Hydrogen Production
Hydrogen Production

Hydrogen Production

Biomass
- Gasification
- Bio-hydrogen

Other?

Natural gas
- Reforming
- Partial oxidation

Wind
- Electrolysis

Solar
- Electrolysis

(Sustainable) Hydrogen

Nuclear
- Electrolysis
- Thermo-catalytic

Petroleum Coke/Residue
- Gasification
  incl. CO₂ sequestration

Coal
- Gasification
  In-situ gasification incl. CO₂ sequestration

Source:
Prof. Dr. J. Schoonman
Delft Institute for Sustainable Energy
Feedstocks Usage in Hydrogen Production

- **Natural gas**: 48%
- **Oil**: 30%
- **Coal**: 18%
- **Electrolysis**: 4%

Source: NAS Study, 2004
Sustainable Paths to Hydrogen

Renewable Energy

- Heat
  - Mechanical Energy
    - Thermolysis
- Biomass
  - Conversion
    - Electrolysis
      - Photolysis

Hydrogen
Hydrogen Production Methods

Most methods of producing hydrogen involve splitting water (H₂O) into its component parts of hydrogen (H₂) and oxygen (O). The most common method involves steam reforming of methane (from natural gas), although there are several other methods.

- **Steam reforming** converts methane (and other hydrocarbons in natural gas) into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst.
- **Electrolysis** uses electrical current to split water into hydrogen at the cathode (+) and oxygen at the anode (-).
- **Steam electrolysis** (a variation on conventional electrolysis) uses heat, instead of electricity, to provide some of the energy needed to split water, making the process more energy efficient.
- **Thermochemical water splitting** uses chemicals and heat in multiple steps to split water into its component parts.
- **Photoelectrochemical systems** use semi-conducting materials (like photovoltaics) to split water using only sunlight.
- **Photobiological systems** use microorganisms to split water using sunlight.
- **Biological systems** use microbes to break down a variety of biomass feed stocks into hydrogen.
- **Thermal water splitting** uses a very high temperature (approximately 1000°C) to split water.
- **Gasification uses** heat to break down biomass or coal into a gas from which pure hydrogen can be generated.
Chemical Hydrogen Production

The Hydrogen on Demand™ System:

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{catalyst}} 4\text{H}_2 + \text{NaBO}_2
\]

- Solution is non-flammable
- Reaction control via (reusable) catalyst
- Controlled H\(_2\) combustion
- No high pressures
- NaBO\(_2\) is non-toxic
- Recycling of NaBO\(_2\) into NaBH\(_4\) is possible
Electrolysis

Anode: $4 \text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$
Cathode: $4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 + 4\text{OH}^-$
Overall: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$

Electrolyte composition:
Pure water ($\sigma < 5\ \mu\text{S/cm}$) + 30% KOH
Electrolysis

Requirements for electrolysis:
• High-purity water
• Electricity

Efficiency: 85-90%
H₂ Purity: >99.9%
Electrolysis of Water

By providing energy from a battery, water (H₂O) can be dissociated into the diatomic molecules of hydrogen (H₂) and oxygen (O₂). This process is a good example of the application of the four thermodynamic potentials (internal energy, U, Helmholtz free energy, F = U-TS; Enthalpy, H = U+pv and Gibbs free energy, G =U+pv-TS).

The electrolysis of one mole of water produces a mole of hydrogen gas and a half a mole of oxygen gas in their normal diatomic forms. A detailed analysis of this process makes use of the thermodynamic potentials and the first law of thermodynamics. This process is presumed to be at 298K and atmospheric pressure.
Electrolysis of Water

System work:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>H₂O</th>
<th>H₂</th>
<th>0.5O₂</th>
<th>Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy</td>
<td>-285.83kJ</td>
<td>0</td>
<td>0</td>
<td>ΔH = -285.83kJ</td>
</tr>
<tr>
<td>Entropy</td>
<td>69.91 J/K</td>
<td>130.68J/K</td>
<td>0.5x205.14J/K</td>
<td>TΔS = 48.7 kJ</td>
</tr>
</tbody>
</table>

\[ W = PΔV = (101.3 \text{ kPa})(1.5 \text{ moles})(22.4x10^{-3}\text{m}^3/\text{mol})(298\text{K}/273\text{K}) = 3715 \text{ J} \]
\[ ΔU = ΔH-PΔV = 285.83\text{kJ}-3.72 \text{ kJ} = 282.1 \text{ kJ} \]
\[ ΔG = ΔH-TΔS = 285.83 \text{kJ}-48.7 \text{ kJ} = 237.1 \text{ kJ} \]
Efficiency

- Energy efficiency of electrolysis =

\[
\frac{\text{Chemical potential}}{\text{Electrolysis potential}} = \frac{1.23}{1.9} = 65\%
\]

- Systems that claim 85%

- Coupling to a 12% PV array gives a solar-to-hydrogen efficiency of:

\[.12 \times .65 = 7.8\%
\]

