An Obvious Choice is Use of Biomass for  
Liquid Hydrocarbon Fuel ....**

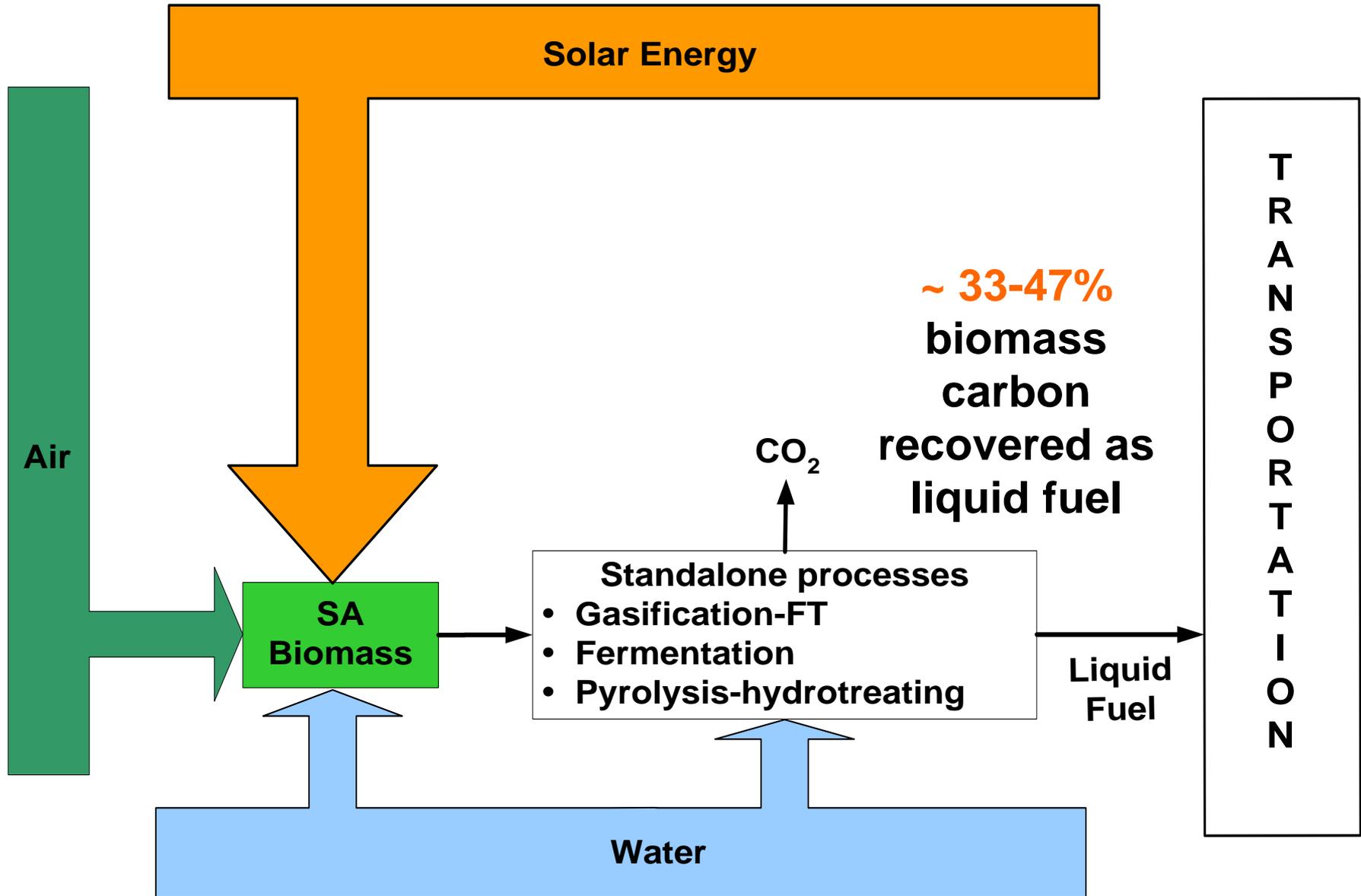
# Liquid fuels from biomass

# Biomass Resource Classification



# What are the process options of converting biomass to liquid fuel?

# Biomass -to-liquid fuel: carbon recovery



1. Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech.*, 2010

2. Agrawal and Singh, *Annual Rev. Chem. Bio. Eng.*, 2010

# Self-contained processes + SA biomass for US transportation

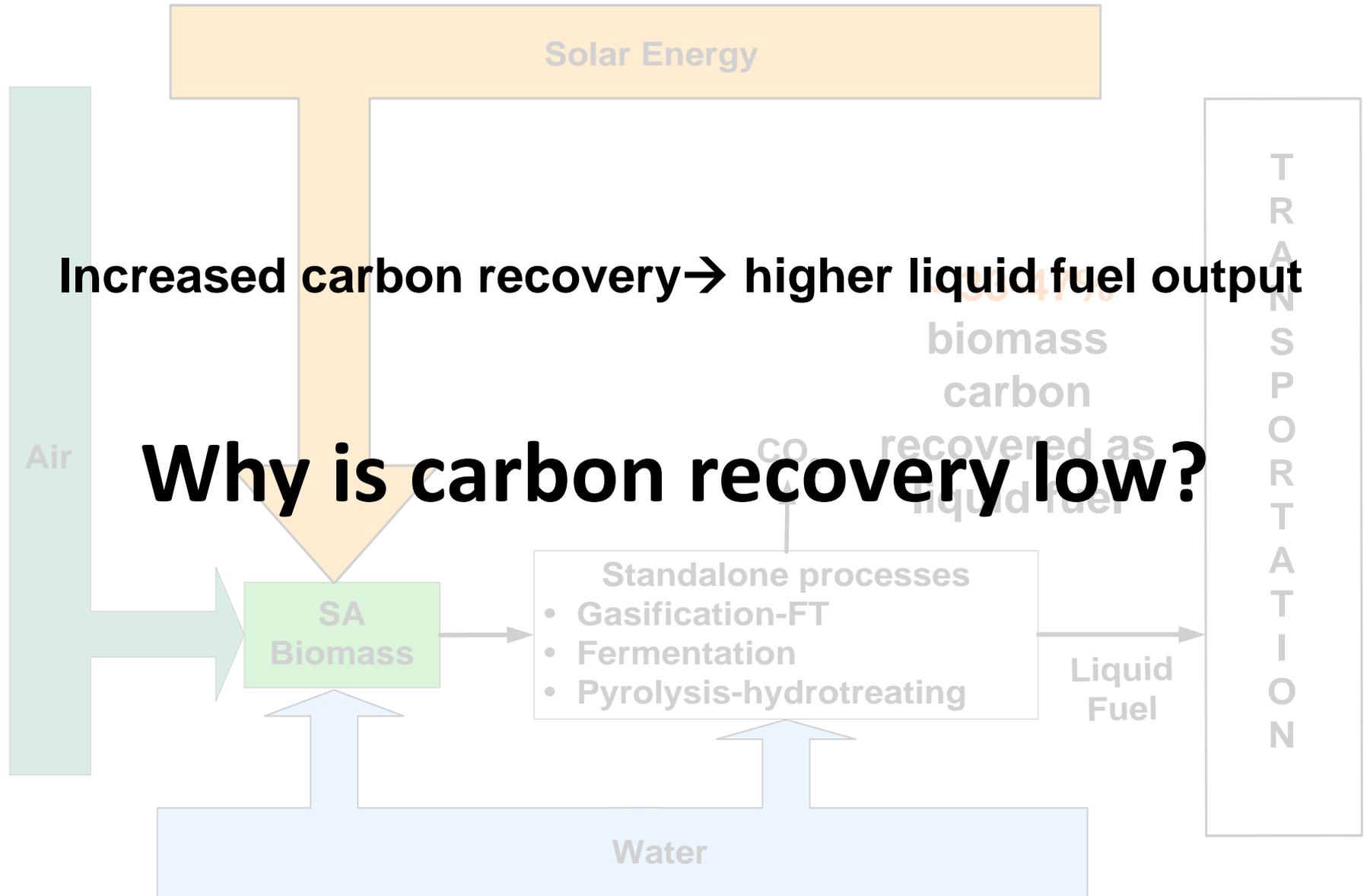
- SA biomass availability potential= 498 Million metric tons/yr<sup>1</sup>
- Transportation fuels use in the USA, 2007 =13.28 Mbbbl/day<sup>2</sup>

**21% (2.8 Mbbbl/day) of current US transportation demand produced using SA biomass with best self-contained process**

1. Liquid transportation fuels NRC report, 2010
2. Davis *et al.*, Transportation energy data book, 2009

**How do we increase liquid fuel from SA biomass?**

# Biomass -to-liquid fuel: carbon recovery



1. Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech.*, 2010

2. Agrawal and Singh, *Annual Rev. Chem. Bio. Eng.*, 2010

**High oxygen content in biomass**



**Energy per carbon atom in biomass is lower than the corresponding energy per carbon atom in high energy density fuels such as gasoline**

