مقدمه ای بر کاتالیزورهای هتروژن

Dr. Vahid Mahmoudi
Assistant Professor,
Department of Chemical Engineering,
University of Gonabad

فصل پنجم

کاتالیزور و انرژی

FUEL CELLS

The future of energy or wishful thinking?

BRIEF HISTORY

- First Developed in 1839 by William Grove
- Improved upon by Francis Thomas Bacon 1930s-1950s
- First Commercial use by NASA
  - Pratt and Whitney
  - Apollo space vehicles

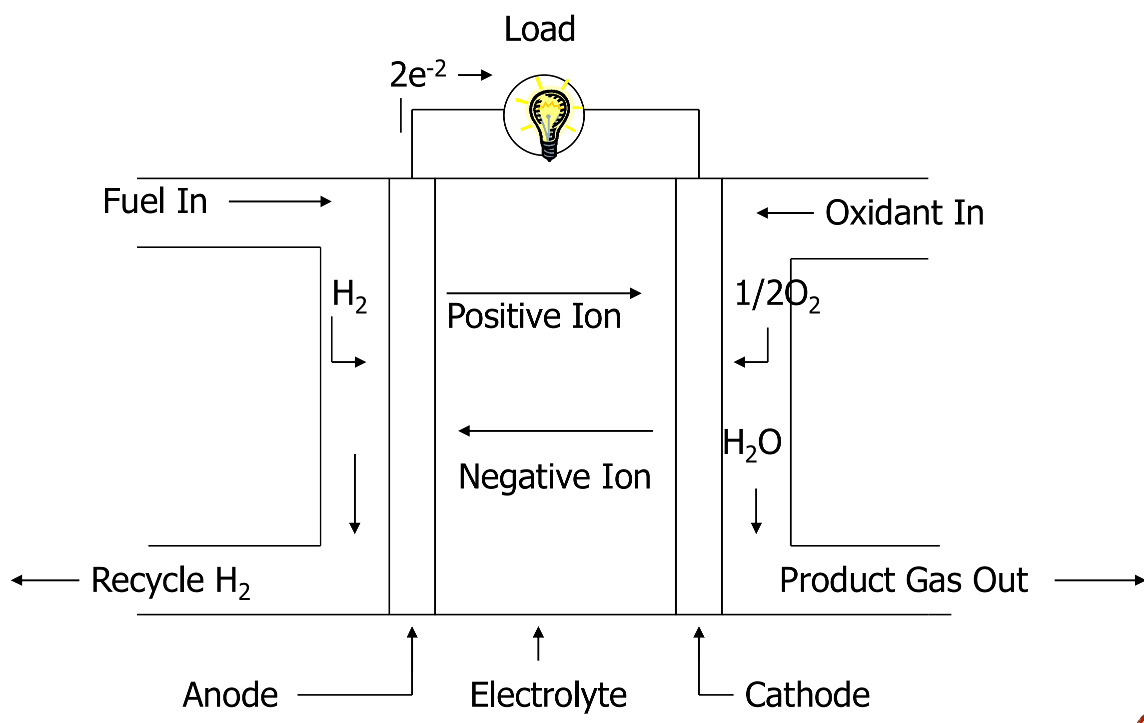
http://www.voltaicpower.com/Biographies/GroveBio.htm

TECHNOLOGY

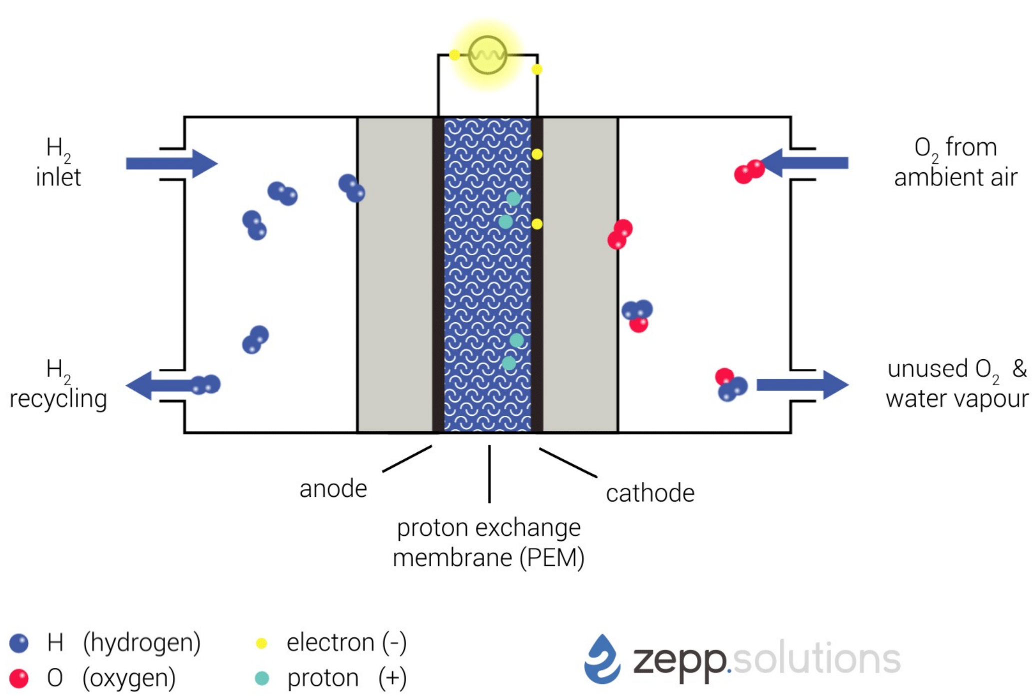
"Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy."