Improved electrolysis efficiency can bring the PV-hydrogen efficiency to about 10%
WATER AVAILABILITY

Reaction:

\[ \text{H}_2 (g) + \text{O}_2 (g) \leftrightarrow \text{H}_2\text{O (l)} + 286 \text{ kJ/mole} \]

Global energy demand: \(4 \times 10^{20} \text{ J/year}\)

\(\text{H}_2\) from water: 1 GJ per 90 liters \(\text{H}_2\text{O}\)

Water needed: \(3.6 \times 10^{13}\) liters

Oceans: \(1.45 \times 10^{21}\) liters

Annual rainfall: \(3.62 \times 10^{17}\) liters

There is enough water to sustain hydrogen!
Hydrogen-Electricity

- Commercial system efficiencies (54-67 kWh/kg)
- Ideal system (HHV of hydrogen 39 kWh/kg)

Graph showing the relationship between H₂ cost (S/kg) and Electricity costs ($/kWh) with a line for commercial system efficiencies and another for an ideal system.
Electrolyzers

> 50 Nm³ H₂/h

5-50 Nm³ H₂/h

< 5 Nm³ H₂/h
Large scale Electrolyzers

Norsk Hydro Electrolyzers
2,000 kW each
The most modern Electrolyzers consume 4.0 kWh per cubic meter of H₂ gas. Electrolysis process takes place by voltage of 1.6-2.0 V and current strength of dozens and hundreds of amperes. When one cubic meter of hydrogen is burnt, 3.55 kWh of energy is released [1].

A money-saving process of decomposition of water molecules into hydrogen and oxygen exists in the nature. This process takes place during photosynthesis. Hydrogen atoms are separated from water molecules and are used as connecting links while forming organic molecules, and oxygen is released into the air.

A question emerges: is it possible to model an electrolytical process of water decomposition into hydrogen and oxygen, which takes place during photosynthesis? A search of a reply to this question has resulted in a simple structure of a cell (Fig. 1), in which the process takes place by voltage of 1.5-2.0 V between the anode and the cathode and amperage of 0.02 amperes [1], [2].
Low Current Electrolysis of Water

The electrodes of the cell are made of steel. It helps to avoid the phenomena, which are appropriate to a galvanic cell. Nevertheless, at the cell electrodes a potential difference of nearly 0.1 V takes place in complete default of electrolytic solution in it. When the solution is charged, the potential difference is increased. The positive sign of the charge appears on the upper electrode always, and the negative sign appears on the lower one. If a direct current source generates pulses, gas output is increased.

As a laboratory model of the low current electrolyzer cell generates small quantity of gases, a solution mass change definition method during the experiment and further calculation of released hydrogen and oxygen is the most reliable method of definition of their quantity. It is known that a gram atom is equal to atomic mass of substance; a gram molecule is equal to molecular mass of substance. For example, the gram molecule of hydrogen in the water molecule is equal to two grams; the gram-atom of the oxygen atom is 16 grams. The gram molecule of water is equal to 18 grams. Hydrogen mass in a water molecule is 2x100/18=11.11%; oxygen mass is 16x100/18=88.89%; this ratio of hydrogen and oxygen is in one liter of water. It means that 111.11 grams of hydrogen and 888.89 grams of oxygen are in 1000 grams of water.

One liter of hydrogen weighs 0.09 g; one liter of oxygen weighs 1.47 g. It means that it is possible to produce 111.11/0.09=1234.44 liters of hydrogen and 888.89/1.47=604.69 liters of oxygen from one liter of water. It appears from this that one gram of water contains 1.23 liters of hydrogen. Energy consumption for production of 1000 liters of hydrogen is 4 kWh and for one liter 4 Wh. As it is possible to produce 1.234 liters of hydrogen from one gram of water, 1.234x4=4.94 Wh is spent for hydrogen production from one gram of water now.
Low Current Electrolysis of Water

A small value of current 0.02 A and voltage 0.062 V allows us to suppose that in the low current electrolyzer the water electrolysis process is similar to the process, which takes place during photosynthesis. At photosynthesis, hydrogen separated from the water molecule is used as a connecting link while organic molecule formation, and oxygen is released in the air. At low current electrolysis, both hydrogen and oxygen are released in the air.

Note: gas release is clearly seen during several hours after the cell is disconnected from the line.

