SOLAR CHEMISTRY HEATS UP

A look at how sunlight is being used to initiate chemical reactions

North Jersey Section AIChE

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  - EI Associates – A/E consulting
  - BOC Gases – industrial gases
  - Schering-Plough - pharmaceuticals
  - ALZO International, Inc. – specialty chemicals

ATTRIBUTIONS

Some information presented on these slides was obtained (with permission) from:

- **Solar Chemistry Heats Up** – Gerald Ondrey, Senior Editor, Chemical Engineering Magazine, March 2018
- **Photochemical Processes in Stirred Tank Reactors** – W. Himmelsbach, et al., EKATO, Chemical Engineering Magazine, June 2018
- **Photoreactor Overcomes Sunlight Variation** – Chemical Processing Magazine, June 2018

- *…as well as over 35 years of experience in the chemical process industry!*

What we will cover:

- **Photochemistry Overview**
  - *What is Photochemistry?*
  - *How does Photochemistry work?*
  - *Industrial photochemical processes and reactors*
- **“Sustainable” Photochemistry?**
  - *HydroGEN Energy Materials Network*
  - *Fisher-Tropsch review*
  - *Photoelectrochemical Cells*
  - *Polymer Electrolyte Fuel Cells*
  - *Thermochemical “water splitting” & the solar thermochemical process*
  - *What about sunlight variations?*
- **Artificial Photosynthesis**
  - *The Rheticus Project*

What is Photochemistry?

- **Photochemistry** is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet *(wavelength from 100 to 400 nm)*, visible light *(400 – 750 nm)* or infrared radiation *(750 – 2500 nm)*[1]

- **Photoexcitation** is the first step in a photochemical process where the reactant is elevated to a state of higher energy, (*i.e.; an excited state*)
  - The first law of photochemistry, known as the ***Grotthuss-Draper Law***, states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place.
  - According to the second law of photochemistry, known as the ***Stark-Einstein Law***, for each photon of light absorbed by a chemical system, no more than one molecule is activated for a photochemical reaction

[1] *Wikipedia*

Reaction Rates & Arrhenius Equation

- For a conventional chemical reaction, the rate can be described as follows:

$$r = k * C_A^{x_A} * C_B^{x_B}$$

*where **k** is the rate coefficient, which follows Arrhenius' Law:*

$$\mathbf{k} = A * e^{-E_A / RT}$$

- **k** is usually too small at ambient temperature to start most reactions
  - Temperature is typically increased, but while enhancing the desired reaction, higher temperatures also enhance side reactions / by-product formation
  - Catalysts allow for lower temperatures by reducing the activation energy, E_A, but catalysts come with costs: *(procurement, handling, disposal, etc.)*
  - Reaction initiation by radiant energy enables reactions to run independently of temperature, and often well below 100^oC
  - Photocatalysts are not used to decrease E_A, but to direct specific mechanisms of the reaction

How Does Photochemistry Work?

- The absorption of electromagnetic radiation of an appropriate wavelength promotes the reactant molecule from its ground state to an electrochemically excited state. From here it undergoes a mostly specific chemical transformation into a stable product or reactive intermediate capable of initiating another reaction

- **Chlorination** example**:**

  ($\lambda = $ 250-450 nm) $Cl_2 \longrightarrow 2\ Cl^*$

  Chain propagation: $Cl^* + R\text{-}H \longrightarrow {}^*R + HCl$

  ${}^*R + Cl_2 \longrightarrow R\text{-}Cl + Cl^*$

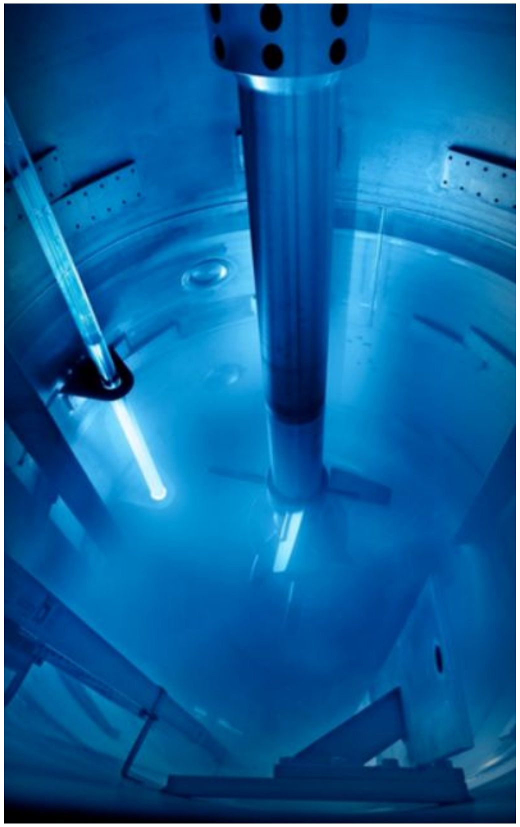
  Chain termination by recombination of radicals:

  $Cl^* + Cl^* \longrightarrow Cl_2$ / $Cl^* + {}^*R \longrightarrow R\text{-}Cl$

Industrial Photochemical Processes

Process	Product(s)	Industry	Mechanism	System
Chlorination	Intermediates, solvents, CPVC, rubbers	Specialties, polymers	Radical	Liquid-gas Liquid-gas-solid
Bromination	Intermediates	Specialties	Radical	Liquid
Sulfoxidation	Intermediates, sulfonic acids, surface-active materials	Specialties, consumer products, polymers	Radical	Liquid – gas
Nitrosylation	Intermediates, Nylon 6 and 12	Specialties, polymers	Radical	Liquid-gas-solid
Hydro-dimerization	Intermediates	Specialties, agrochemicals	Radical	Liquid
Oxidation	Intermediates, surface active materials	Specialties, perfumes, pharmaceuticals	Radical, sensitized, catalytic	Liquid, Liquid-gas Gas-solid Liquid-gas-solid
Isomerization	Intermediates	Specialties, pharmaceuticals	Electron density distribution, sensitized	Liquid
Polymerization	Intermediates	Specialties, polymers	Radical, ionic, catalytic	Liquid, Liquid-gas Liquid-solid Liquid-gas-solid

Industrial Photochemical Reactors



https://www.ekato.com/en/products/process-plants/photochemical-reactors/

“Sustainable” Photochemistry?

- There are three basic ways to make chemicals from sunlight:
  1. Sunlight can be used as photons for photosynthesis
  2. Sunlight can be transformed into electrons in photovoltaic cells, (e.g.; solar panels)
  3. Sunlight can be used as heat in thermochemical processes
- For industrial applications, however; solar radiation is a rather diluted energy source, limited to about 1kW / m^2 of irradiated reactor surface….
- …and only a fraction of that is available with the right wavelengths
- From an industrial point of view then, it is necessary to concentrate solar radiation – either in the form of heat or electricity – to be able to use it efficiently in chemical processes

Splitting Water

- The electrolysis of water into H_2 and O_2 has been used industrially for many years, especially in areas with cheap electricity
- With lower PV technology costs, renewable H_2 production is now making its way into the chemical process industries
  - Royal Dutch Shell has announced plans to build the world's largest water-electrolysis plant to produce H_2 for use in its Rheinland Refinery in Germany
  - This 10 MW plant will produce 1,300 metric tons per year of H_2 using renewable energy, when it starts up in 2020
- Meanwhile, there are ongoing efforts to develop alternative methods of making H_2 from water – the so-called "advanced water-splitting" technologies (AWS)…

HydroGEN Energy Materials Network

- **One of many AWS initiatives is the HydroGEN Energy Materials Network (EMN) consortium:**
  - **Led by the U.S. DOE's National Renewable Energy Laboratory, and including:**
    - » *Lawrence Berkeley National Laboratory*
    - » *Sandia National Laboratories*
    - » *Lawrence Livermore National Laboratory*
    - » *Savanna River National Laboratory*
- **Among the technologies being investigated are:**
  - *Low-temperature anionic-exchange membrane (AEM) and*
  - *Proton-exchange membrane (PEM) electrolysis*
  - *High-temperature electrolysis:*
    - » *Photoelectrochemical (PEC) pathways*
    - » *Solar thermo-chemical (STCH) water splitting*

https://www.h2awsm.org/

Fischer-Tropsch Review:

- The Fischer–Tropsch process is a collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons.
- The process was first developed by Franz Fischer and Hans Tropsch in Germany in 1925.
- The Fischer–Tropsch process is an important reaction in both coal liquefaction and gas-to-liquids technology for producing liquid hydrocarbons.
  - In the usual implementation, carbon monoxide and hydrogen, (the feedstocks for F-T), are produced from coal, natural gas or biomass in a process known as gasification. The Fischer–Tropsch process then converts these gases into a synthetic lubrication oil and synthetic fuel.

Fischer-Tropsch Review:

- **The Fischer–Tropsch process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula (C_nH_{2n+2}). The more useful reactions produce alkanes as follows:**

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$$

  - *Where n is typically 10–20.*
  - *The formation of methane (n = 1) is unwanted.*
  - *Most of the alkanes produced tend to be straight-chain, suitable as diesel fuel.*
  - *In addition to alkane formation, competing reactions give small amounts of alkenes, as well as alcohols and other oxygenated hydrocarbons.*

Photoelectrochemical Cells

- Photoelectrochemical cells or PECs are solar cells that produce electrical energy or hydrogen in a process similar to the electrolysis of water.
- This type of cell electrolyzes water to hydrogen and oxygen gas by irradiating the anode with electromagnetic radiation.
- This has been referred to as "artificial photosynthesis" and has been suggested as a way of storing solar energy in hydrogen, for use as fuel.
- Two types of photochemical systems operate via ***photocatalysis***.
  - *One type uses semiconductor surfaces as catalysts. In these devices the semiconductor surface absorbs solar energy and acts as an electrode for water-splitting.*
  - *The other method utilizes in-solution metal complexes as catalysts.*

