HYDROGEN PRODUCTION

Natural gas reforming is an advanced and mature production process that builds upon the existing natural gas pipeline delivery infrastructure. Today, 95% of the hydrogen produced in the United States is made by natural gas reforming in large central plants. This is an important technology pathway for near-term hydrogen production.

How Does It Work?

Natural gas contains methane (CH_4) that can be used to produce hydrogen with thermal processes, such as steam-methane reformation and partial oxidation.

Although today most hydrogen is produced from natural gas, the Fuel Cell Technologies Office is exploring a variety of ways to produce hydrogen from renewable resources.

STEAM-METHANE REFORMING

Most hydrogen produced today in the United States is made via steam-methane reforming, a mature production process in which high-temperature steam (700°C–1,000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic—that is, heat must be supplied to the process for the reaction to proceed.

Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

Steam-methane reforming reaction
$CH_4 + H_2O$ (+ heat) $\rightarrow CO + 3H_2$

Water-gas shift reaction
$CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

PARTIAL OXIDATION

In partial oxidation, the methane and other hydrocarbons in natural gas react with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and carbon monoxide (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of carbon dioxide and other compounds. Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen.

Partial oxidation is an exothermic process—it gives off heat. The process is, typically, much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction
$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (+ heat)

Water-gas shift reaction
$CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

Why Is This Pathway Being Considered?

Reforming low-cost natural gas can provide hydrogen today for fuel cell electric vehicles (FCEVs) as well as other applications. Over the long term, DOE expects that hydrogen production from natural gas will be augmented with production from renewable, nuclear, coal (with carbon capture and storage), and other low-carbon, domestic energy resources.

Petroleum use and emissions are lower than for gasoline-powered internal combustion engine vehicles. The only product from an FCEV tailpipe is water vapor but even with the upstream process of producing hydrogen from natural gas as well as delivering and storing it for use in FCEVs, the total greenhouse gas emissions are cut in half and petroleum is reduced over 90% compared to today's gasoline vehicles.

The U.S. Department of Energy (DOE) Office of Fossil Energy supports activities to advance coal-to-hydrogen technologies, specifically through the process of coal gasification with carbon capture, utilization, and storage. DOE anticipates that coal gasification for hydrogen production with carbon capture, utilization, and storage could be deployed in the mid-term time frame.

HOW DOES IT WORK?

Chemically, coal is a complex and highly variable substance that can be converted into a variety of products. The gasification of coal is one method that can produce power, liquid fuels, chemicals, and hydrogen. Specifically, hydrogen is produced by first reacting coal with oxygen and steam under high pressures and temperatures to form synthesis gas, a mixture consisting primarily of carbon monoxide and hydrogen.

Coal gasification reaction (unbalanced):
$CH_{0.8} + O_2 + H_2O \rightarrow CO + CO_2 + H_2$ + other species

After the impurities are removed from the synthesis gas, the carbon monoxide in the gas mixture is reacted with steam through the water-gas shift reaction to produce additional hydrogen and carbon dioxide. Hydrogen is removed by a separation system, and the highly concentrated carbon dioxide stream can subsequently be captured and stored. Learn more about carbon capture, utilization, and storage.