**Biomass  
~450 kJ/mol C**

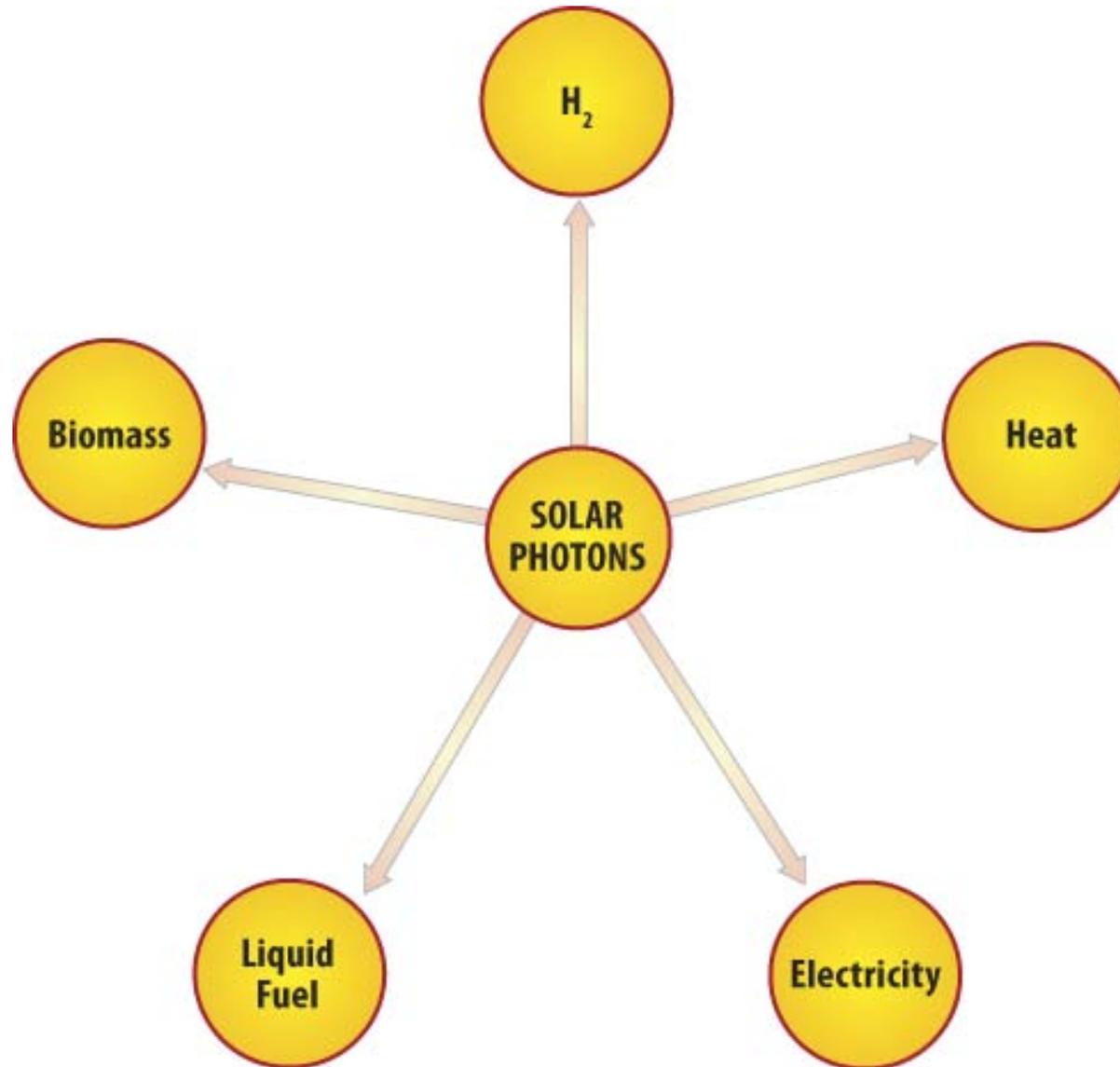
**Gasoline  
605 kJ/mol C**



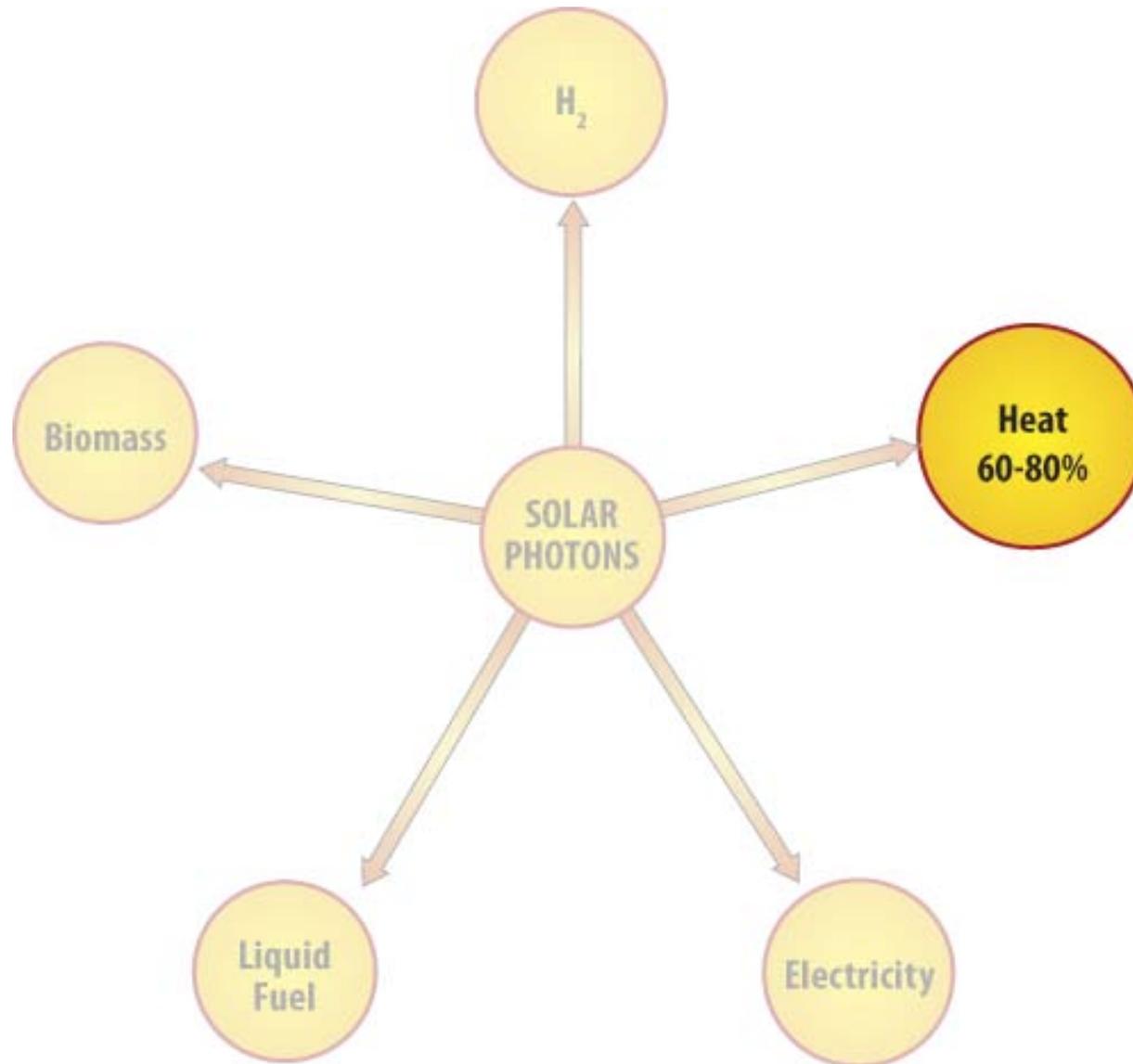
**Lower carbon recovery during conversion to high energy density liquid Fuel**