$$2H^{+} + \frac{1}{2} O_2 + 2e^{-1} = H_2O$$

FUEL CELL SCHEMATIC



HOW DOES A FUEL CELL WORK?

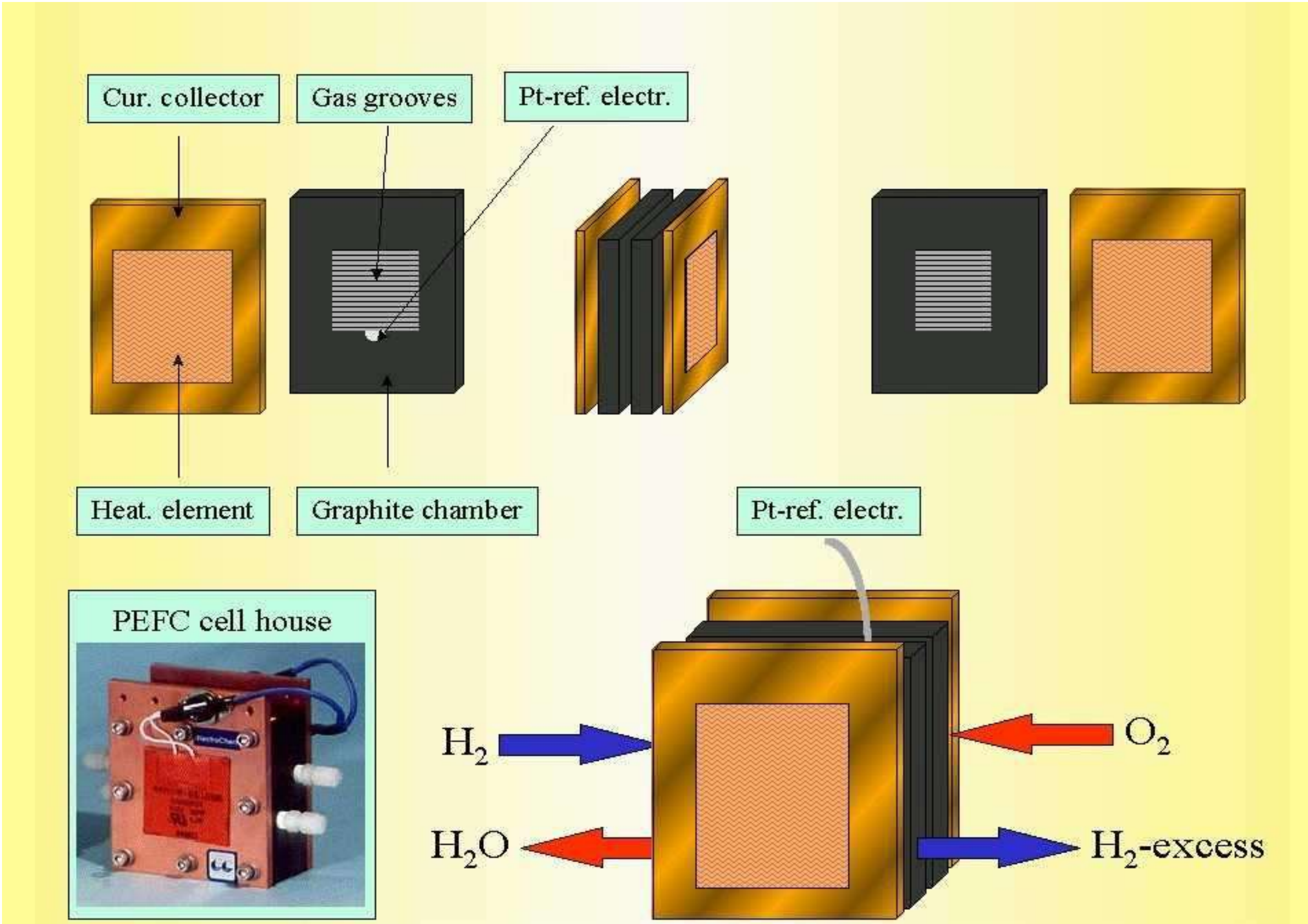


TYPES OF FUEL CELLS

- Polymer Electrolyte Fuel Cell (PEFC)
  - Proton Exchange Membrane Fuel Cell (PEMFC)
- Alkaline Fuel Cell (AFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)
  - Intermediate Temperature (ITSOFC)
  - Tubular (TSOFC)
  - Flat Plate (FPSOFC)

MAJOR DIFFERENCES

	PEFC	AFC	PAFC	MCFC	ITSOFC	TSOFC
Electrolyte	Ion Exchange Membrane	Potassium Acid	Liquid Phosphoric Acid	Liquid Molten Carbonate	Ceramic	Ceramic
Operating Temperature	80ºC	65-220ºC	205ºC	650ºC	600-800ºC	800-1000ºC
Charge Carrier	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}	O^{2-}
Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites	Perovskites



http://www.materiale.kemi.dtu.dk/FUELCELL/Pemfc.htm

ADVANTAGES/DISADVANTAGES

AFC

- Excellent performance with H_2