REFERENCES

Producing hydrogen from water, without electrolysis

Electrochemical potential difference drives the reaction

Researchers at DOE’s National Energy Technology Laboratory and Argonne National Laboratory have patented a "Method of Generating Hydrogen by Catalytic Decomposition of Water." The invention potentially leapfrogs current capital and energy intensive processes that produce hydrogen from fossil fuels or through the electrolysis of water. According to co-inventor Arun Bose, "Hydrogen can be produced by electrolysis, but the high voltage requirements are a commercial barrier. The invention provides a new route for producing hydrogen from water by using mixed proton-electron conducting membranes." Water is decomposed on the feed surface. The hydrogen is ionized and protons and electrons travel concurrently through the membrane. On the permeate side, they combine into hydrogen molecules.
Photoelectrolysis

Hydrogen Production by Photo-electrolysis of Water

The photo-electrolysis of water into hydrogen and oxygen using solar energy is potentially a clean and renewable source of hydrogen fuel for the hydrogen economy. The energy conversion efficiency of water photo-electrolysis is determined mainly by the properties of the materials used as electrodes in the photo-electrochemical cell. Obstacles to direct photo-electrolysis of water are the lack of efficient light absorption, corrosion of the semiconductor photo-catalyst and energetics. The aim of research work is to engineer materials with appropriate optical, electronic and chemical properties for use as photo-catalysts in efficient and cost effective photo-electrochemical cells.
Photoelectrolysis

Photoelectrolysis: Water + Sunlight = H₂ + O₂
  • Indirect photoelectrolysis
    → solar cell + electrolyzer
  • Direct photoelectrolysis
    → Water splitting by photo-generated electrons

Direct PE: Holy Grail of electrochemistry!
Requirements:
  • H₂/O₂ fuel value ≥ 10% of incident energy
  • Long lifetime
Direct Conversion

Photoelectrochemical-Based Direct Conversion Systems

- Combines a photovoltaic system (light harvesting) and an electrolyzer (water splitting) into a single monolithic device.
  - Electrolysis area approximates that of the solar cell - the current density is reduced.
- Balance of system costs reduced.
  - Capital cost of electrolyzer eliminated
- Semiconductor processing reduced.
- Efficiency 30% higher than separated system.
Photoelectrolysis

Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions

\[ 2H_2O + 2e^- = 2OH^- + H_2 \uparrow \]
\[ H_2O + 2h^+ = 2H^+ + 1/2 O_2 \uparrow \]
Photoelectrolysis

Overall reaction:
2 H₂O + light → 2 H₂ + O₂
Photoelectrolysis

Photoelectrolysis: Doped oxides

Electrical wire

Sunlight

4 H₂O + 4 e⁻ → 2 H₂ + 4 OH⁻

1.23 eV

4 OH⁻ → O₂ + 2 H₂O + 4 e⁻

Overall reaction:
2 H₂O + light → 2 H₂ + O₂
Photoelectrolysis

Material and Energetic Requirements

Bandgap
- Band edge overlap
- Fast charge transfer

All three energetic conditions must be satisfied SIMULTANEOUSLY + Stability

Diagram:
- p-type semiconductor
- $E_g > 1.7 \text{ eV}$
- $1.23 \text{ eV}$
- $H_2O/H_2$ and $H_2O/O_2$
- Counter Electrode
Bandgap Considerations

The diagram shows the distribution of radiation energy in terms of photon energy (eV) and wavelength (μm). The visible spectrum is indicated by a dashed line, with a peak energy of 1.23 eV.
Bandedge Energetic Considerations

Technical Challenges

• Stability
  – The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.

• Efficiency (Bandgap)
  – For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with bandgaps in this range are photochemically unstable in water.

• Energetics
  – In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energies where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.
Technical Challenges

- **Catalysts:**
  - Oxygen (most important -- highest energy loss).
  - Hydrogen
  - Transparency might be necessary
- Band edge engineering.
- Semiconductor hybrid designs
- Low cost system designs featuring passive controls.
Photoelectrolysis

Photoelectrolysis: Solutions

Materials: metal oxides

- Tandem cells
  - Dye-sens. TiO$_2$ (red, H$_2$) / WO$_3$ (blue, O$_2$), 4.5%
    (Grätzel, Nature 414 (2001) 338)
  - p-GaAs/n-GaAs/p-GaInP$_2$, 12.4%
    (Khaselev, Science 280 (1998) 425)

- Oxides with metal 3d valence band
  - MoS$_2$, NiTiO$_3$
  - In$_{1-x}$Ni$_x$TaO$_4$ (?), <1%
    (Zou et al., Nature 414 (2001) 625)

- Sensitization by doping
  - TiO$_2$ doped with Cr, Fe, Mn, Cd, etc.
  - SrTiO$_3$ doped with e.g. Cr
Photoelectrolysis

Comparison of PV/Electrolysis with Photoelectrolysis

- For 12% PV system with an electrolysis efficiency of 65% (1.9V), we have a solar-to-hydrogen efficiency of 7.8%.
- For a direct conversion system with a base 12% PV efficiency, operating at an equivalent 1.45V, we can have a solar-to-hydrogen efficiency of 10.2%.

Equivalent electrolysis efficiency of 85% equals a 30% decrease in coverage area.