**Let us examine efficiencies at which supplemental forms of energy are recovered from Sunlight**

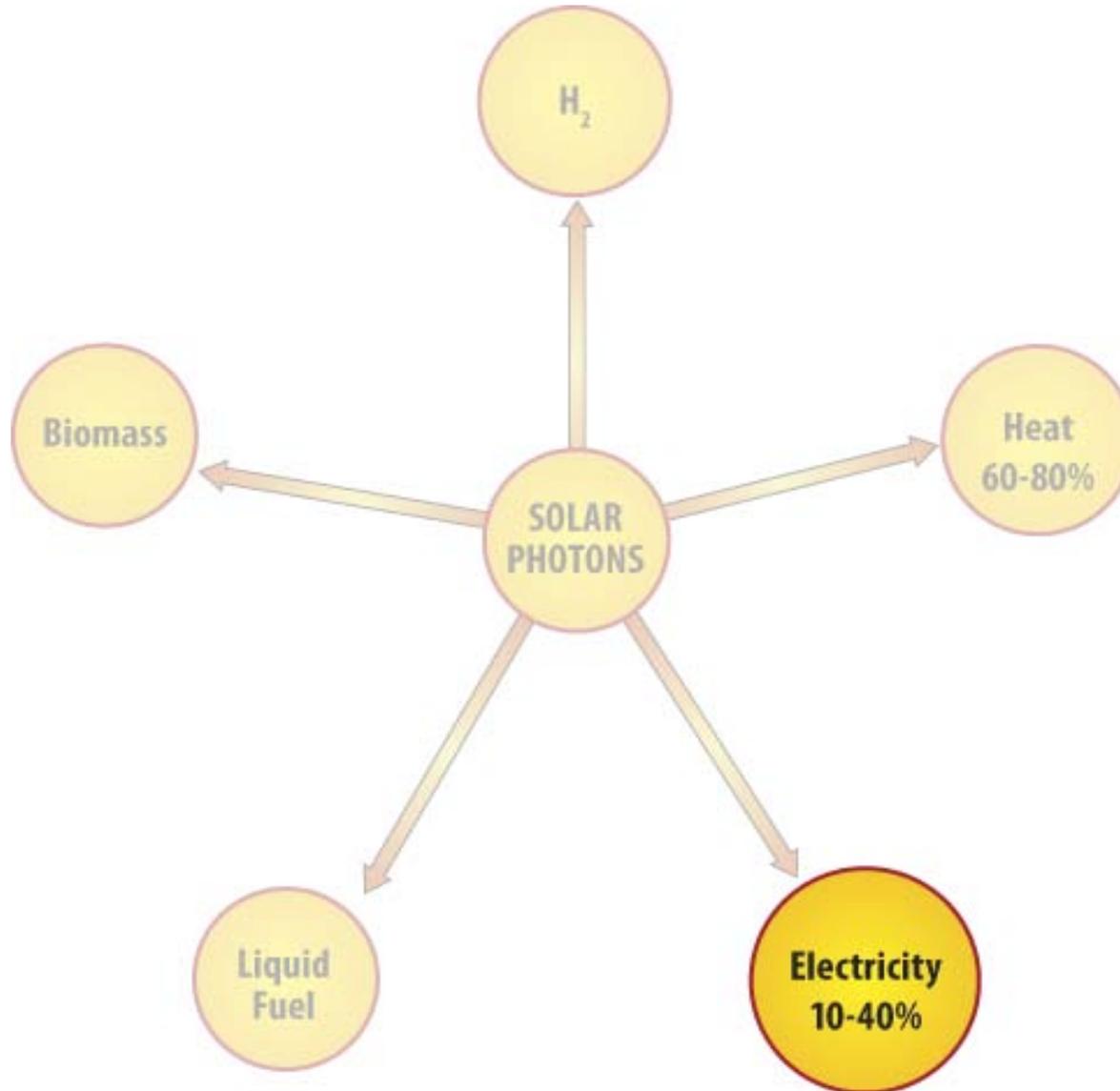
# Efficiencies of Solar Energy Recovery



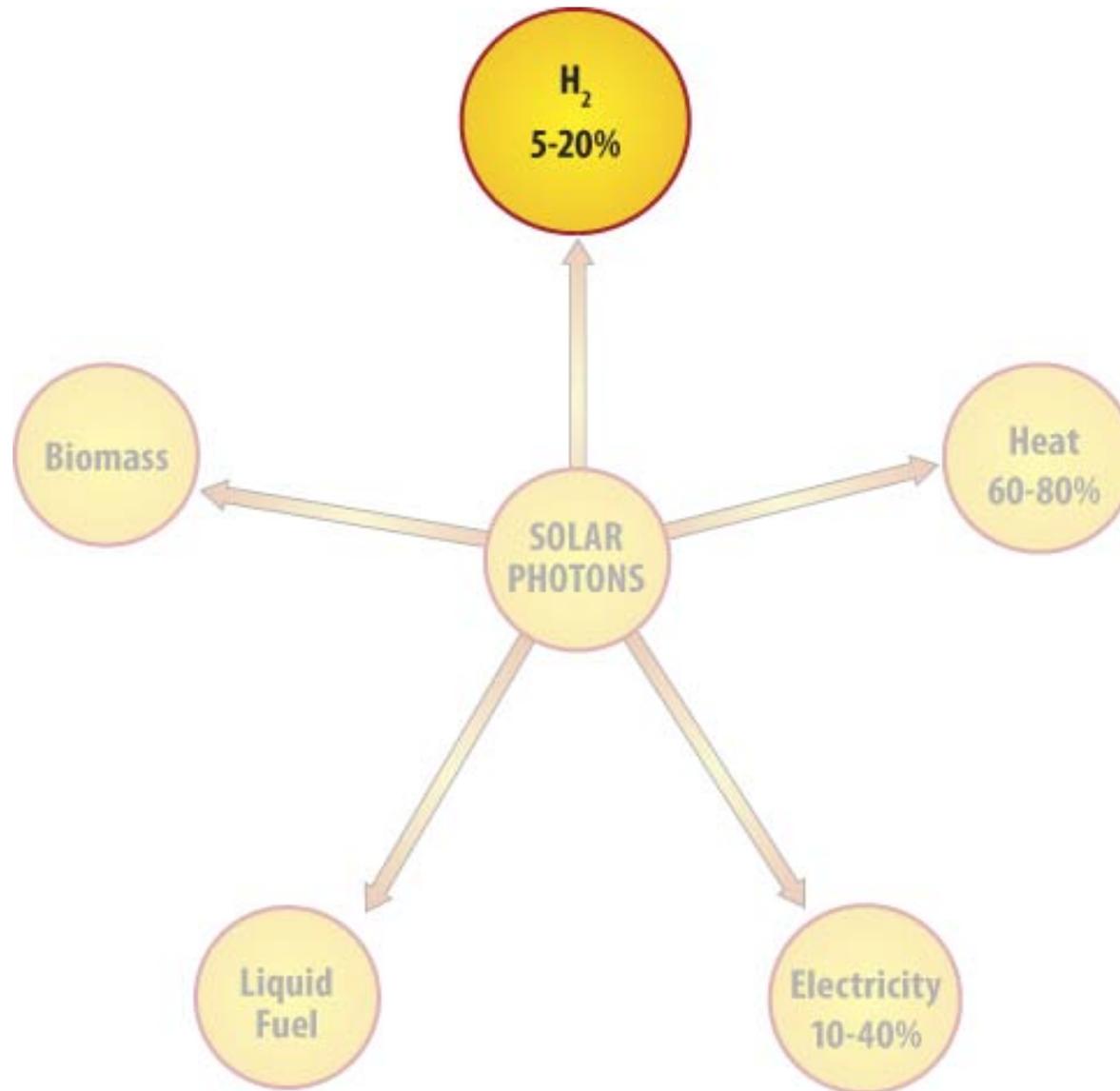
# Efficiencies of Solar Energy Recovery



# Efficiencies of Solar Energy Recovery



# Efficiencies of Solar Energy Recovery

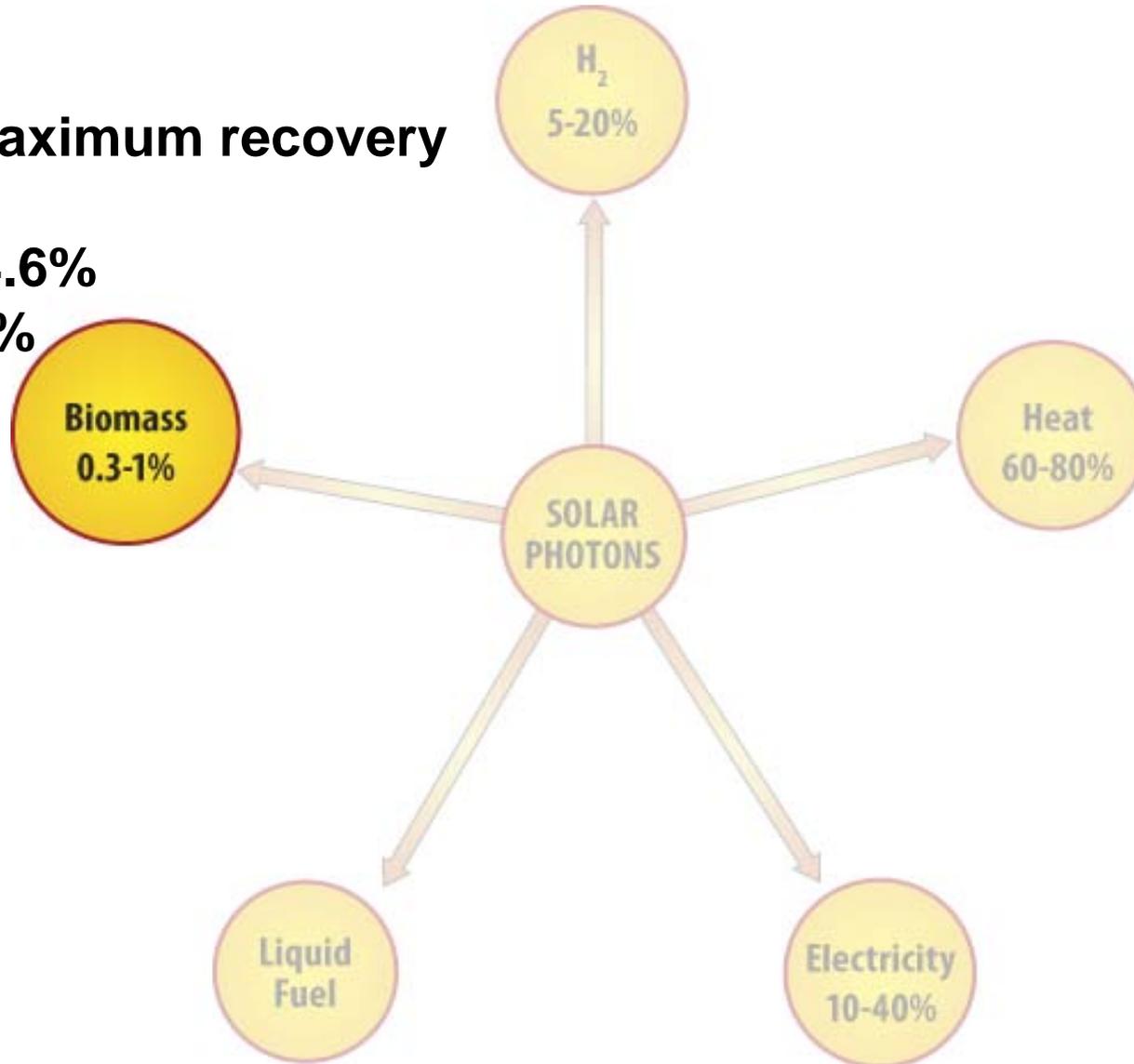


# Efficiencies of Solar Energy Recovery

Estimated maximum recovery efficiency <sup>1</sup>

•C3 crops= 4.6%

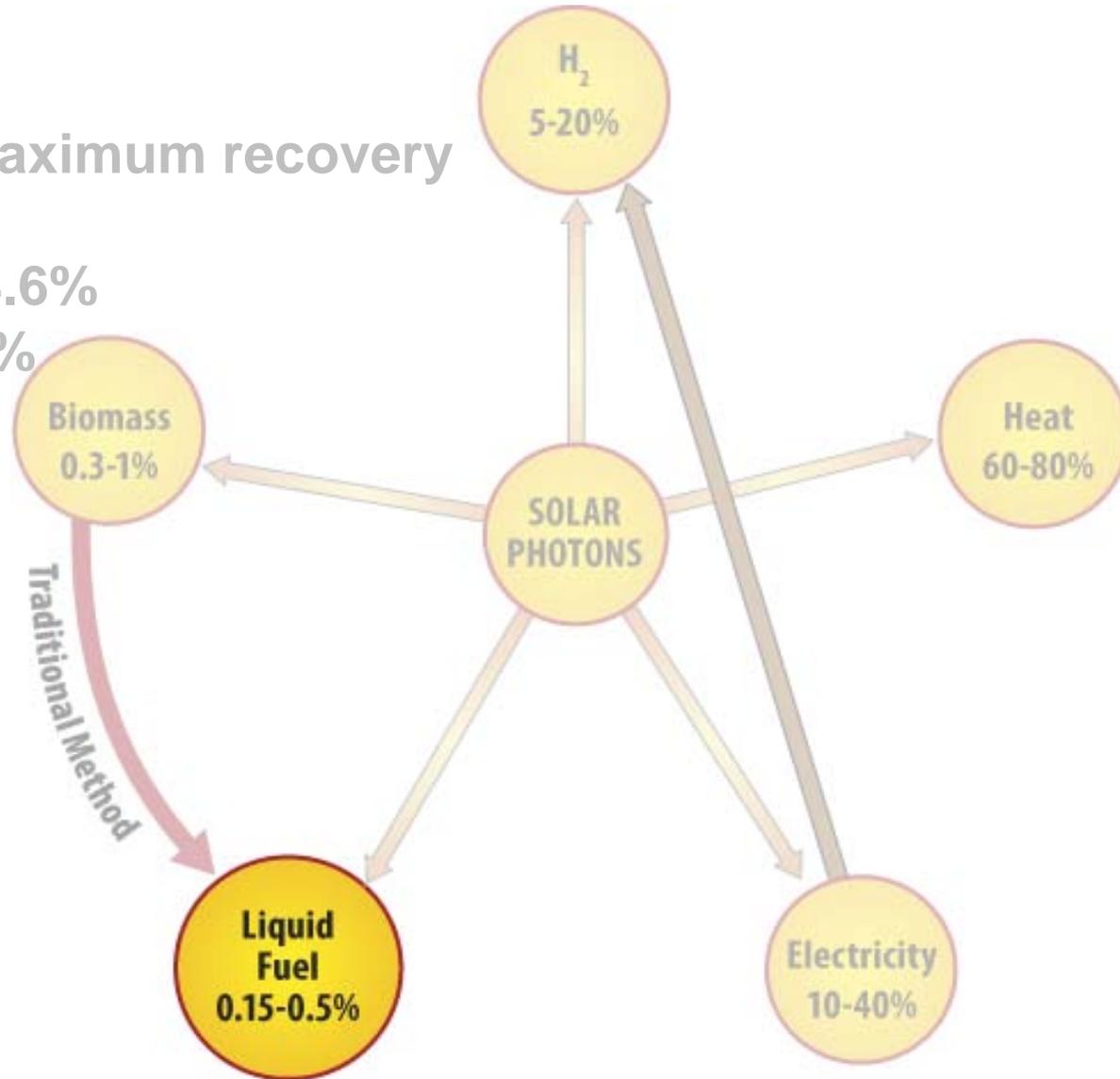
•C4 crops=6%



# Efficiencies of Solar Energy Recovery

Estimated maximum recovery efficiency <sup>1</sup>

- C3 crops= 4.6%
- C4 crops=6%



## An Observation

**Biomass Should be Viewed as a Source of Carbon  
and  
NOT as a Primary Source of Energy**

## **An Observation**

**Biomass Should be Viewed as a Source of Carbon  
and  
NOT as a Primary Source of Energy**

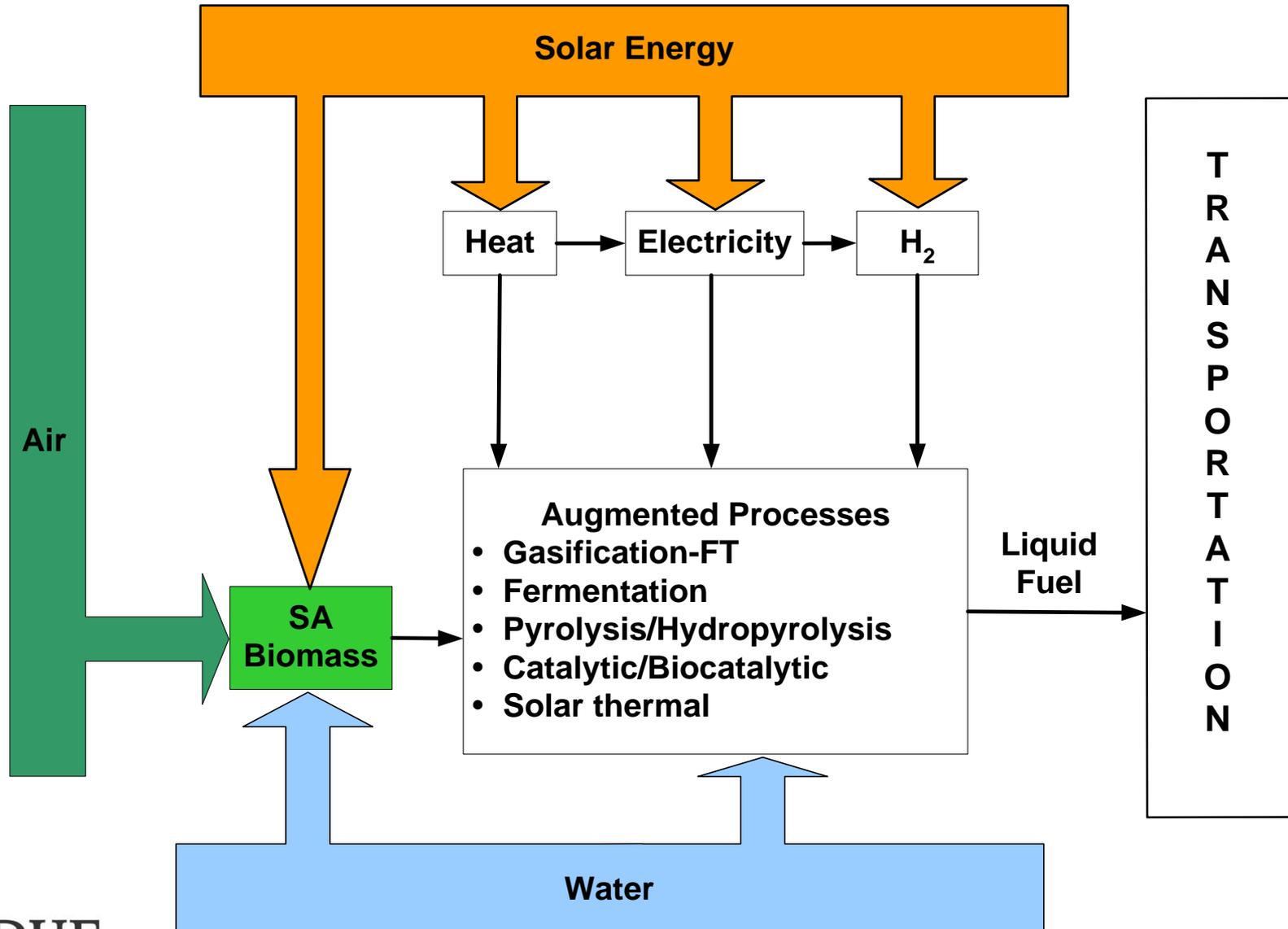
**Challenge & Opportunity:**

**Design New Processes to increase biomass carbon recovery**

# Available forms of supplementary energy to increase biofuel yield

- Heat