  - Cathode: $O_2 + 2H_2O + 4e^{-1} \rightarrow 4OH^{-1}$
  - Anode: $H_2 + 2OH^{-1} \rightarrow 2H_2O + 2e^{-1}$
- Wide range of electrocatalysts
- Low tolerance of impurities
  - $CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$
- Very Corrosive

ADVANTAGES/DISADVANTAGES

PAFC

- Tolerance of CO_2
- Less Complex Fuel Conversion
- Rejected heat and can be recycled
- Lower efficiency (37-42%)
- High Cost for precious metal catalysts
- Electrochemical Reaction:
  - Anode: $H_2 \rightarrow 2H^+ + 2e^{-1}$
  - Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^{-1} \rightarrow H_2O$

ADVANTAGES/DISADVANTAGES

MCFC

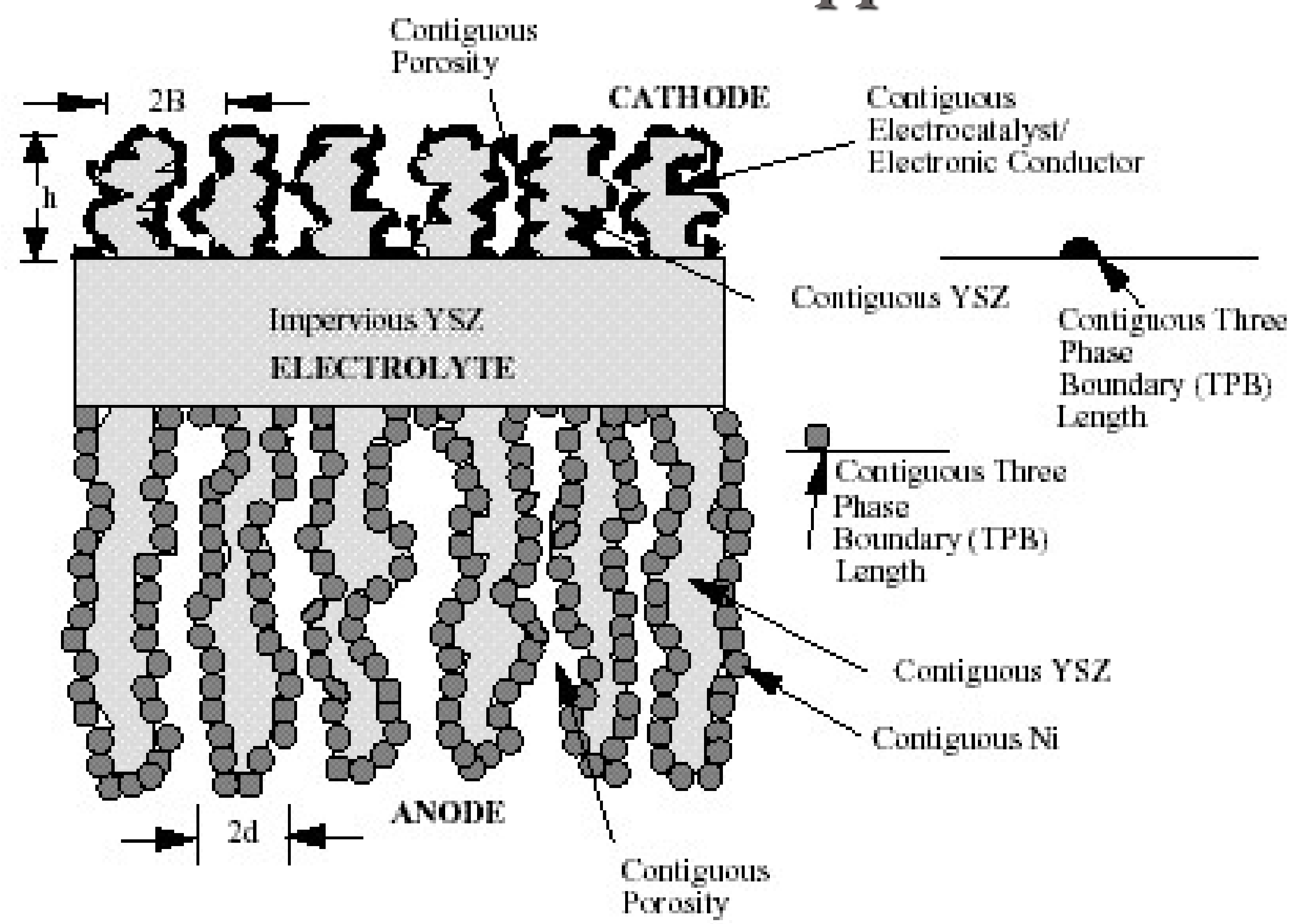
- Advantages of Higher Operating Temperature
- CO_2 tolerance
- Corrosive and mobile electrolyte
- Material problems
- Electrochemical Reaction:
  - Anode: $H_2 + CO_3^{2-} \rightarrow CO_2 + 2e^{-1}$
  - Cathode: $\frac{1}{2} O_2 + CO_2\ e^{-1} \rightarrow CO_3^{2-}$