A strong motivation for improved electrolysis process
Historical Perspective


Allen J. Bard & Marye Anne Fox “Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen”

Water splitting “Holy Grail” definition: “We want an efficient and long-lived system for splitting water to $H_2$ and $O_2$ with light in the terrestrial (AM1.5) solar spectrum at an intensity of one sun. For a practical system, an energy efficiency of at least 10% appears to be necessary. This means that the $H_2$ and $O_2$ produced in the system have a fuel value of at least 10% of the solar energy incident on the system...and will not be consumed or degraded under irradiation for at least 10 years.”
Historical Perspective

First reported direct water splitting: A. Fujishima, K. Honda, *Nature* 238, p 37. 1972,
- Single crystal TiO$_2$ with chemical (pH) bias of 840 mV.

Best unbiased single semiconductor material efficiency to date is $\sim$ 1% (solar-to-hydrogen)

Best multijunction/PV bias is:
- 4.5% (M. Grätzel et.al., *Nature*, 414, p338 2001)
- 8.5% (S. Kahn et.al., *Science*, 297, p2243 2002)
Thermal Decomposition of Water

By heating water to over 2,000°C, it is broken down into hydrogen and oxygen. This is considered to be an interesting and inexpensive method of producing hydrogen directly from solar energy. Research is also being done on the use of catalysts to reduce the temperature for dissociation. One central problem is the separation of gases at high temperatures to avoid recombining. The efficiency factor is uncertain.

Chemical Reactions

\[ H_2O \rightarrow H_2 + \frac{1}{2}O_2 \]

\[ H_2 \rightarrow 2H \]

\[ O_2 \rightarrow 2O \]

\[ O + H \rightarrow OH \]
Thermochemical Production from Nuclear Energy

Hydrogen can be produced from water using thermal energy

- **Electric power generation → Electrolysis**
  - Proven technology
  - Overall efficiency ~24% (LWR), ~36% (Hi T Reactors)
    (efficiency of electric power generation x efficiency of electrolysis)

- **Heat → Thermochemical water-splitting**
  - Net plant efficiencies of up to ~50%
  - Developing technology

- **Electricity + Heat → High temperature electrolysis or Hybrid cycles**
Thermochemical Production

A set of coupled, thermally-driven chemical reactions that sum to the decomposition of water into H₂ and O₂

- All reagents returned within the cycle and recycled
- Only high temperature heat and water are input, only low temperature heat, H₂ and O₂ are output

High efficiency is possible – at high temperature

A developing technology

- Explored extensively in the 1970s
- Numerous possible cycles identified and explored
- Never commercialized
Identified the Sulfur-Iodine (S-I) as best suited for hydrogen production from a nuclear heat source

- Higher efficiency, easier handling
- France, Japan have also selected the S-I cycle (or "I-S cycle")

Ref.: Brown, et al, AIChE 2002

- Invented at GA in 1970s
  - Serious investigations for nuclear and solar
  - Chemistry reactions all demonstrated
  - Materials candidates selected and tested

- Advantages:
  - All fluid continuous process, chemicals all recycled; no effluents
  - H₂ produced at high pressure ~ 22 - 84 atm.
  - Highest cited projected efficiency, ~50%

- Challenges:
  - Requires high temperature, ≥800°C
  - Must be demonstrated as a closed loop under prototypical conditions
The S-I cycle is a thermally-driven chemical process

Follows the rules of chemistry and thermodynamics (Carnot)

High predicted efficiency: ~50% at 900°C
Possible production of heat by solar thermal plant

- Process is coupled to nuclear heat source by an intermediate loop with 2 heat exchangers \(\sim 50^\circ C \Delta T\)
- Earlier studies used \(827^\circ C\), achieved 42% efficiency
- >50% efficiency requires >900°C peak process T
- Reactor outlet T \(\geq 950^\circ C\) desired
We completed the S-I process design

- Used chemical process design code Aspen Plus
- Designed the three main chemical process systems
  - Prime or Bunsen reaction
    \[(2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI)\]
  - Sulfuric acid decomposition
    \[2H_2SO_4 \rightarrow 2SO_2 + 2H_2O + O_2\]
  - Hydrogen iodide decomposition
    \[2HI \rightarrow I_2 + H_2\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Flow rate tons/day</th>
<th>Inventory tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>H_2O</td>
<td>1,800</td>
<td>40</td>
</tr>
<tr>
<td>H_2SO_4</td>
<td>9,800</td>
<td>100</td>
</tr>
<tr>
<td>I_2</td>
<td>203,200</td>
<td>2,120</td>
</tr>
</tbody>
</table>

- We estimate high efficiency (52% at 900°C) and reasonable cost (~$250/kWt)
  - Benefit of high reactor outlet temperature important

- Experimental verification is needed
  - HI, H_2O, I_2 Vapor-Liquid Equilibrium data needed
  - Confirmation of HI Reactive Distillation analysis important, may allow further cost savings

Solar Production of Hydrogen is an appealing goal

- **Solar receivers can deliver high temperature**
  - NREL/U.Colorado demonstrated 51% collection efficiency at 2000°C in the process fluid for thermal cracking of methane