Photoelectrochemical Cell

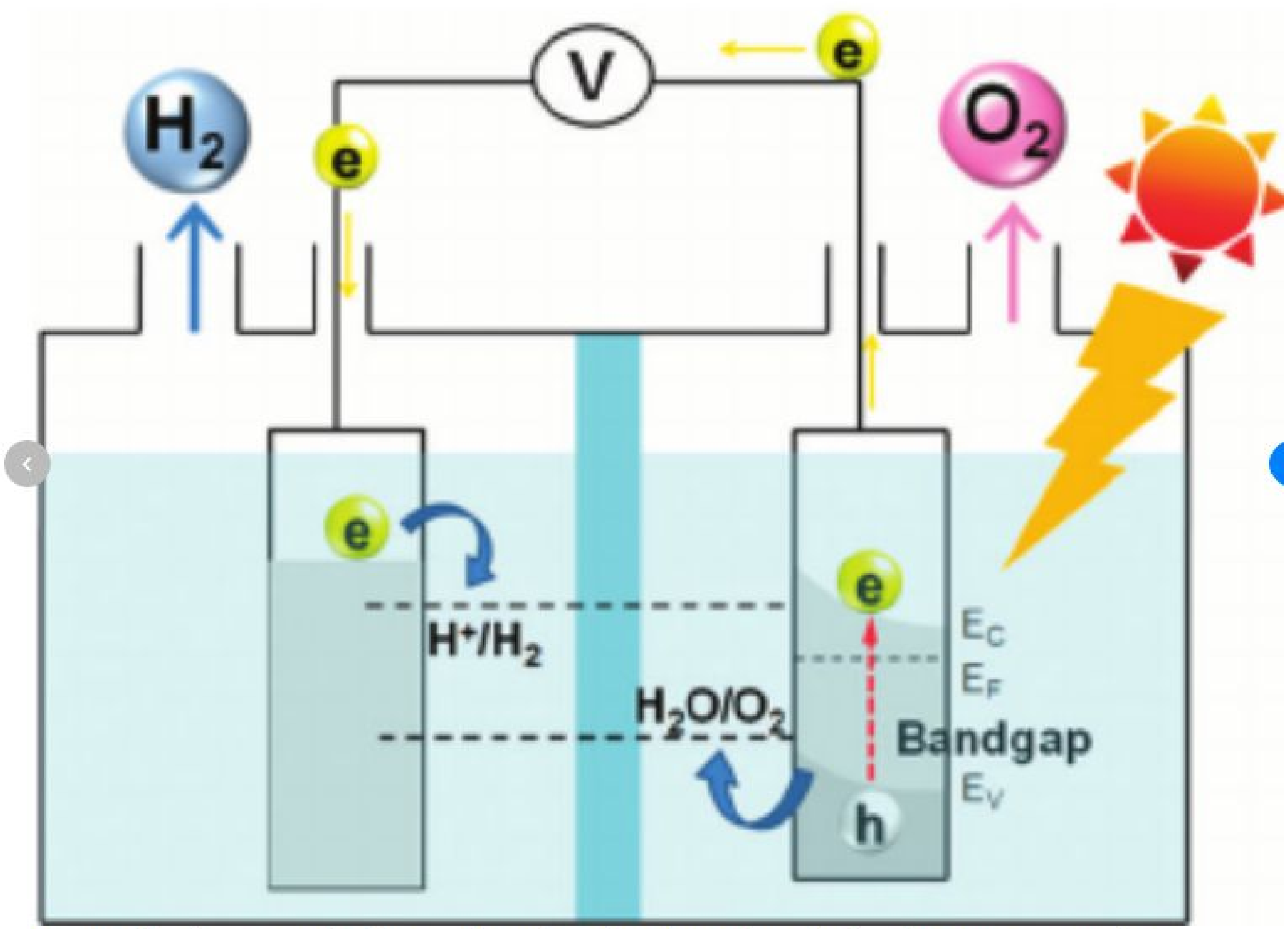
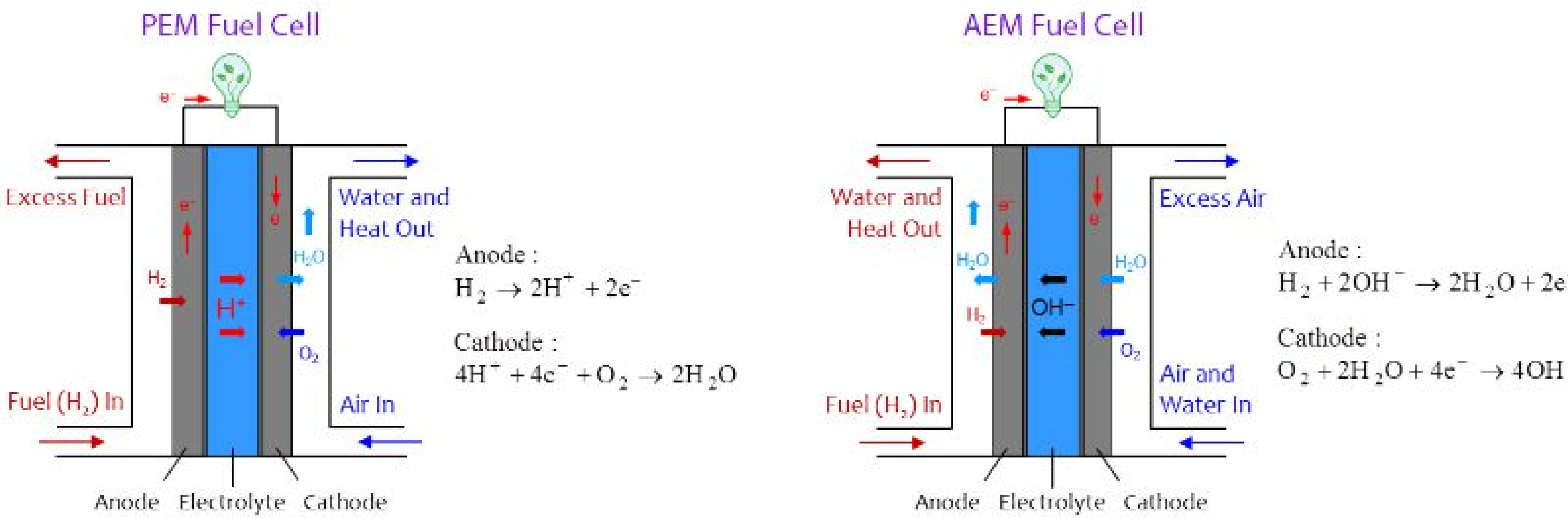