- Electricity
- H<sub>2</sub>

# Augmented Processes : up to 100% biomass carbon recoverable as liquid fuel



# Augmented processes using H<sub>2</sub>

# 100% SA biomass carbon recovery for US transportation

- SA biomass availability potential= 498 Million metric tons/yr<sup>1</sup>
- Transportation fuels use in the US, 2007 =13.28 Mbbbl/day<sup>2</sup>

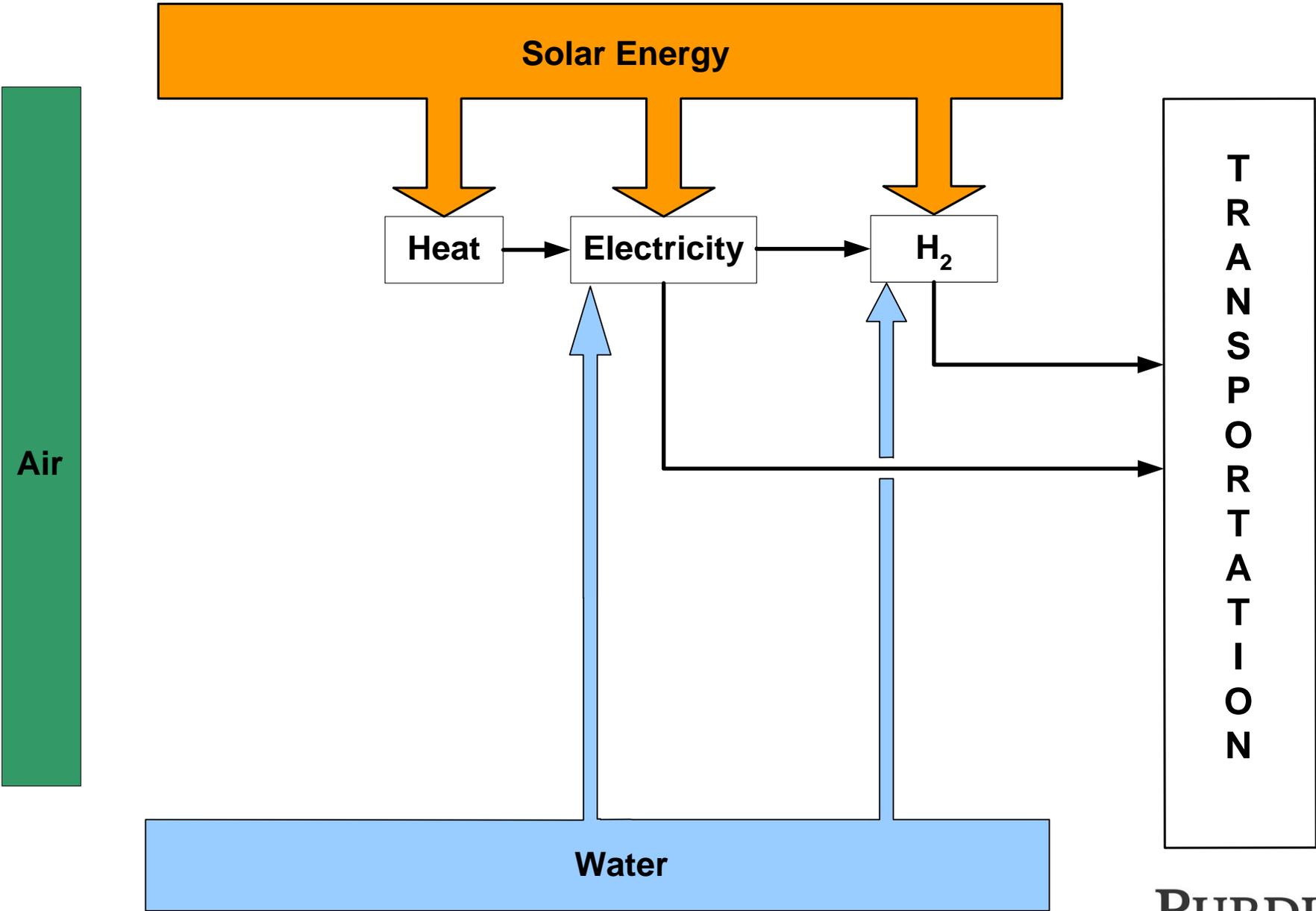
47% (6.2 Mbbbl/day) of current US transportation demand produced using SA biomass with H<sub>2</sub>CAR process

1. Liquid transportation fuels NRC report, 2010
  2. Davis *et al.*, Transportation energy data book, 2009
- H<sub>2</sub>CAR estimated yield: 329 ethanol-gallon-equivalent/ton

**Still >50% of deficit liquid fuel demand exists**

**How can we harness incident solar energy  
efficiently to meet the demand?**

# Use other efficient secondary energy forms from Sun



# Use other efficient secondary energy forms from Sun

- Electricity via PHEVs for light duty vehicles (LDV)
- H<sub>2</sub> for Fuel Cell Vehicles

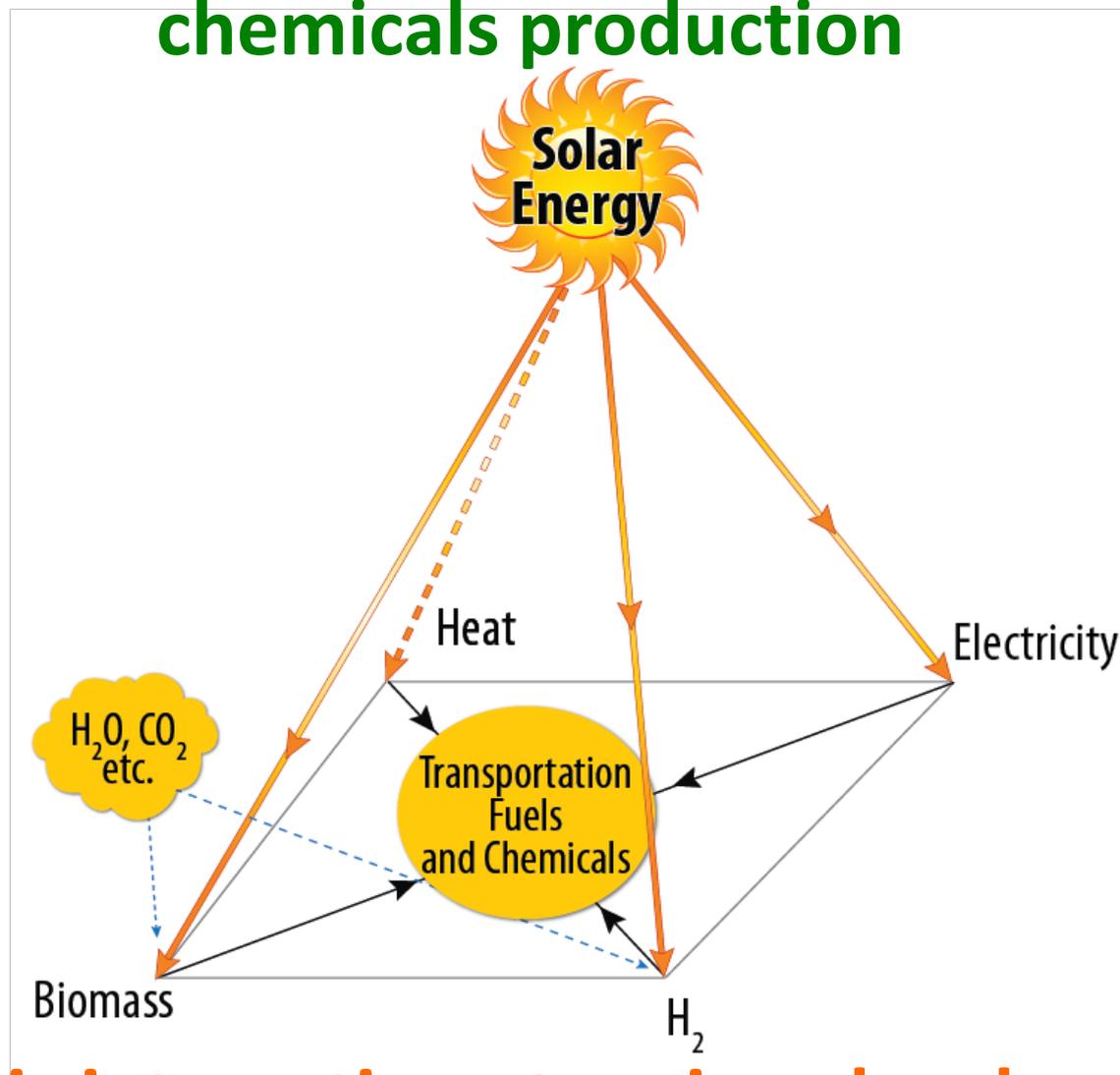
# Use of PHEVs + Augmented processes (H<sub>2</sub>CAR)