- **Solar diurnal cycle is a real limitation**
  - ~ 8 hours of useful energy per day
  - 8/24 = 33% duty cycle
  - Capital equipment only earning revenue 1/3 of the time
  - Hydrogen unit cost increased 3x

- **Solar can deliver higher temperatures than nuclear -- can we use it effectively to off-set the low duty cycle?**

Photos of NREL Solar Furnace
Preliminary estimates of Solar thermochemical hydrogen production are encouraging

- Start with nuclear-matched S-I cycle coupled to solar receiver
  - NREL heliostat/collector: 1 kW/m², 51% capture, $130/m², 8 hr/day
  - Lower capital cost than nuclear, but low duty cycle hurts
- Increase temperature to maximum S-I can use – 1100°C
  - NREL advanced heliostat/collector: $75/m²
  - Better – but doesn’t use the full temperature potential of solar
- Assume hypothetical thermochemical cycle at 2000°C
  - Assume same 79% of Carnot efficiency as S-I → 65% heat to H₂ efficiency
  - Assume same $/kWt capital cost as S-I
- While the assumptions are unproven, the result is interesting

<table>
<thead>
<tr>
<th>Process</th>
<th>Nuclear S-I</th>
<th>Solar S-I</th>
<th>Solar Hi T S-I</th>
<th>V Hi T Cycle</th>
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</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>900</td>
<td>900</td>
<td>1100</td>
<td>2000</td>
</tr>
<tr>
<td>Efficiency - Heat to H₂</td>
<td>52%</td>
<td>52%</td>
<td>56%</td>
<td>65%</td>
</tr>
<tr>
<td>Hydrogen cost, $/kg</td>
<td>1.42</td>
<td>3.45</td>
<td>2.50</td>
<td>2.15</td>
</tr>
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</table>
# Hydrogen From Water

<table>
<thead>
<tr>
<th>Process Temperature (°C)</th>
<th>Heat-to-Hydrogen Efficiency (%)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis</td>
<td>20-25</td>
<td>Commercial</td>
</tr>
<tr>
<td>Sulfur-iodine thermochemical cycle</td>
<td>850</td>
<td>45-49</td>
</tr>
<tr>
<td>Calcium-bromine thermochemical cycle</td>
<td>760</td>
<td>36-40</td>
</tr>
<tr>
<td>Copper-chlorine thermochemical cycle</td>
<td>550</td>
<td>41*</td>
</tr>
</tbody>
</table>

* Energy efficiency calculated based on thermodynamics
Solar Thermochemical Production

Concentrated Solar Energy

- H₂O
- Thermolysis
- Thermochemical Cycles
- Reforming
- Cracking
- Gasification
- CO₂/C Sequestration
- Carbothermic Reduction

Fossil Fuels

- H₂O

Solar Hydrogen

- hydrolysis

Solar Metals

Source: Aldo Steinfeld
Solar Thermochemical Production

Concentrated Solar Radiation

Receiver
Concentrator

Receiver
Heliostats

Receiver
Concentrator
Solar Thermochemical Production

Concentrated Solar Radiation

Absorption

Heat

$Q_{H,T_H}$

$H_2O$ \rightarrow \text{Chemical Reactor} \rightarrow H_2 + \frac{1}{2}O_2
Copper-Chlorine Cycle

Hydrogen Production (160°C)
2Ag + 2HCl → \( \text{H}_2(g) \) + 2AgCl

Intermediate Reaction (40°C)
2AgCl + 2CuCl + 8NH₃(g) → 2Ag + 2CuCl₂ + 8NH₃(a)
The reaction takes place in an aqueous media.

Oxygen Formation (550°C)
2CuCl₂ + 2MgO + \( \text{H}_2\text{O} \) → \( \frac{1}{2}\text{O}_2(g) \) + 2HCl + 2CuCl + 2MgO
Reaction consists of a complex set of reactions in which MgO is chlorinated to MgCl₂ Åù H₂O at 270°C and transformed back into MgO at 550°C.

Net Reaction: \( \text{H}_2\text{O}(l) \) → \( \text{H}_2(g) \) + \( \frac{1}{2}\text{O}_2(g) \)

Solar Thermochemical Production

\[ H_2O = H_2 + \frac{1}{2} O_2 \]
ZnO Disassociation

ZnO = Zn + \( \frac{1}{2} \) O\(_2\)

\( \Delta H = 557 \text{ kJ/mol} \)
\( T = 2000 \text{ K} \)

\( \frac{1}{2} \) O\(_2\)  
Zn  
H\(_2\)

H\(_2\)O

Zn + H\(_2\)O = ZnO + H\(_2\)

\( \Delta H = -62 \text{ kJ/mol} \)
\( T = 700 \text{ K} \)

ZnO serves the functions of radiant absorber, thermal insulator, and chemical reactant.
**ZnO Disassociation**