ADVANTAGES/DISADVANTAGES

SOFC

- No corrosion or mobility
- Fast cell kinetics
- Internal reforming
- Thermal expansion mismatches (~1000°C)
- Sealing problems
- Material constraints
- Electrochemical Reaction:
  - Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^{-1}$
  - Cathode: $\frac{1}{2} O_2 + 2e^{-1} \rightarrow O^{2-}$

Schematic of Anode Supported Cell



ADVANTAGES/DISADVANTAGES

ITSOFC

- Ceramic used for electrodes and electrolytes
- Internal reforming
- No corrosion or mobility
- Electrolyte conductivity and electrode kinetics drops

BARRIERS

- Infrastructure
- Hydrogen Source
- Hydrogen Distribution and Storage
- Market Acceptance

INFRASTRUCTURE

- Fueling Stations
- Pipelines
- A mechanic that knows how to fix your car?
- Parts

"Hydrogen filling stations capable of supplying 100 vehicles a day, built in sufficient numbers to realize respective economics of scale, could sell the fuel at a price comparable to that of gasoline."

-Ford Motors

HYDROGEN SOURCE

HYDROGEN IS NOT FOUND NATURALLY, SO WHERE IS IT COMING FROM?

- Ethanol
- Methanol
- Electrolysis
- Gasoline
- Natural Gas
- Synthetic fuels
- Diesel

"Gas-to-Liquid"

$$2H_2O \rightarrow 2H_2 + O_2$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$

$$C_8H_{18} + 16O_2 \rightarrow 8CO_2 + 9H_2$$

HYDROGEN DISTRIBUTION AND STORAGE

- Compressed Hydrogen
- Liquefying Hydrogen
- Metal Hydrides
- Carbon Nanotubes
- Glass Microspheres