- SA biomass availability potential= 498 Million metric tons/yr<sup>1</sup>
- Transportation fuels use in the US, 2007 =13.28 Mbbl/day<sup>2</sup>
- Liquid fuel produced from SA biomass = 6.2 Mbbl/day
- Oil potentially displaced by PHEV40 = 5.5 Mbbl/day<sup>3</sup>

**88.1% (11.7 Mbbl/day equivalent) of current US transportation demand could now be met**

1. Liquid transportation fuels NRC report, 2010
2. Davis *et al.*, Transportation energy data book, 2009
3. Parks, Denholm and Markel, *NREL/TP-640-41410*, 2007

# Systems analysis of the transportation sector and chemicals production



**Synergistic integration at various levels needed!**

# **Summary – Transformation of solar Energy:**

## **Analysis of Energy System**

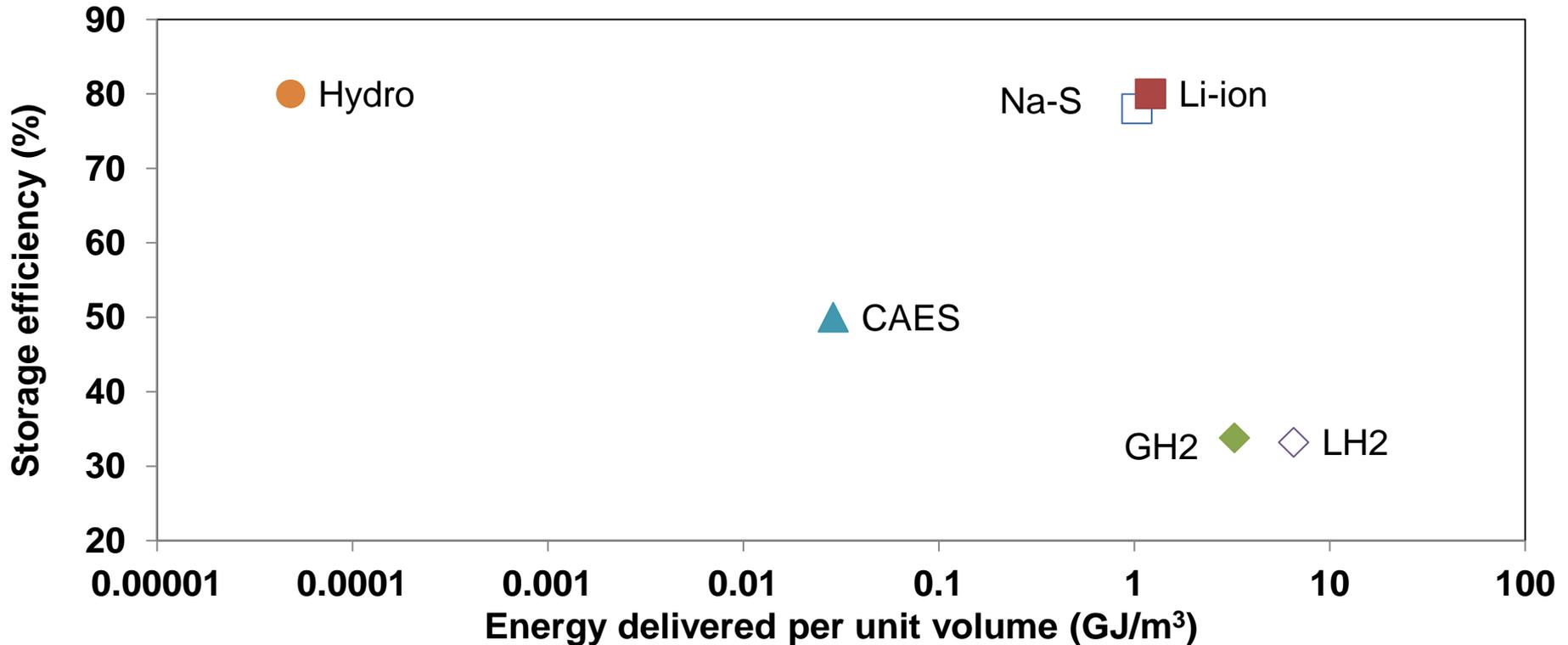
- **Energy Systems Analysis is important – it provides valuable insights.**
- **Must develop efficient and cost effective solutions for a world driven by renewable energy.**
- **Must provide solutions for transition from fossil to renewable energy**
- **Energy Systems Analysis is Fun!**

# A Three Part Presentation .....

1. Harnessing of Solar Energy -- Solar Cells from Nanocrystal Inks
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3. **Storage** of Solar Energy -- A Chemical Storage Cycle

# GWh level Electrical Energy Storage

# Some energy storage options

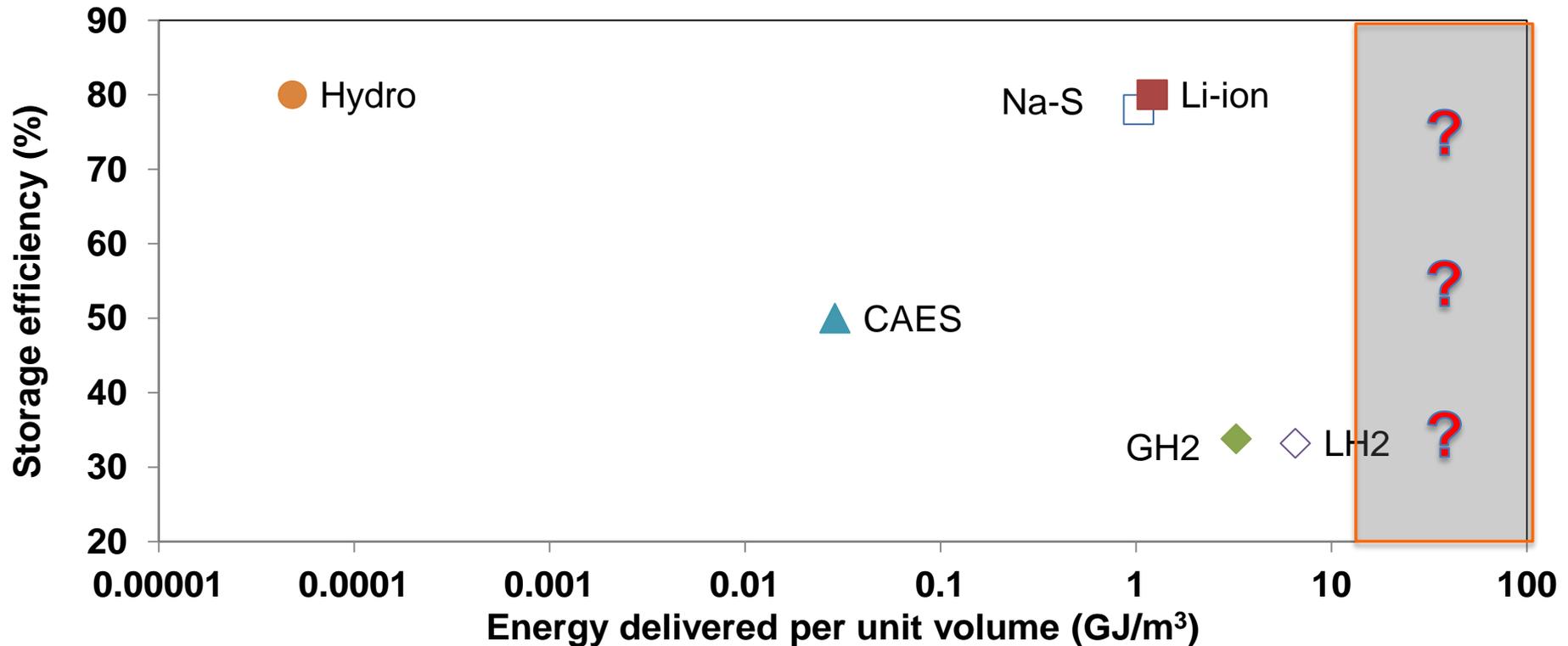


**Need- high energy density and storage efficient solutions!**

Reference: EPRI report on Storage Technologies, 2010

Hydro= pumped hydroelectric power, CAES= compressed air energy storage

# Carbon fuels for energy storage

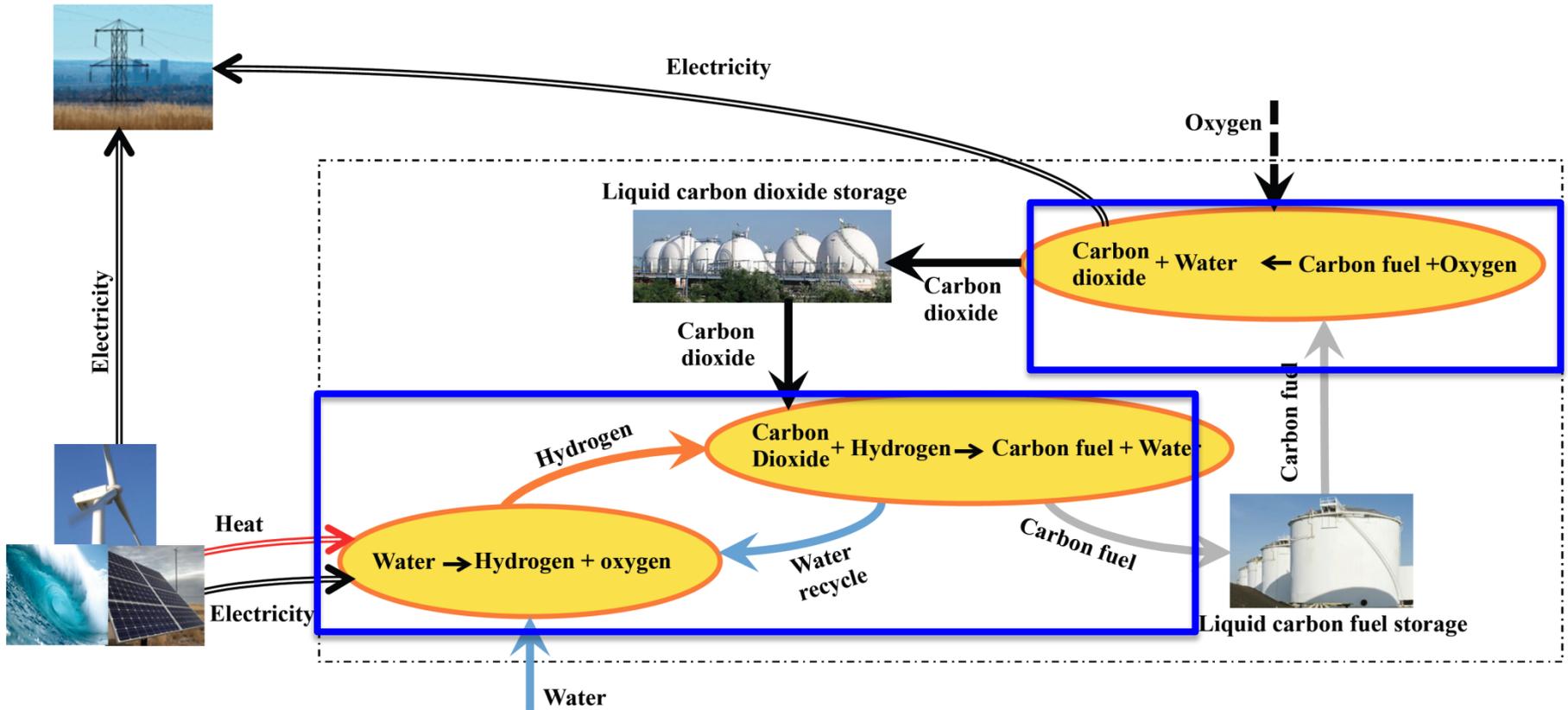


- Store as liquid to minimize volumes
- Avoid handling large volume of pressurized gas