**Thermal Dissociation**

\[ \text{ZnO} \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \]

**Carbon (coke, biomass, ...)**

\[ \text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO} \]

**\( \text{CH}_4 \) (NG, biomass, ...)**

\[ \text{ZnO} + \text{CH}_4 \rightarrow \text{Zn} + 2\text{H}_2 + \text{CO} \]
Decarbonization of Fossil Fuels

NG Fossil Fuels $\xrightarrow{Q_{\text{Solar}}}$ Cracking Reactor $\xrightarrow{\text{H}_2}$ Fuel Cell $\xrightarrow{W_{\text{out}}}$ Sequestration

CH$_{0.4}$O$_{0.03}$ anthracite Fossil Fuels $\xrightarrow{Q_{\text{Solar}}}$ Gas. / Ref. Reactor $\xrightarrow{\text{Syngas}}$ Shift-Reactor $\xrightarrow{\text{H}_2/\text{CO}_2}$ Separation $\xrightarrow{\text{CO}_2}$ Fuel Cell $\xrightarrow{\text{H}_2}$ $\xrightarrow{\text{O}_2}$

Graphs:
- NG-cracking + C-sequestration + 65%-\(\eta\) FC
- NG-cracking + C-gasification + 65%-\(\eta\) FC
- NG-combustion + 55%-\(\eta\) combined cycle

Graph:
- C-gasification to syngas + 55%-\(\eta\) CC
- C-gasification to H$_2$ + 65%-\(\eta\) fuel cell
- C-combustion + 35%-\(\eta\) Rankine cycle
Timeline

Concentrated Solar Energy

Thermochemical Cycles

Thermolysis

H₂O

Fossil Fuels

H₂O

Fossil Fuels

M₉O₇

Reforming

C₀₂

Cracking

Gasification

Carbothermic Reduction

Long-Term

Short/Mid-Term Transition to Solar Hydrogen

Solar Hydrogen

hydrolysis

Solar Metals
Efficiency

\[ \eta_{\text{maximum}} = \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \]

\[ \eta_{\text{absorption}} = \left(1 - \frac{\sigma T_H^4}{C \cdot I}\right) \]

Concentrated Solar Radiation

Absorption

Heat

Heat Engine

\[ Q_H T_H \]

\[ Q_L T_L \]

\[ W \]
Efficiency

Concentrated Solar Radiation

\[ \eta_{\text{maximum}} = \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \]

\[ \eta_{\text{absorption}} = 1 - \frac{4 \sigma T_H^4}{C \cdot I} \]

For:

- \( I = 1 \text{ kW/m}^2 \) (1 sun)
- \( \sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \)

<table>
<thead>
<tr>
<th>( C )</th>
<th>( T_{\text{stagnation}} )</th>
<th>( T_{\text{optimal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>2049 K</td>
<td>1106 K</td>
</tr>
<tr>
<td>5000</td>
<td>3064 K</td>
<td>1507 K</td>
</tr>
<tr>
<td>10000</td>
<td>3644 K</td>
<td>1724 K</td>
</tr>
</tbody>
</table>
CSIRO in collaboration with industry partner Solar Systems Pty Ltd has demonstrated a concept for integrating solar thermal energy and methane gas to produce a range of solar-enriched fuels and synthesis gas (CO and H2) that can be used as a power generation fuel gas, as a metallurgical reducing gas or as chemical feed stock e.g. in methanol production. The main chemical processes are:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O}_{(g)} + 250 \text{ kJ} &\rightarrow \text{CO} + 3\text{H}_2 \quad (\text{Reaction 1}) \\
\text{CO} + \text{H}_2\text{O}_{(g)} &\rightarrow \text{CO}_2 + \text{H}_2 + 3 \text{ kJ} \quad (\text{Reaction 2}) \\
\text{CO} + \text{H}_2\text{O}_{(l)} &\rightarrow \text{H}_2 + \text{CO}_2 + 3 \text{ kJ}
\end{align*}
\]
Solar to Hydrogen Conversion Efficiency

a: Direct thermal hydrogen
b: Silicon photovoltaic cells and alkaline electrolyzer
c: Solar dish Stirling generator and alkaline electrolyzer
d: National Renewable Energy Laboratory goal
e: Multi-junction single crystal gallium arsenide solar cells and alkaline electrolyzer
f: Direct thermal hydrogen process potential