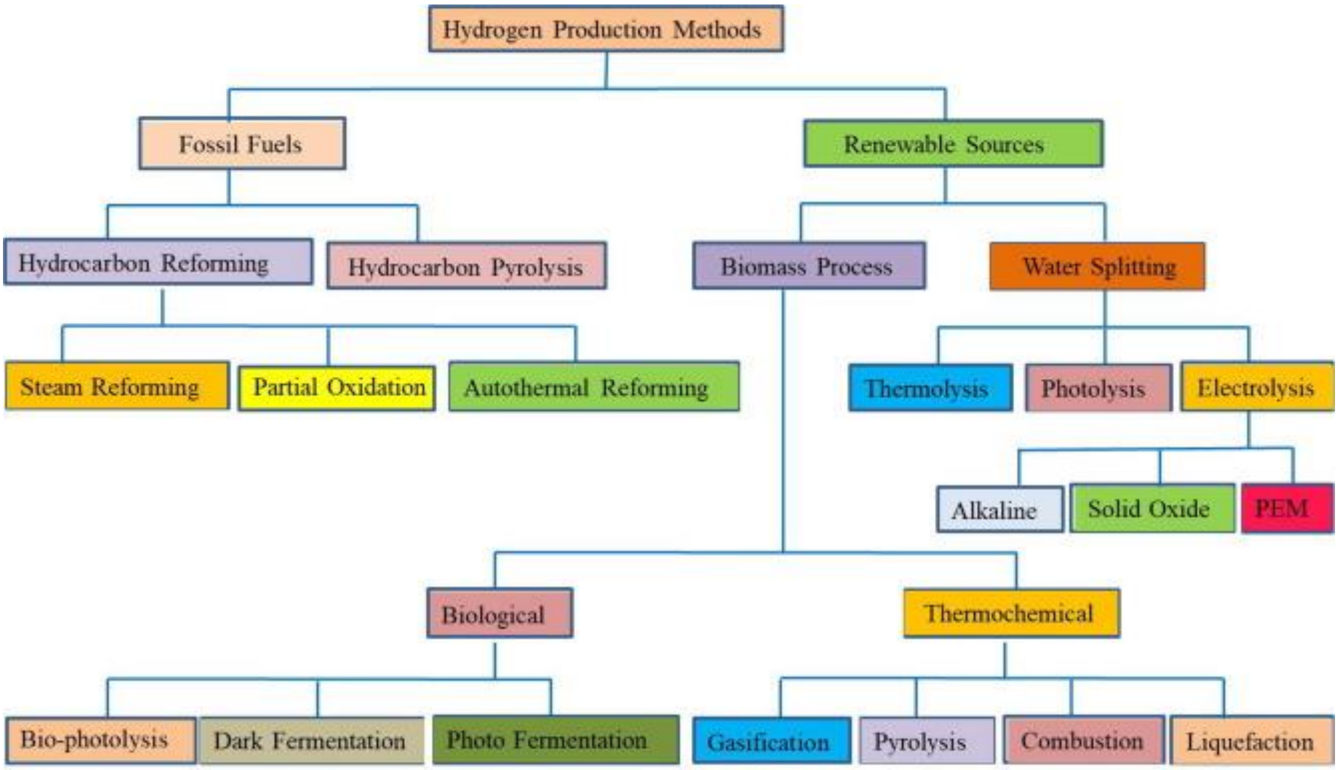
WHY IS THIS PATHWAY BEING CONSIDERED?

The United States has an abundant, domestic resource in coal. The use of coal to produce hydrogen for the transportation sector can reduce America's total energy use and its reliance on imported petroleum while helping create jobs through the creation of a domestic industry. The production of hydrogen from coal also offers environmental benefits when integrated with advanced technologies in coal gasification, power production, and carbon capture, utilization, and storage. The integration of these technologies facilitates the capture of multiple pollutants such as sulfur oxides, nitrogen oxides, mercury, and particulates, as well as greenhouse gases such as carbon dioxide. When hydrogen is used in efficient fuel cell vehicles, emissions from the transportation sector can be nearly eliminated.

RESEARCH FOCUSES ON OVERCOMING CHALLENGES

There are several challenges to using coal gasification to produce hydrogen at target costs and with near-zero greenhouse gas emissions. Additional R&D is needed to:

- Develop carbon capture, utilization, and storage technologies that ensure minimal carbon dioxide is released in the production process
- Develop new technologies that can replace the cryogenic process currently used to separate the required oxygen from air.



Hydrogen production Method	**Advantages**	**Disadvantages**	**Efficiency**
Steam Reforming	Developed technology & Existing infrastructure	Produced CO, CO_2 Unstable supply	74–85
Partial Oxidation	Established technology	Along with H_2 Production, produced heavy oils and petroleum coke	60–75
Auto thermal Reforming	Well established technology & Existing infrastructure	Produced CO_2 as a byproduct, use of fossil fuels.	60–75
Bio photolysis	Consumed CO_2, Produced O_2 as a byproduct, working under mild conditions.	Low yields of H_2, sunlight needed, large reactor required, O_2 sensitivity, high cost of material.	10–11
Dark Fermentation	Simple method, H_2 produced without light, no limitation O_2, CO_2-neutral, involves to waste recycling	Fatty acids elimination, low yields of H_2, low efficiency, necessity of huge volume of reactor	60–80
Photo Fermentation	Involves to waste water recycling, used different organic waste waters, CO_2-neutral.	low efficiency, Low H_2 production rate, sunlight required, necessity of huge volume of reactor, O_2-sensitivity	0.1
Gasification	Abundant, cheap feedstock and neutral CO_2.	Fluctuating H_2 yields because of feedstock impurities,	30–40

Hydrogen production Method	Advantages	Disadvantages	Efficiency
		seasonal availability and formation of tar.	
Pyrolysis	Abundant, cheap feedstock and CO_2-neutral.	Tar formation, fluctuating H_2 amount because of feedstock impurities and seasonal availability	35–50
Thermolysis	Clean and sustainable, O_2-byproduct, copious feedstock	High capital costs, Elements toxicity, corrosion problems.	20–45
Photolysis	O_2 as byproduct, abundant feedstock, No emissions.	Low efficiency, non-effective photocatalytic material, Requires sunlight.	0.06
Electrolysis	Established technology Zero emission Existing infrastructure O_2 as byproduct	Storage and Transportation problem.	60–80

However, hydrogen production efficiency through water electrolysis is very low to be economically competitive due to the high energy consumption and low hydrogen evolution rate. Therefore in order to increase the efficiency and reduce the energy consumption, many researchers have been done their work related to development of alternative low cost electrocatalysts, efficiency and energy reduction. In this review, various hydrogen production methods from renewable energy sources along with recent developments on efficiency, durability, cost effective electrocatalysts and its challenges have been discussed and summarized.