Reference: EPRI report on Storage Technologies, 2010

Hydro= pumped hydroelectric power, CAES= compressed air energy storage

# Closed carbon cycle for energy storage liquid CO<sub>2</sub> ↔ liquid fuel



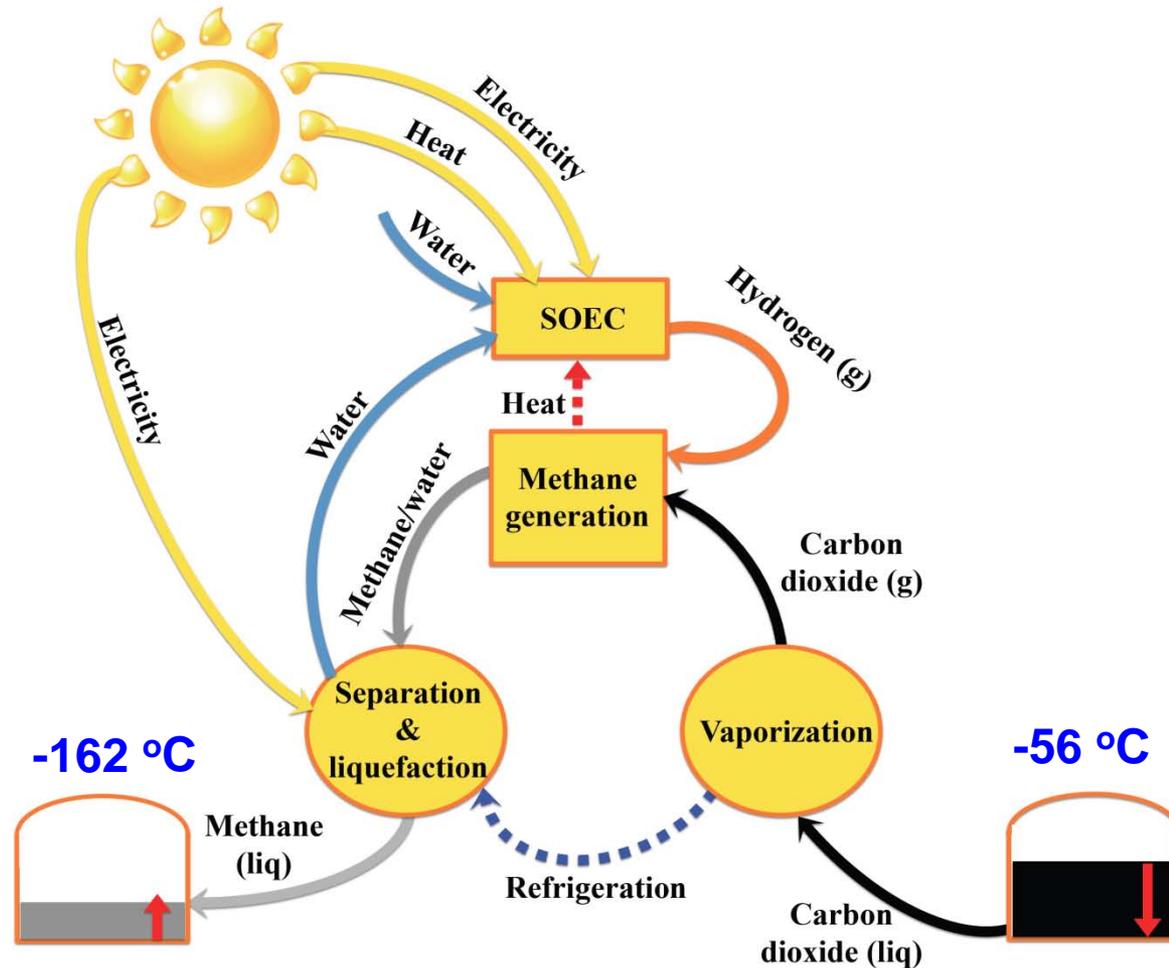
**Very little external carbon required as make up!**

# Among carbon fuels.. ... consider the use of methane

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

- **CH<sub>4</sub> → highest energy content per carbon**
- **Liquefaction energy penalty (-162 °C)**

# Methane-cycle (Storage mode)

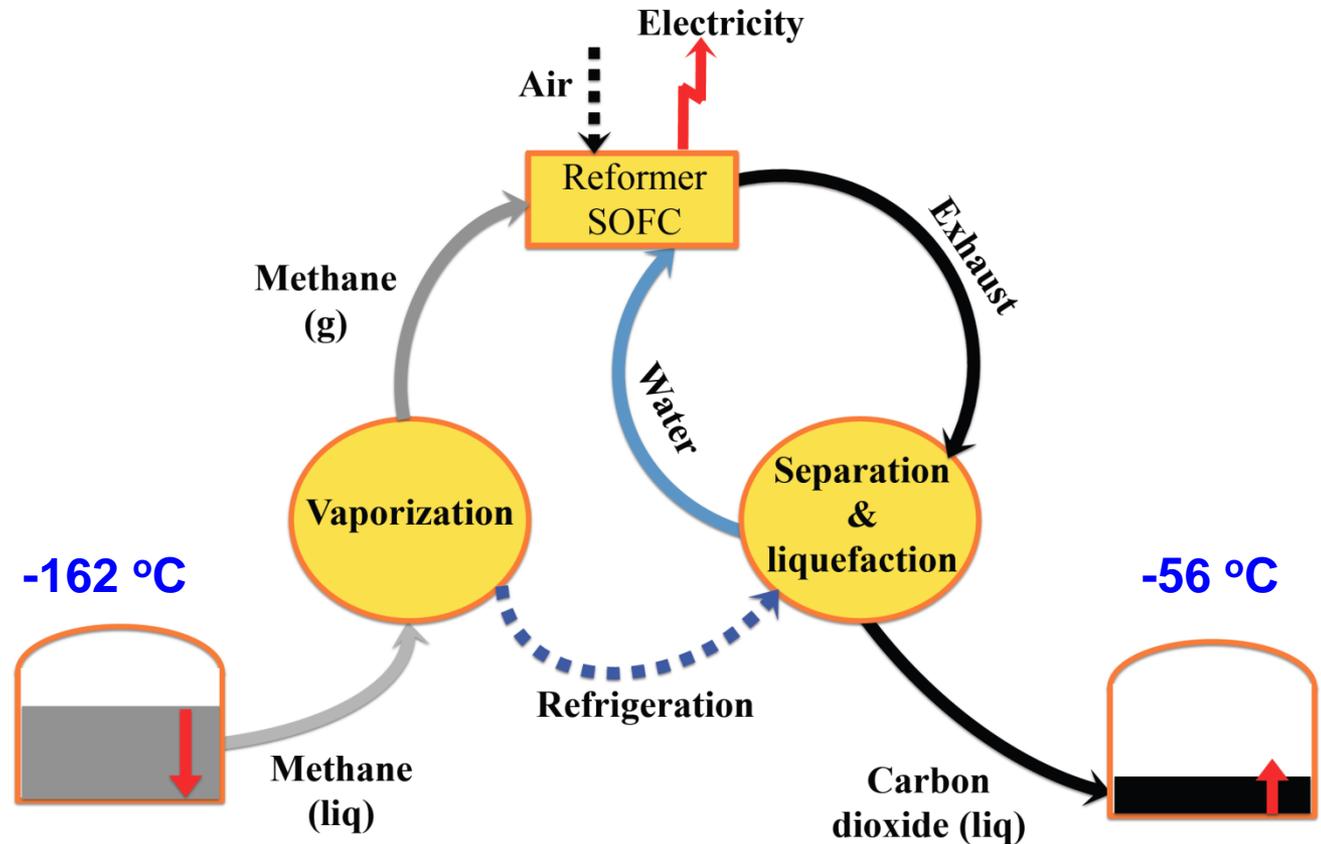


Minimize solar energy penalty of  $\text{CH}_4$  liquefaction

SOEC=Solid Oxide Electrolysis

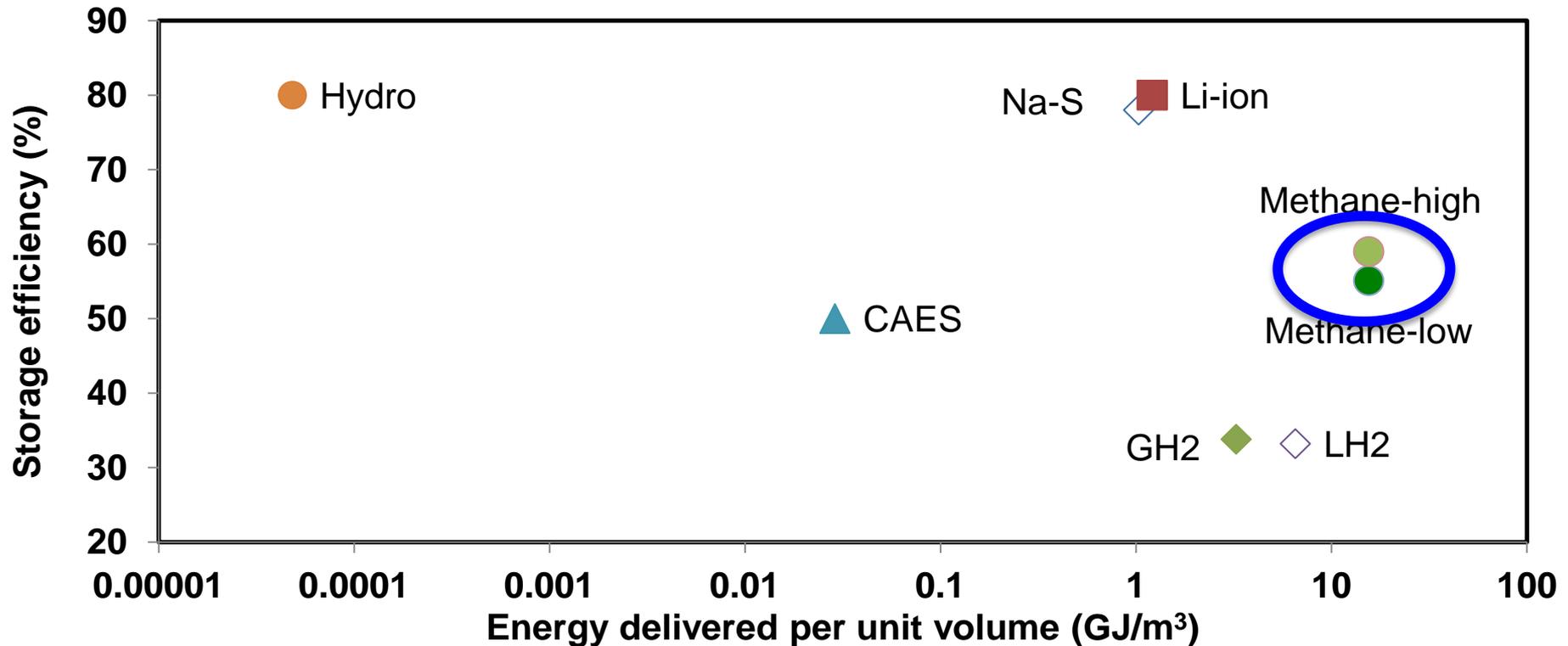
# Methane-cycle (Delivery mode)