Biomass to Hydrogen

BioResource

Biological
- Anaerobic Digestion
- Fermentation
- Metabolic Processing

Thermochemical
- Gasification
- High Pressure Aqueous
- Pyrolysis

CH₃CH₂OH/CO₂
- Reforming
- Pyrolysis
- Photo-biology
- H₂/C
- H₂/O₂

H₂/CO
- Synthesis
- Reforming
- H₂/CO₂

CH₄/CO₂
- Reforming
- H₂/CO₂
- H₂/C

CH₄/CO₂
- Reforming
- H₂/CO₂
- H₂/C

CH₃OH/CO₂
- Reforming
- H₂/CO₂
- H₂/C

Severe
Biomass to Hydrogen

Biofuel Processes for Vehicle Fuel

- Biomass and Waste
  - Gasification
    - Reforming
      - Natural Gas
      - Synthesis Gas
        - DME
        - Methanol
        - FT Diesel
        - H₂
### Fuel Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Gasoline</th>
<th>No. 2 Diesel Fuel</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>MTBE</th>
<th>Propane</th>
<th>Compressed Natural Gas (CNG)</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Formula</strong></td>
<td>C_{4} to C_{12}</td>
<td>C_{3} to C_{25}</td>
<td>CH_{2}OH</td>
<td>C_{2}H_{5}OH</td>
<td>(CH_{3})_{2}C=O</td>
<td>C_{3}H_{8}</td>
<td>CH_{4}</td>
<td>H_{2}</td>
</tr>
<tr>
<td><strong>Molecular Weight</strong></td>
<td>100–105({a})</td>
<td>100–200</td>
<td>32.04</td>
<td>46.07</td>
<td>88.15</td>
<td>44.1</td>
<td>16.04</td>
<td>2.02({a})</td>
</tr>
<tr>
<td><strong>Composition, Weight %</strong></td>
<td>Carbon</td>
<td>85–88({b})</td>
<td>84–87</td>
<td>37.5</td>
<td>52.2</td>
<td>66.1</td>
<td>82</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Hydrogen</td>
<td>12–15({b})</td>
<td>33–16</td>
<td>12.6</td>
<td>13.1</td>
<td>13.7</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>0</td>
<td>0</td>
<td>49.9</td>
<td>34.7</td>
<td>18.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Specific gravity, 60° F/60° F</td>
<td>0.72–0.78({b})</td>
<td>0.81–0.89({d})</td>
<td>0.796({c})</td>
<td>0.796({c})</td>
<td>0.744({m})</td>
<td>0.508</td>
<td>0.424</td>
</tr>
<tr>
<td></td>
<td>Density, lb/gal @ 60° F</td>
<td>6.0–6.5({b})</td>
<td>6.7–7.4({d})</td>
<td>6.82({b})</td>
<td>6.61({b})</td>
<td>6.19({m})</td>
<td>4.22</td>
<td>1.07({r})</td>
</tr>
<tr>
<td></td>
<td>Boiling temperature, °F</td>
<td>80–437({b})</td>
<td>370–850({d})</td>
<td>140({c})</td>
<td>172({c})</td>
<td>131({c})</td>
<td>44</td>
<td>-259</td>
</tr>
<tr>
<td></td>
<td>Reid vapor pressure, psi</td>
<td>8–15({d})</td>
<td>0.2</td>
<td>4.6({d})</td>
<td>2.2({d})</td>
<td>7.8({d})</td>
<td>206</td>
<td>2,400</td>
</tr>
<tr>
<td><strong>Octane no.</strong></td>
<td>Research octane no.</td>
<td>90–100({l})</td>
<td>--</td>
<td>107</td>
<td>108</td>
<td>112</td>
<td>112</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Motor octane no.</td>
<td>81–90({e})</td>
<td>--</td>
<td>92</td>
<td>92</td>
<td>101({l})</td>
<td>97</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>(R + M/2)</td>
<td>88–94({e})</td>
<td>N/A</td>
<td>100</td>
<td>100</td>
<td>103({l})</td>
<td>104</td>
<td>128+</td>
</tr>
<tr>
<td></td>
<td>Cetane no.({l})</td>
<td>5–20</td>
<td>40–55</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><strong>Water solubility, @ 70° F</strong></td>
<td>Fuel in water, volume %</td>
<td>Negligible</td>
<td>Negligible</td>
<td>100({c})</td>
<td>100({b})</td>
<td>4.3({e})</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Water in fuel, volume %</td>
<td>Negligible</td>
<td>Negligible</td>
<td>100({c})</td>
<td>100({b})</td>
<td>1.4({e})</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Freezing point, °F</td>
<td>40(1)</td>
<td>-40–30({d})</td>
<td>-142.5</td>
<td>-173.2</td>
<td>-164({e})</td>
<td>-305.8</td>
<td>-236</td>
</tr>
<tr>
<td><strong>Viscosity</strong></td>
<td>Centipoise @ 60° F</td>
<td>0.37–0.44({x})</td>
<td>2.6–4.1</td>
<td>0.59({l})</td>
<td>1.19({l})</td>
<td>0.35({l})</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Flash point, closed cup, °F</td>
<td>165({d})</td>
<td>165({d})</td>
<td>52({e})</td>
<td>55({e})</td>
<td>-14({e})</td>
<td>-100 to -150</td>
<td>-300</td>
</tr>
<tr>
<td></td>
<td>Autoignition temperature, °F</td>
<td>495({b})</td>
<td>600</td>
<td>897({b})</td>
<td>793({b})</td>
<td>815({e})</td>
<td>850–950</td>
<td>1,004</td>
</tr>
<tr>
<td><strong>Flammability limits, volume %</strong></td>
<td>Lower</td>
<td>1.4({b})</td>
<td>1</td>
<td>7.3({e})</td>
<td>4.3({e})</td>
<td>1.6({e})</td>
<td>2.2</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Higher</td>
<td>7.9({b})</td>
<td>6</td>
<td>36({e})</td>
<td>19({e})</td>
<td>8.4({e})</td>
<td>9.5</td>
<td>15</td>
</tr>
<tr>
<td><strong>Latent heat of vaporization</strong></td>
<td>Btu/gal @ 60° F</td>
<td>≤500({b})</td>
<td>≤700</td>
<td>3.34({b})</td>
<td>2.37({b})</td>
<td>883({f})</td>
<td>775</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Btu/lb @ 60° F</td>
<td>≤150({b})</td>
<td>≤100</td>
<td>506({b})</td>
<td>396({b})</td>
<td>136({b})</td>
<td>193.1</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td>Btu/lb air for stoichiometric mixture @ 60° F</td>
<td>≤10({b})</td>
<td>≤8</td>
<td>78.4({b})</td>
<td>44({b})</td>
<td>11.8</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
### Fuel Properties