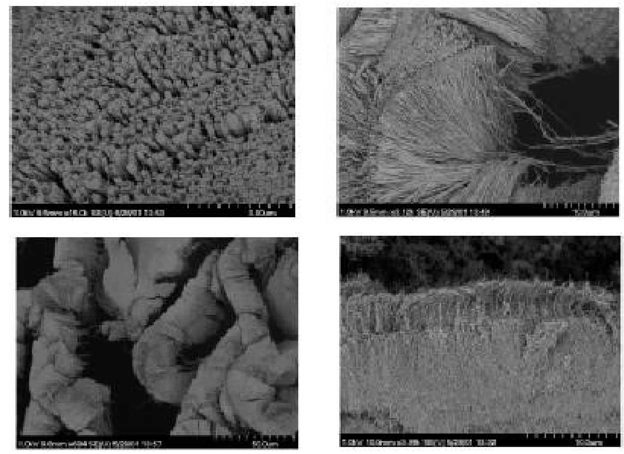


Fig. 1 Consistent structure doped carbon nanotubes

MARKET ACCEPTANCE

- Hydrogen Misconceptions

“35 people died in the flames - and nobody knew why. Sabotage? A bolt of lightning? The mystery surrounding the disaster has never been resolved - until now. In many years of research, a NASA scientist at Cape Canaveral has found proof that neither the hydrogen in the hull nor a bomb was to blame, but the fabric of the Hindenburg's outer skin and a new protective coating. A single spark of static electricity was enough to make it burn like dry leaves. The ‘infallible’ German engineers had designed a flying bomb just waiting to explode.”

http://www.vidicom-tv.com/tohiburg.htm

MARKET ACCEPTANCE

- Cost will be a major factor in the acceptance of fuel cells
- Technology and Fuel will need to be competitive with current technologies

FUEL CELLS: THE FUTURE

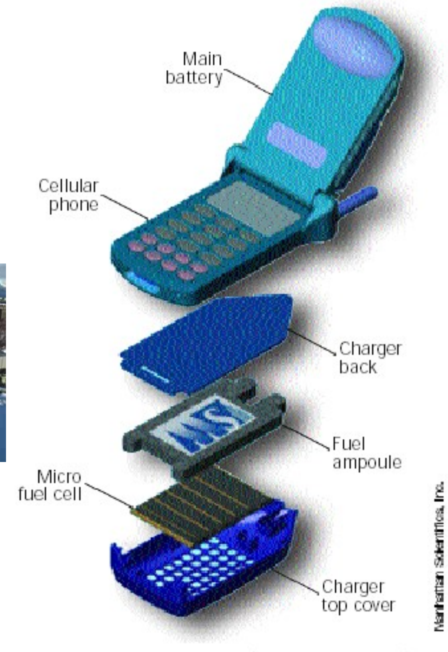
- "Fuel-cell technology is going to take a long time to bring to some sort of affordable fruition. There is not going to be a silver bullet. It is a long, slow haul, requiring a lot of consistent work in the areas of research and infrastructure, but there will be some very exciting episodes along the way with very small fleets built."

Richard Parry-Jones, Ford Group Vice President

- Ford is looking 15-25 years into the future before the fuel cell is a viable alternative to the internal combustion engine

CURRENT USES

- Appliance Applications
- Residential
- Commercial
- Transportation



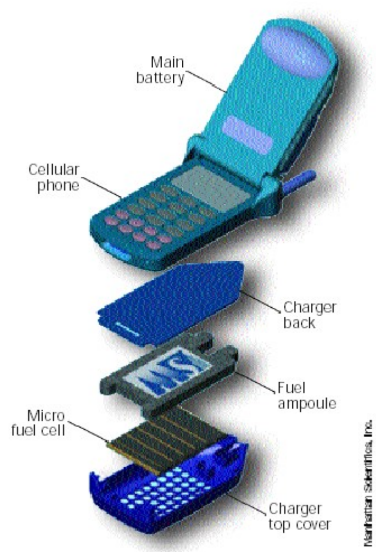
http://www.tipmagazine.com/tip/INPHFA/vol-7/iss-4/p14.pdf

http://www.ballard.com/tD.asp?pgid=32&dbid=0

http://www.hfcletter.com/letter/february00/index.html

APPLIANCE APPLICATION

- Replace the Battery in Portable Electronics
  - Cell Phones
  - Laptops
- Fuel Cell runs 20x longer cadmium batteries



RESIDENTIAL

- Solid Oxide Fuel Cells
- Stationary Fuel Cells for Homes
- UTC Fuel Cells: 5kW Proton Exchange Membrane (PEM) power plant -- called the *Energy Center*

http://www.utcfuelcells.com/residential/overview.shtml

COMMERCIAL CASE STUDY: UTC FUEL CELLS

- First National Bank of Omaha
- Anchorage Mail Processing Center
- Conde Nast Building NY, NY
- City of Portland

http://www.utcfuelcells.com/commercial/applications.shtml

TRANSPORTATION

- PEMFC
- Georgetown University
- DaimlerChrysler: Mercedes-Benz and Jeep

- http://www.fta.dot.gov/research/equip/buseq/fucell/fucell.htm

http://www.daimlerchrysler.com/index_e.htm?/news/top/2000/t01107a_e.htm

CASE STUDY: BALLARD

- CaFCP
  - ZEbus Demonstration Program
- Chicago and Vancouver Demonstration Programs
- European Fuel Cell Bus Project