Diagram of the basic principles of water splitting for a photoelectrochemical cell with an n-type semiconductor photoanode where oxygen is evolved and a photocathode (Pt sheet) where hydrogen is evolved.

https://www.researchgate.net/figure/Diagram-of-the-basic-principles-of-water-splitting-for-a-photoelectrochemical-cell-with_fig1_228324324

Polymer Electrolyte Fuel Cells



In a **PEFC**, fuel - typically hydrogen - and oxygen from air are combined electrochemically across a solid polymer membrane generating electricity, water and heat. PEFCs are classified primarily by the transport of ions (either proton or anion), namely **proton-exchange-membrane (PEM) fuel cells** and **anion-exchange-membrane (AEM) fuel cells** as illustrated above, each with its own advantages, limitations, and potential applications.

https://www.staff.ncl.ac.uk/prodip.das/modeling.html

Anion Exchange Membrane (AEM)

- Anion exchange membrane (AEM) water electrolysis is a hydrogen production method that is achieved with an AEM, using electricity.
- One of the major advantages of AEM water electrolysis is the replacement of conventional noble metal electrocatalysts with low cost transition metal catalysts.
- AEM electrolysis is still a developing technology, with a view to using it to eventually achieve commercially viable hydrogen production.
- AEM electrolysis requires further investigation and improvements, specifically regarding its power efficiency, membrane stability, robustness, ease of handling, and cost reduction.

Proton Exchange Membrane (PEM)

- **Proton-exchange membrane fuel cells, also known as polymer electrolyte membrane fuel cells (PEMFC), are being developed mainly for transport applications, as well as for stationary and portable fuel cell applications.**

- **Their distinguishing features include lower temperature and pressure ranges *(e.g.; 50° to 100°C*), and a special proton-conducting polymer electrolyte membrane.**

- **PEMFCs generate electricity and operate on the opposite principle to AEM electrolysis, which consumes electricity.**

- **PEMFCs are a leading candidate to replace the aging alkaline fuel cell technology technology, which was used in the Space Shuttle.**

Polymer Electrolyte Fuel Cells

- The operation of a PEFC involves a complex overlap of interrelated physicochemical processes, which include electrochemical reactions as well as transport of ions, electrons, energy, and species in gas and liquid phases across a heterogeneous medium.
- Though PEFCs have shown promising performance improvement in terms of efficiency and durability over the last three decades, the level of robustness required for operation in widely varying conditions, while matching the current power sources in terms of cost, stifles the commercial utilization of PEFCs.
- Any further improvements could be greatly aided by a better understanding of the complex processes of fuel-cell operation.

Thermochemical Water-splitting

- **Thermochemical water splitting processes use high-temperature heat (500°–2,000°C) to drive a series of chemical reactions that produce hydrogen.**
  - **The chemicals used in the process are reused within each cycle, creating a closed loop that consumes only water and**
  - **This is a long-term technology pathway, with potentially low or no greenhouse gas emissions.**
- **The necessary high temperatures can be generated in the following ways:**
  - **Concentrating sunlight onto a reactor tower using a field of mirror "heliostats“.**
  - **Using waste heat from advanced nuclear reactors.**

Thermochemical Water-splitting

- Numerous solar thermochemical water-splitting cycles have been investigated for hydrogen production, each with different sets of operating conditions, engineering challenges, and hydrogen production opportunities. In fact, more than 300 water-splitting cycles are described in the literature.