**Solid Oxide  
Fuel Cell for  
electricity**



**No additional power consumed for CO<sub>2</sub> capture and liquefaction!**

# Methane storage simulation results



- **Efficiency:** Methane superior to H<sub>2</sub>
- **Volume:** Methane superior to other options

Simulations carried out using Aspen Plus

# Summary – Storage of solar Energy: A Chemical Storage Cycle

- High storage efficiency cycles using methane and carbon dioxide storage.
- Other chemicals should also be explored.

# In Conclusion...

- **Solar Economy is a must for long term existence of human civilization.**
- **We will have to learn to harness, transform and store solar energy on a time scale of use.**
- **Need for a careful systems analysis to identify synergies and create efficient conversion and use technologies.**

# Overall Summary

**“Great time to be a Scientist & an Engineer”**

# Acknowledgments (Current Collaborators)

## Energy Systems Analysis and Distillation:

**Prof. Mohit Tawarmalani** (Krannert School of Management)

## Biomass To Liquid Fuel:

**Prof. Nick Delgass** (Chemical Engineering)

**Prof. Fabio Ribeiro** (Chemical Engineering)

**Prof. Maureen McCann** (Biological Sciences Molecular Biosciences)

**Prof. Nick Carpita** (Agriculture- Botany and Plant Pathology)

**Prof. Hilikka Kenttämäa** (Chemistry)

**Prof. Mahdi Abou-omar** (chemistry)

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**Dr. Eric Stach** (Brookhaven National Lab)

**Dr. Hans Werner Schock and Thomas Unold** (HZB, Berlin)

# Funding Acknowledgment

**NSF Solar Economy IGERT**

**DOE Distillation**

**DOE Liquid Fuels**

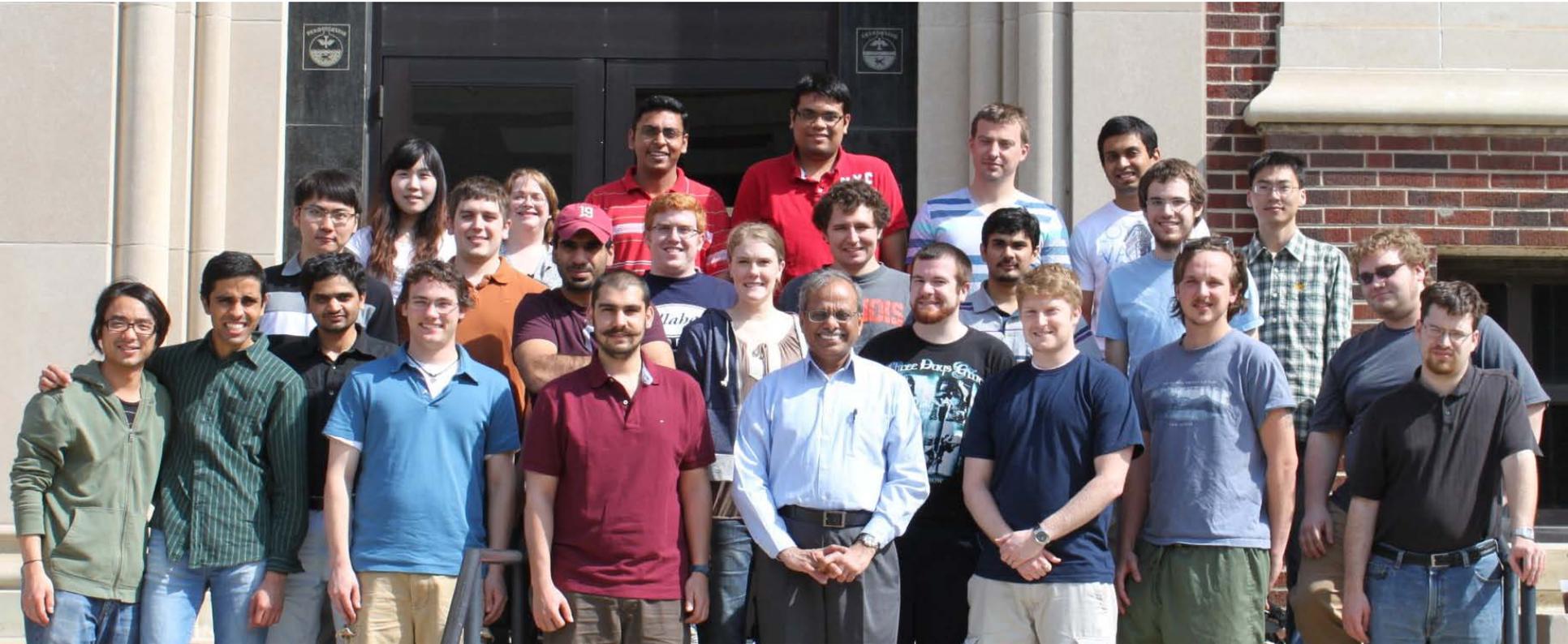
**DOE C3Bio EFRC**

**AFSOR Liquid Fuel**

**NSF EFRI**

**DOE SunShot**

# The Research Team

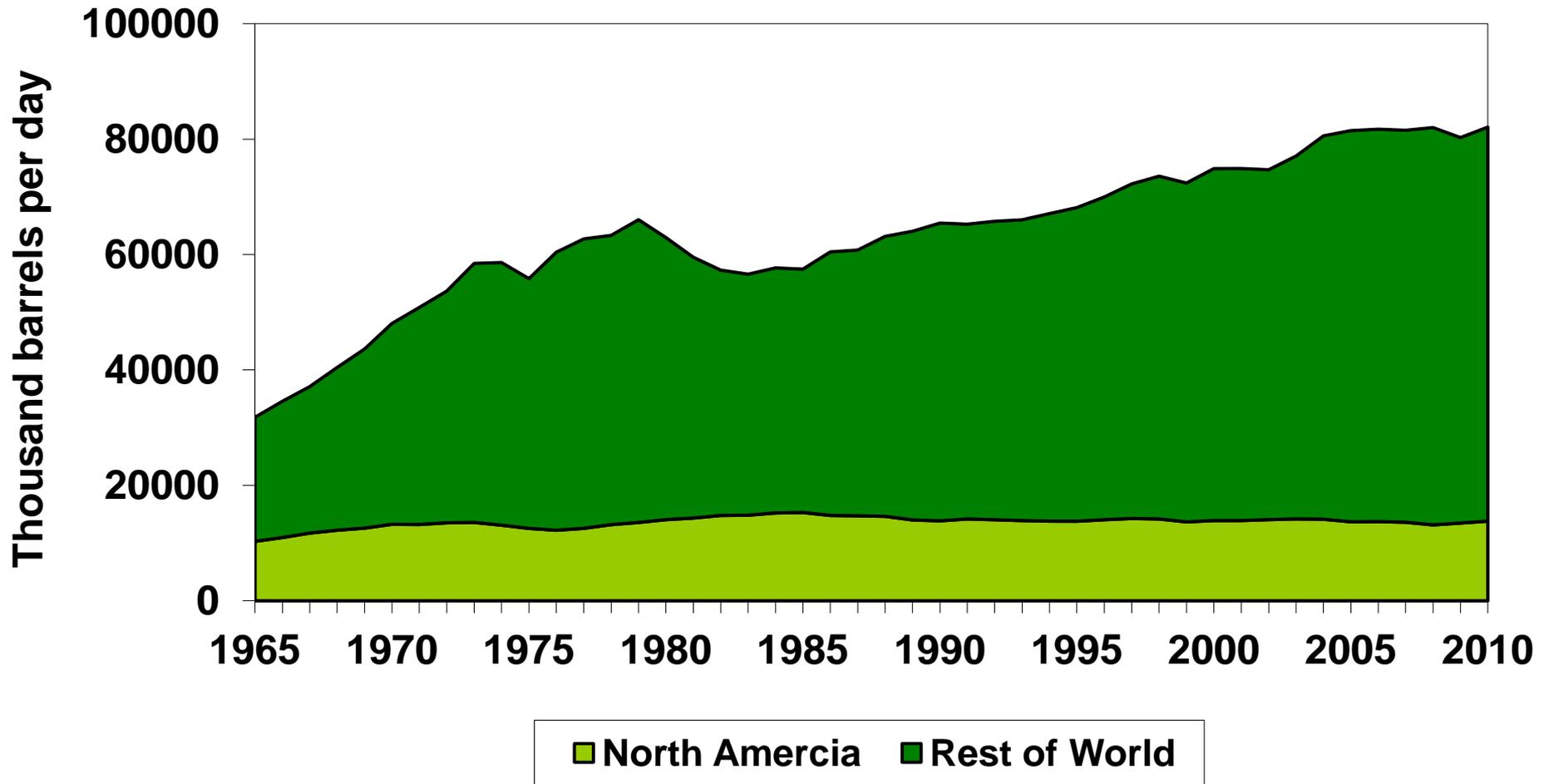


An aerial photograph of the Purdue University campus. The image shows a large, multi-story brick building complex surrounding a central quad. The quad features a large, white, abstract sculpture in the center, surrounded by green lawns and paved walkways. The text "...Thank you" is overlaid in blue on the central part of the image.