California Fuel Cell Partnership
DRIVING FOR THE FUTURE

http://www.ballard.com/tD.asp?pgid=31&dbid=0

http://www.ballard.com/tD.asp?pgid=28&dbid=0

http://www.ballard.com/tD.asp?pgid=30&dbid=0

BUILDING AN INFRASTRUCTURE

- Hydrogen Filling Station in Munich, Germany
- Hydrogen Filling Station plan unveiled in Reykjavik, Iceland

WORLD WIDE HYDROGEN FUELING STATIONS

- Davis, California
- El Segundo, California
- 2X Thousand Palms, California
- Sacramento, California
- 2X Torrance, California
- Oxnard, California
- Chula Vista, California
- Richmond, California
- San Jose, California
- Chicago, Illinois
- Dearborn, Michigan
- Phoenix, Arizona
- Northern Nevada
- Torino, Italy
- 2X Munich, Germany
- 2X Hamburg, Germany
- Nabem, Germany
- Wolfsburg, Germany

- Russelsheirr, Germany
- Sindelfingen, Germany
- 2X Berlin, Germany
- Copenhager
- Lisbon
- Erlangen, Germany
- Obersidorf Spa, Germany
- Stuttgart, Germany
- Stockholm, Sweden
- London, United Kingdom
- Amsterdam, The Netherlands
- City of Luxemburg
- Oporto, Portugal
- Madrid, Spain
- Barcelona, Spain
- Reykjavik, Iceland
- Perth, Australia
- Victoria, Australia
- South Korea

- Beijing, China
- Shanghai, China
- Cairo, Egypt
- Mexico City, Mexico
- New Delhi, India
- Sao Paulo, Brazil
- Osaka, Japan
- Takamatsu, Japan
- Tsurumi, Japan
- 2X Yokohama, Japan
- Tokai, Japan
- 2X Tokyo, Japan
- Kawasaki City, Japan
- Vancouver, Canada
- Montreal, Canada
- Surrey, BC Canada
- Torino, Canada
- Oostmalle, Belgian
- Leuven, Belgian

These examples are case studies, and are by no means the only examples of fuel cells currently being utilized worldwide

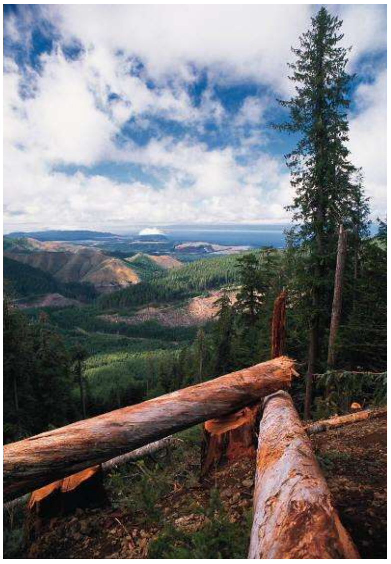
BIOMASS

BIOENERGY

- In 2001, biomass provided over half of the renewable energy in US
- Globally, biomass meets about 14% of the world's energy needs

BIOMASS

- organic matter which can be converted to energy or fuels
- Use of existing resources
  - "Cut it down, process it, then burn it"
- Active creation of organic material or "energy crops"
  - "Grow it, process it, then burn it"
- Use of plant and animal byproducts
  - "you get the picture"



FEEDSTOCKS

- Biomass byproducts used for fueling power plants
  - Wood residue
    - Mill Residues
    - Urban Wood Residues
    - Tree Trimmings
    - Forest Residues
  - Agriculture residue
    - Bagasse
    - Rice husks
  - Energy crops
    - Crops grown specifically for fuel
    - fast-growing trees, shrubs, and grasses, hybrid poplar, willow, switchgrass, and eucalyptus.

OTHER SOURCES

- Municipal Solid Waste (landfills)
- Animal waste
  - Manure, bedding from swine, cattle, poultry
- Human Waste (sewage and sludge)

COMBUSTION

Direct combustion

- burning of unprocessed material by direct heat to produce heat or steam to generate electric power
- direct combustion is the simplest biomass technology
- wood, garbage, manure, straw, and biogas

COMBUSTION

- Residential
  - burning wood fireplace or woodstove
  - pellets stoves and compacted/ manufactured logs
  - space heating, cooking
- Industry
  - Industrial biomass includes:
    - wood
    - agricultural residues
    - wood pulping liquor
    - municipal solid waste
  - Furnaces - burns fuel in a combustion chamber to create hot gases
  - Boiler - transfers the heat of combustion into steam used for electricity, mechanical energy or heat
    - pile burners
    - stationary or traveling grate combustors
    - fluidized-bed combustors.