- For more information, search on: ***Solar Thermochemical Hydrogen production Research: Thermochemical Cycle Selection and Investment Priority.***

Thermochemical water-splitting

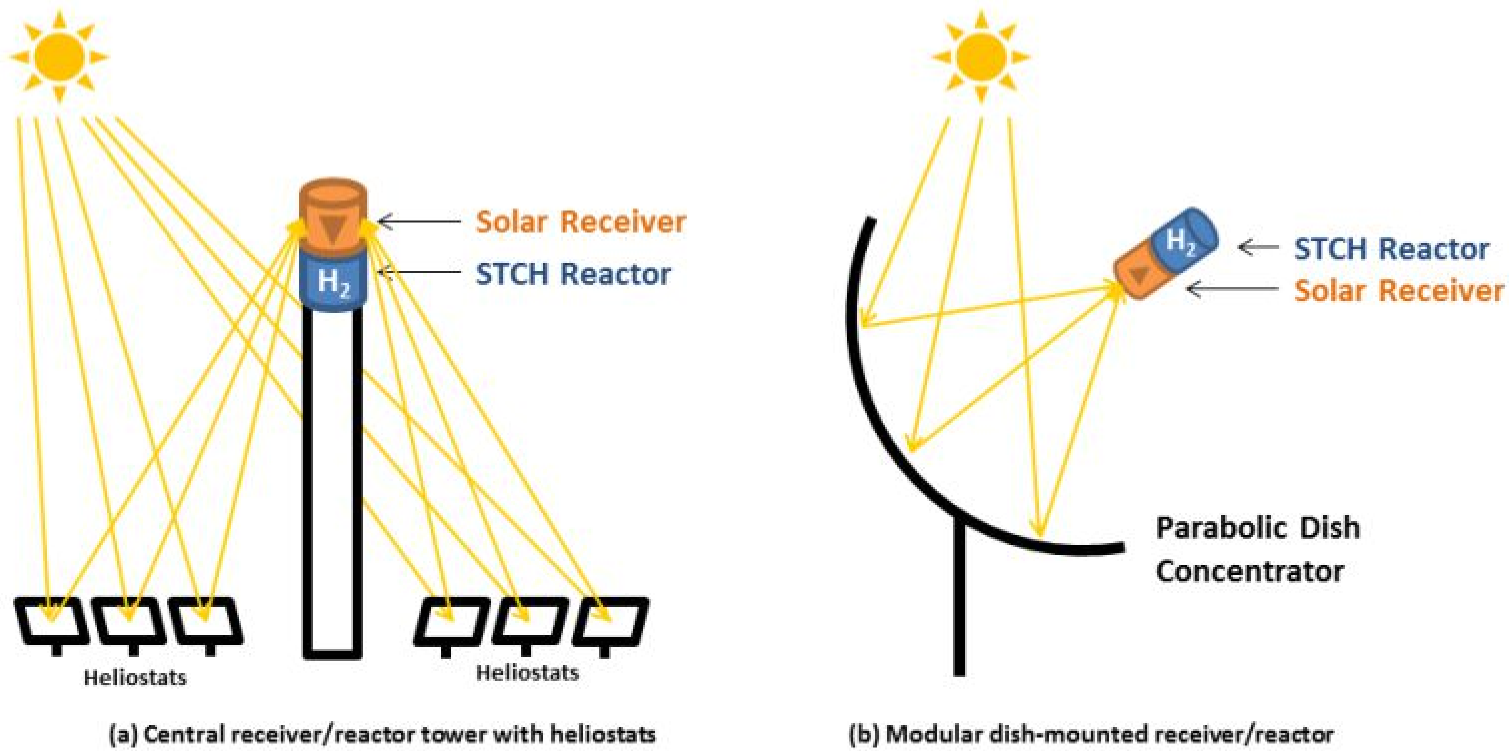
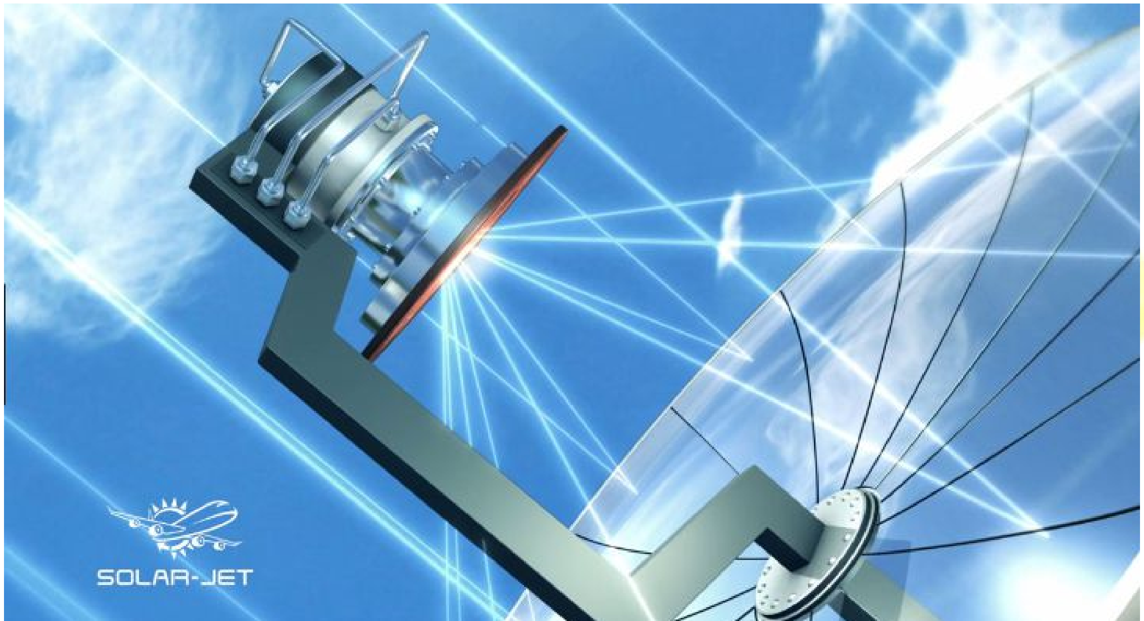
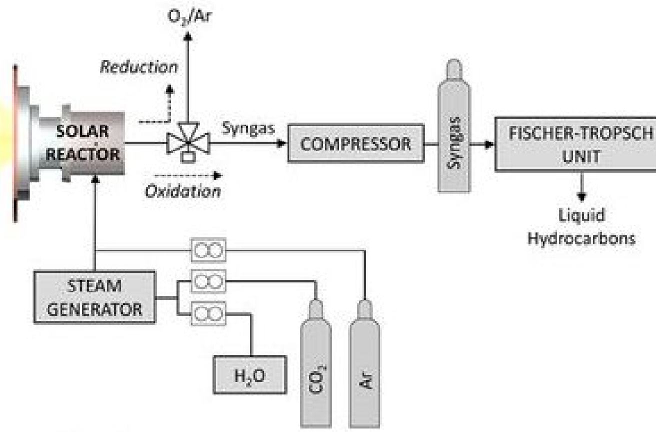