....Thank you

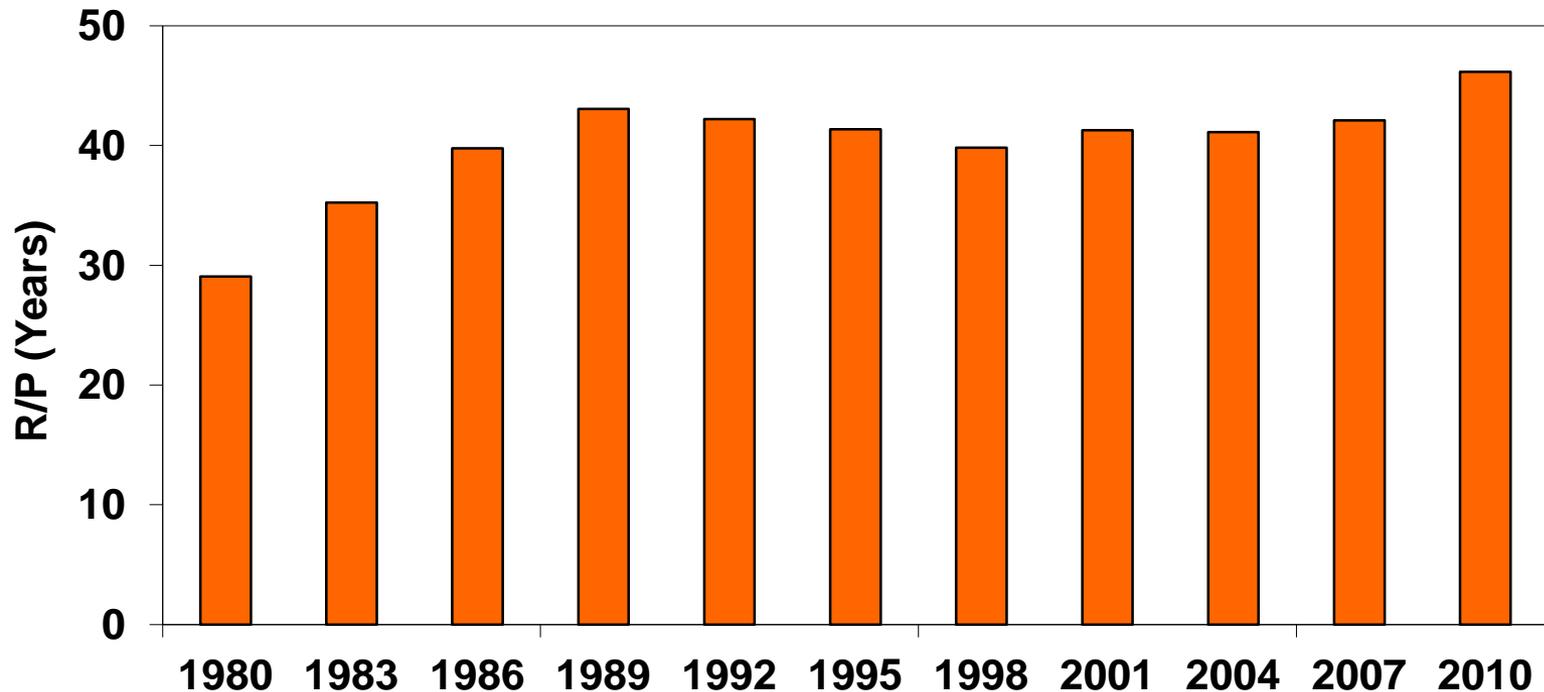
# Availability of Primary Energy Sources

# World Oil Production



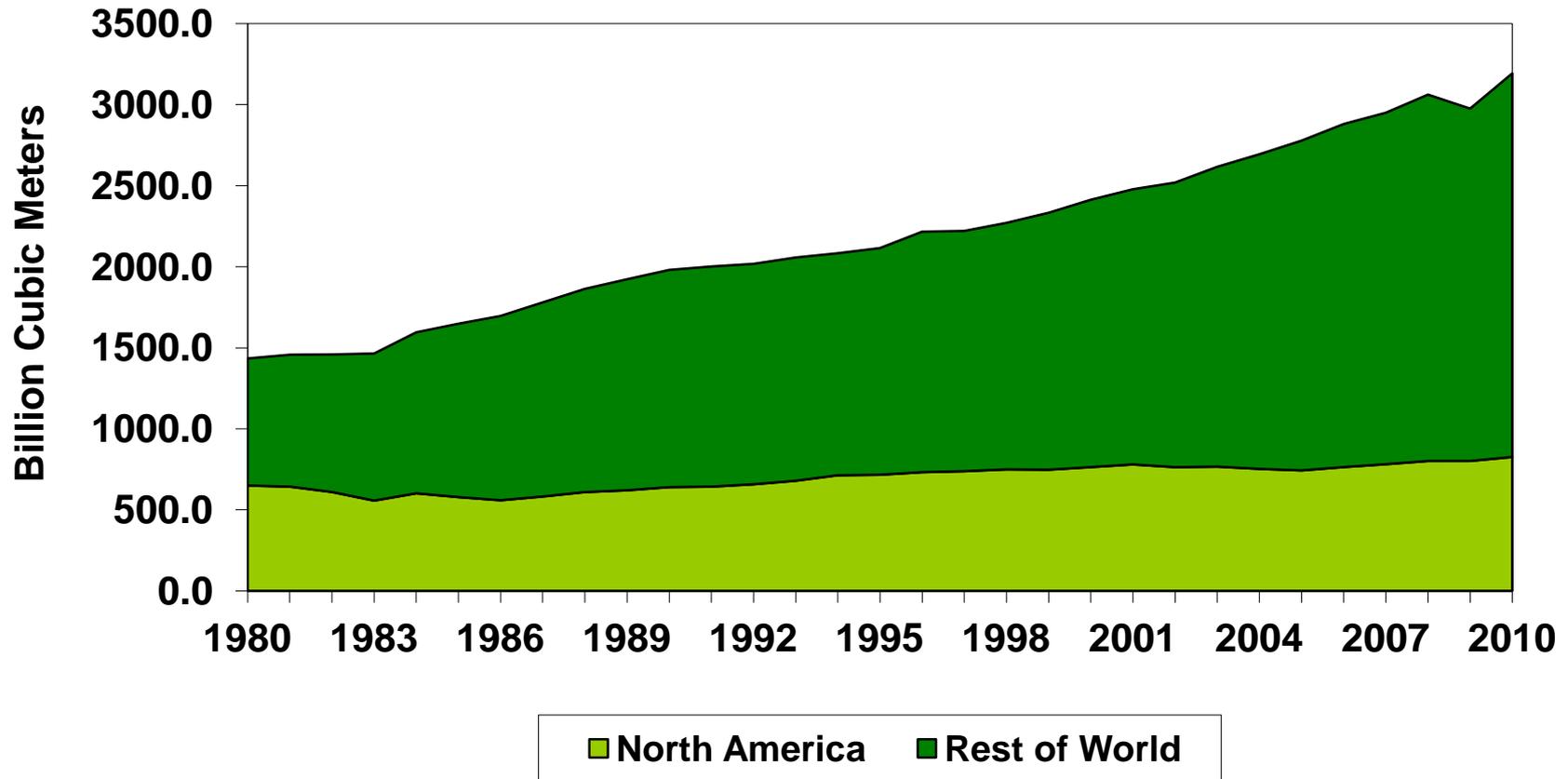
**Total proven conventional oil reserve = 1383 billion bbl**

# World Oil Reserves-to-Production (R/P) Ratios



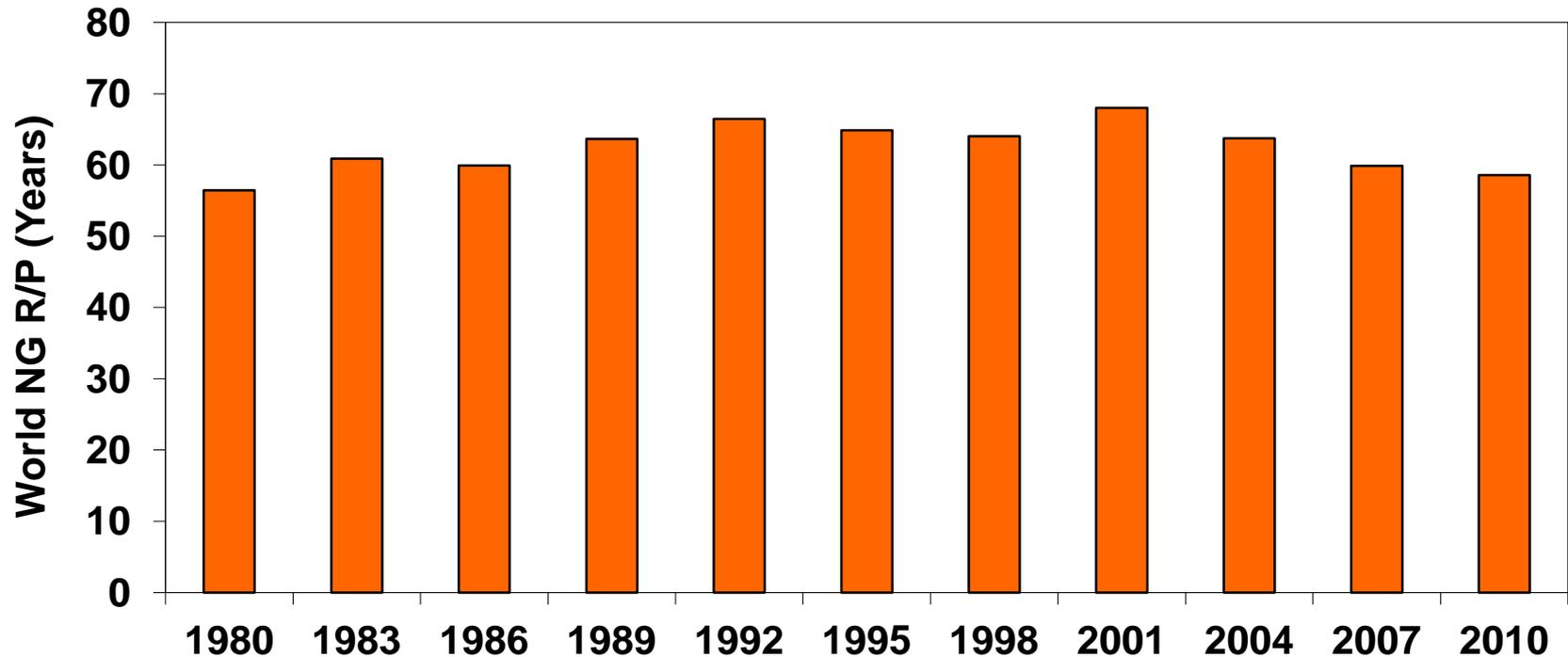
- Reserves are 29% above 1997 level
- Production is 14% higher than 1997 level
- USA R/P = 11.3 years
- USA R/Consumption = 4.4 years

# Natural Gas Production



- Total proven gas reserve = 187.1 trillion m<sup>3</sup>
- Natural gas demand continues to rise

# Natural Gas Reserves-to-Production Ratios



- Reserves are 64% above 1997 level
- Production is 14% higher than 1997 level
- USA R/P = 118 years\*
- In USA, natural gas production has remained flat over the last decade, but sudden spike since 2007

Source : BP Statistical Review of world Energy 2011

\* US Energy Information Administration

# Coal

- **Proven World Reserve = 860 billion tons**
- **World Reserve-to-Production Ratio = 118 years**
- **USA Reserve-to-Production Ratio = 241 years**

**It seems that there is enough hydrocarbon fuel to last for the next fifty years!**

**It seems that there is enough hydrocarbon fuel to last for the next fifty years!**

**However.....**