COMBUSTION

Cogeneration

- combustion facilities that produce electricity from boilers and steam-driven turbine-generators
  - conversion efficiency of 17 to 25 percent (85% improvement of overall system efficiency)
- Bottoming Cycle:
  - steam product used first in an industrial process first and then routed through a turbine to generate electricity
- Topping Cycle:
  - steam passes first through a turbine to produce electric power and then exhaust from the turbine is then used for industrial processes or for space and water heating
  - More common process

COMBUSTION

Direct-Fired Gas Turbine

- Pretreated fuel (particle size <2mm, moisture content <25%)
- fuel burned with compressed air

Co-Firing with Coal

- secondary fuel (~20%)in a coal-burning power plant using high-sulfur coal
- decreases CO_2 emissions from the power plant

Alkali Fouling

- Allows the burning of agriculture products containing alkali compounds (K, Na)
- Special boilers with low exit temperatures to reduce slag

GASIFICATION

- Process that converts biomass into a combustible "producer" gas
  - contains carbon monoxide, hydrogen, water vapor, carbon dioxide, tar vapor and ash particles
  - 70 – 80% of potential energy from feedstock
  - gas burned directly for space heat or drying
  - gas can be burned in a boiler to produce steam
- Gas is cleaned by filters and scrubbers
  - internal combustion engine
  - fuel cells
- **Pyrolysis** (first stage of gasification) 450° to 600° C
  - Vaporization of volatile components with controlled heat in absence of air
  - carbon monoxide, hydrogen, methane, volatile tars, carbon dioxide, water and charcoal
- **Char conversion** (last stage of gasification) 700° to 1200° C
  - The charcoal residue + oxygen = carbon monoxide

DIGESTER GAS

- **Anaerobic digestion**
  - Biomass is mixed with water and then put in a digester tank without air.
  - converts organic matter to:
    - a mixture of methane and CO_2
    - syngas, a mixture of carbon monoxide and hydrogen
    - hydrogen
  - Sewage, manure, and food processing wastes

DIGESTER GAS

- **Landfill gas**
  - created from anaerobic digestion or decomposition of buried trash and garbage in landfills
  - gas generated consists of ~50% methane

BIODIESEL FUEL

- Substitute for petroleum diesel
- Made by chemical conversion process that converts oilseed crops into biodiesel fuel
  - mechanical press extraction
  - solvent extraction
- Vegetable oils, such as rapeseed, corn or safflower, can be used as a diesel fuel without further processing
- Trans-esterification
  - reduces the high viscosity of vegetable oil
  - higher-quality fuel
  - oil reacts with alcohol in the presence of a catalyst to produce glycerol and rapeseed methyl or ethyl ester (RME or REE)
  - used straight or in a blend with petroleum diesel.

FUEL ALCOHOL

Methanol (wood alcohol)

- wood and agricultural residues, but most from natural gas

- From biomass: made through high temp/pressure gasification
  - carbon monoxide and hydrogen catalyzed to condense into liquid methanol
- Fuel alternative
  - Methanol is a high-octane fuel that offers excellent acceleration and vehicle power
  - Methanol-fueled trucks and buses emit practically no particulate matter less nitrogen oxides than diesel

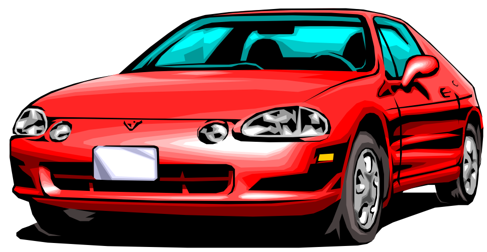
https://www.formula1.com/en/latest/article/formula-1-on-course-to-deliver-100-sustainable-fuels-for-2026.1szcnS0ehW3I0HJeelwPam

FUEL ALCOHOL

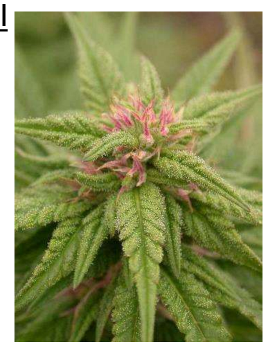
- **Ethanol (grain alcohol)**
  - converting starch to sugar → fermenting sugar to alcohol with yeast → distilling alcohol water mixture → **ethanol**
  - wheat, barley, potatoes, waste paper, sawdust, and straw contain either sugar, starch, or cellulose for fermenting
  - alternative fuel for internal combustion engines.