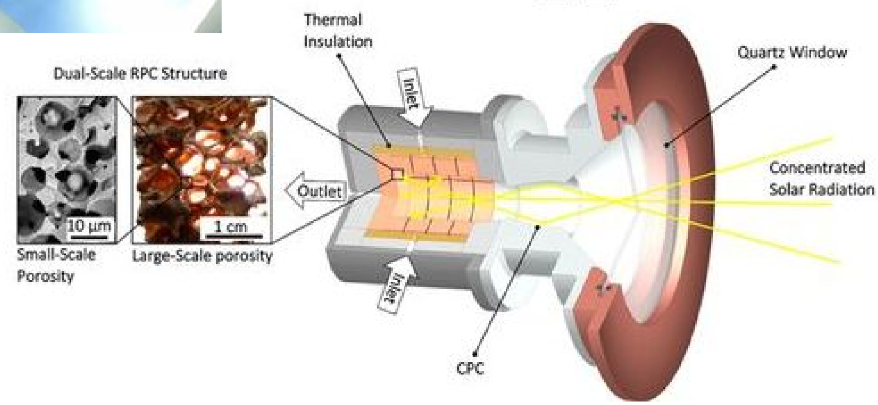
Figure 1. Two mirror-based approaches for focusing sunlight on a thermochemical reactor to produce temperatures up to 2,000°C are illustrated: (a) a field of heliostat mirrors concentrates sunlight onto a central reactor tower; and (b) dish mirrors focus sunlight onto an attached reactor module. The solar-generated high-temperature heat can be used to drive thermochemical reactions that produce hydrogen.

https://www.energy.gov/eere/fuelcells/hydrogen-production-thermochemical-water-splitting

Solar-Thermochemical Process (STCH)







SCTH Advantages

- **The thermochemical route to renewable fuels has three main advantages over other processes:**

  1. **Higher energy conversion efficiency** – commercial solar concentrating infrastructure collects solar light spectrum delivering high-temperature process heat directly to the reactor
  2. **Requires 12 times less area than biofuels derived from biomass –** additionally, this would not require agricultural areas, but deserts, i.e.; regions with high solar radiation
  3. **Uses high-temperature process heat** – can be stored on a large scale by inexpensive thermal energy storage systems enabling continuous, uninterrupted operation 24/7

Let’s see how it works……..