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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Heating value (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Higher (liquid fuel-liquid water)</td>
<td>18,000–20,400</td>
<td>19,200–20,000</td>
<td>9,750(2)</td>
<td>12,000(4)</td>
<td>18,290(4)</td>
<td>21,600</td>
<td>23,600</td>
<td>61,002(4)</td>
</tr>
<tr>
<td>Btu/lb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower (liquid fuel-water vapor)</td>
<td>18,000–19,000</td>
<td>18,000–19,000</td>
<td>8,570(3)</td>
<td>11,500(4)</td>
<td>15,100(4)</td>
<td>19,900</td>
<td>21,300</td>
<td>51,532(4)</td>
</tr>
<tr>
<td>Btu/lb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Higher (liquid fuel-liquid water)</td>
<td>124,800</td>
<td>138,700</td>
<td>64,250</td>
<td>84,100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Btu/gal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower (liquid fuel-water vapor)</td>
<td>115,000</td>
<td>128,400</td>
<td>56,800(5)</td>
<td>76,000(5)</td>
<td>93,500(4)</td>
<td>84,500</td>
<td>19,800(8)</td>
<td></td>
</tr>
<tr>
<td>Btu/gal @ 60° F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating value, stoichiometric mixture</td>
<td>95.2(3)</td>
<td>96.9(5, q)</td>
<td>92.5(3)</td>
<td>92.9(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixture in vapor state, Btu/cubic foot @ 60° F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel in liquid state, Btu/lb or air</td>
<td>1,290(3)</td>
<td></td>
<td>1,330(3)</td>
<td>1,280(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific heat, Btu/lb °F</td>
<td>0.49(3)</td>
<td>0.43</td>
<td>0.60(3)</td>
<td>0.57(3)</td>
<td>0.5(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichiometric air/fuel, weight</td>
<td>14.7(3)</td>
<td>14.7</td>
<td>6.49(3)</td>
<td>9(3)</td>
<td>11.7(3)</td>
<td>15.7</td>
<td>17.2</td>
<td>34.3(3)</td>
</tr>
<tr>
<td>Volume % fuel in vaporized stoichiometric mixture</td>
<td>2(3)</td>
<td></td>
<td>12.3(3)</td>
<td>6.5(3)</td>
<td>2.7(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

1. Octane values are for pure components. Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with hydrocarbons. Similar problems exist for cetane rating procedures.

2. The higher heating value is cited for completeness only. Since no vehicles in use, or currently being developed for future use, have powerplants capable of condensing the moisture of combustion, the lower heating value should be used for practical comparisons between fuels.

3. Calculated.

4. Pour Point, ASTM D 97 from Reference ( c ).

5. Based on cetane.

6. For compressed gas at 2,400 psi.

**Sources:**

(a) The basis of this table and associated references was taken from: American Petroleum Institute (API), Alcohols and Ethers, Publication No. 4261, 2nd ed. (Washington, DC, July 1988), Table B-1.


(e) ARCO Chemical Company, 1987.

Fuel Properties

(h) American Petroleum Institute Research Project 44, NBS C-461.
(l) Based on isooctane.
(n) BP America, Sohio Oil Broadway Laboratory.
(r) Value at 90 degrees F with respect to the water at 60 degrees F (Mueller & Associates).
(s) National Institute for Petroleum and Energy Research, Petroleum Product Surveys, Motor Gasolines, Summer 1992, NIPER-179 PPS 93/1 (Batresville, OK, January 1993), Table 1.