ETHANOL

- Ethanol is already penetrating the transportation market as gasohol as replacement fuel
- Higher blends of ethanol, specifically E85, are becoming increasingly available in certain regions of the US
- Nearly 150 stations in 20 states in the Midwest and Rocky Mountains
- All major automobile manufacturers have models that can operate on E85, gasoline, or any mixture of the two.



http://hightimes.com/photooftheweek.html

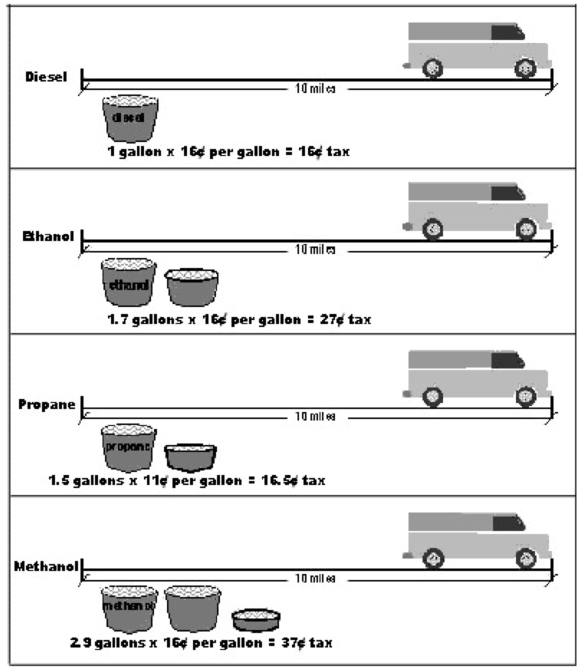


HEMP

- 10 tons per acre in four months
- contains 77% cellulose
  - compared to wood containing 60% cellulose
- requires no special equipment to plant or harvest
- drought resistant
- removes less nutrients from the soil than any other feedstock
- hemp can yield up to eight times as much methanol per acre as corn
- equals 1,000 gallons of methanol per acre per year
- hemp is perhaps the only plant capable of producing sufficient biomass to provide an alternative to fossil fuels

TAX INCENTIVES ~ RENEWABLE FUELS

- **Case Study: Hawaii**
  - Act 143 (HB1345, Relating to Energy Content of Fuels)
  - encourages use of alternative fuels (less energy per gallon)
  - adjusting the fuel tax to reflect the energy content of alternative fuels
  - reducing the fuel tax rate of alternative fuels for several years
  - Offsets discouragement to use alternative fuels that were once taxed higher



http://www.hawaii.gov/dbedt/ert/fueltax-act143.html

BIOMASS METHODS

Technology	Conversion Process Type	Major Biomass Feedstock	Energy or Fuel Produced
Direct Combustion	Thermochemical	wood agricultural waste municipal solid waste residential fuels	heat steam electricity
Gasification	Thermochemical	wood agricultural waste municipal solid waste	low or medium-Btu producer gas
Pyrolysis	Thermochemical	wood agricultural waste municipal solid waste	synthetic fuel oil (biocrude) charcoal
Anaerobic Digestion	Biochemical (anaerobic)	animal manure agricultural waste landfills wastewater	medium Btu gas (methane)
Ethanol Production	Biochemical (aerobic)	sugar or starch crops wood waste pulp sludge grass straw	ethanol
Biodiesel Production	Chemical	rapeseed soy beans waste vegetable oil animal fats	biodiesel
Methanol Production	Thermochemical	wood agricultural waste municipal solid waste	methanol

http://www.energy.state.or.us/biomass/TechChart.htm

ENVIRONMENT BENEFITS

- Theoretically inexhaustible fuel source
- Biomass absorbs carbon dioxide during growth
  - Recycling Process
- Reduce Landfill usage
- Available to produce everywhere!
- Low levels of sulfur and ash
  - Does not contribute to acid rain
- Nitrous oxide emissions can be controlled
- Co-firing with biomass helps existing power plants comply with clean-air laws

BIOMASS ECONOMICS

- In 1992, biomass grossed $1.8 billion in personal and corporate income in US
- 66,000 jobs supported by biomass energy
- economic benefits expected to triple by 2010
- supports agriculture and rural America
- Tax credits
  - 1.5 ¢/kWh relief for electricity generated from "closed-loop biomass"

BIOMASS DISADVANTAGES

- If burned directly, contributes CO_2 and particulates just like coal and petroleum!
- expensive source
  - producing the biomass and converting it to alcohols
- On a small scale there is most likely a net loss of energy
  - energy must be put in to grow the plant mass!

Any Question?