What about sunlight variations?

- Eindhoven University of Technology researchers in The Netherlands are testing ways to overcome sunlight variation and its effect on their micro-photoreactor
- Their reactor makes pharmaceuticals using solar energy and microchannels
- Reports are that their “mini factory” can keep production at the same level, regardless of variations in sunlight due to clouds or time of day
- Real-time feedback system designed, costing less than $60, that automatically slows or speeds production
  - Too much light = unwanted by-products
  - Too little light = no, or sluggish reactions

What about sunlight variations?

- **Their real-time reaction control system consisted of:**
  1. **A sensor that measured the amount of light reaching the microchannels,**
  2. **A micro-controller to translate that signal into pump speed,**
  3. **A pump that moved the fluids through the channels at that speed**
     - *The required pump speed for a specific light intensity was determined through experimentation*
- **The feedback loop was tested at both artificial and natural light and a yield setting of 90% kept production stable for 1 hour at between 86% and 93%**
  - ***The same system without the feedback loop varied dramatically between 55% and 97%***
- **The feedback loop increased the average yield by about 20%**

What about sunlight variations?

Leaf-Inspired Microphotoreactors
Figure 1. The amount of light captured by the microphotoreactors is visible, lit up bright red. As liquid is pumped through thin channels or "veins" in the leaves, light causes the reactions. *Source: Bart van Overbeeke.*

The leaf, made from silicone rubber, can operate in diffuse light. "It can be easily cleaned with some solvent and subsequently reused," says Noel.

"Theoretically, you could use this device to make drug compounds with solar energy anywhere you want," he adds.

The next step is to further improve energy efficiency and increase output.

Artificial Leaf Spurs Energy-Efficient Reactions

Micro photoreactor uses solar energy and microchannels to manufacture pharmaceuticals

By Chemical Processing Staff
Mar 06, 2017

Artificial Photosynthesis?

- **The inability to effectively store excess renewable electricity reduces the efficiency of the renewable energy installations.**
- **Additionally, projects to pull carbon dioxide emissions out of the air will be a necessary transitional measure to continue energy-spurred growth while converting to renewable energy sources.**
- **The Rheticus Project offers solutions for both conundrums. Researchers from two German industrial giants, Siemens and Evonik, announced that they will team up to demonstrate the feasibility of "technical photosynthesis". The idea is to use eco-electricity and harness the power of nature to convert CO_2 into more complex chemical building blocks, like the alcohols butanol and hexanol.**

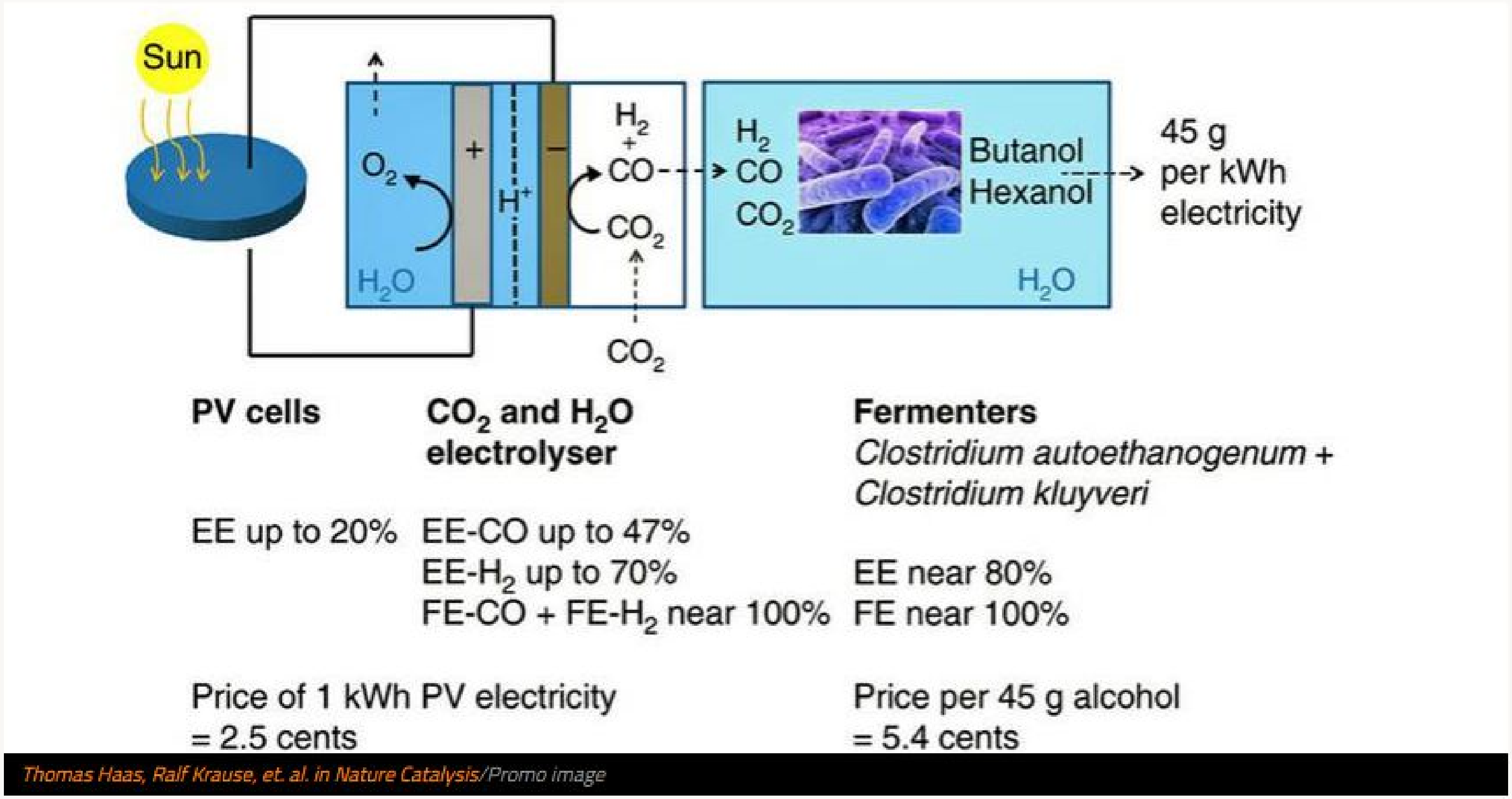
Artificial Photosynthesis?

- **Energy storage -** The ability to productively use as much renewable energy as can be generated is a major benefit of this concept:
  - ***The process effectively "stores" excess electricity in a CO-rich gas mixture, known as syngas.***
  - ***The syngas then serves as the nutrients for anaerobic microbes that produce the value-added alcohols like butanol and hexanol as a by-product.***
  - ***The valuable alcohols are easily separated from the reaction mixture in a process that promotes the re-use of the major components of the process, furthering the efficiency and reducing the potential waste generation of the process.***

Artificial Photosynthesis?

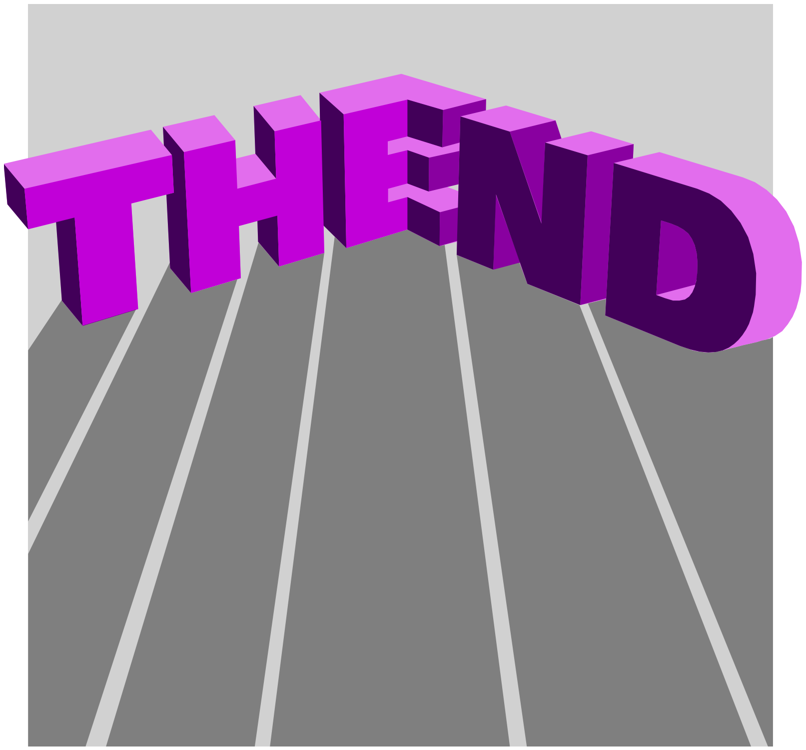
- With the **Rheticus Project**, syngas is produced electrolytically, using electricity generated by renewable sources:
  - *CO_2 is reduced into syngas at the cathode, while water is split into O2 and H^+ ions at the anode*
  - *The syngas is then fermented into alcohols using aerobic micro-organisms*
  - *The complete process has been demonstrated at small scale*
  - *The study demonstrated that the conversion achieved close to 100% Faradic efficiency*
  - *A test plant is expected to be on-stream by 2021 with the next step potentially being at 20,000 m.t./year plant*

Artificial Photosynthesis?



The alcohols generated by the process have a value of 2.2 times the cost of the electricity, assuming photovoltaic efficiency of 20%.

https://www.treehugger.com/biomimicry/rheticus-project-teams-german-giants-harvest-co2-artificial-photosynthesis.html


THE END

"There is no expedient to which a man will not resort to avoid the real labor of thinking."

Sir Joshua Reynolds

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