Hydrogen as a fuel

Hydrogen is considered an alternative fuel. It is due to its ability to power fuel cells in zero-emission electric vehicles, its potential for domestic production, and the fuel cell's potential for high efficiency. In fact, a fuel cell coupled with an electric motor is two to three times more efficient than an internal combustion engine running on gasoline. Hydrogen can also serve as fuel for internal combustion engines. The energy in 2.2 pounds (1 kilogram) of hydrogen gas contains about the same as the energy in 1 gallon (6.2 pounds, 2.8 kilograms) of gasoline.

Potential Applications

- Production of electricity, heat and water for various end uses
- Industrial applications
- Vehicular transportation
- Residential applications
- Commercial applications, including in telecom towers for providing back-up power

Advantages and disadvantages of Hydrogen fuel cells

Advantages

- **It is readily available**. It is a basic earth element and is very abundant. However, it time consuming to separate hydrogen gas from its companion substances. While that may be the case, the results produce a powerful clean energy source.
- **It doesn't produce harmful emissions.** When it is burned, it doesn't emit harmful substances. Basically, it reacts with oxygen without burning and the energy it releases can be used to generate electricity used to drive an electric motor. Also, it doesn't generate carbon dioxide when burnt, not unlike other power sources.
- **It is environmentally friendly**. It is a non-toxic substance which is rare for a fuel source. Others such as nuclear energy, coal and gasoline are either toxic or found in places that have hazardous environments. Because hydrogen is friendly towards the environment, it can be used in ways that other fuels can't even possibly match.
- **It can be used as fuel in rockets.** It is both powerful and efficient. It is enough to provide power for powerful machines such as spaceships. Also, given that it is environmentally friendly, it is a much safer choice compared to other fuel sources. A fun fact: hydrogen is three times as powerful as gasoline and other fossil fuels. This means that it can accomplish more with less.
- **It is fuel efficient.** Compared to diesel or gas, it is much more fuel efficient as it can produce more energy per pound of fuel. This means that if a car is fueled by hydrogen, it can go farther than a vehicle loaded with the same amount of fuel but using a more traditional source of energy. Hydrogen-powered fuel cells have two or three times the efficiency of traditional combustion technologies. For example, a conventional combustion-based power plant usually generates electricity between 33 to 35 percent efficiency. Hydrogen fuel cells are capable of generating electricity of up to 65 percent efficiency.
- **It is renewable**. It can be produced again and again, unlike other non-renewable sources of energy. This means that with hydrogen, you get a fuel source that is limited. Basically, hydrogen energy can be produced on demand.

Disadvantages

- **It is expensive.** While widely available, it is expensive. A good reason for this is that it takes a lot of time to separate the element from others. If the process were really simple, then a lot would have been doing it with relative ease, but it's not. Although, hydrogen cells are now being used to power hybrid cars, it's still not a feasible source of fuel for everyone. Until technology is developed that can make the whole process a lot more simpler, then hydrogen energy will continue to be an expensive option.
- **It is difficult to store.** Hydrogen is very hard to move around. When speaking about oil, that element can be sent though pipelines. When discussing coal, that can be easily carried off on the back of trucks. When talking about hydrogen, just moving even small amounts is a very expensive matter. For that reason alone, the transport and storage of such a substance is deemed impractical.
- It is not easy to replace existing infrastructure. Gasoline is still being widely used to this day. And as of the moment, there just isn't any infrastructure that can support hydrogen as fuel. This is why it becomes highly expensive to just think about replacing gasoline. Also, cars need to be refitted in order to accommodate hydrogen as fuel.
- **It is highly flammable.** Since it is a very powerful source of fuel, hydrogen can be very flammable. In fact, it is on the news frequently for its many number of risks. Hydrogen gas burns in air at very wide concentrations – between 4 and 75 percent.
- It is dependent on fossil fuels. Although hydrogen energy is renewable and has minimal environmental impact, other non-renewable sources such as coal, oil and natural gas are needed to separate it from oxygen. While the point of switching to hydrogen is to get rid of using fossil fuels, they are still needed to produce hydrogen fuel.

Applications of Hydrogen as an energy source in India

Current sources of Hydrogen production in India

- Hydrogen is a by - product in Chlor - Alkali industries. Earlier, a part of it was used for non - energy applications and rest was either flared or vented out in the atmosphere. With the passage of time awareness about its usage for energy applications increased and up to 2013 - 14 around 90% of by - product hydrogen was utilized for production of chemicals and captive (mainly energy) applications.
- Hydrogen is produced for non - energy applications e.g. in fertilizer industries and petroleum refineries.

National Hydrogen Energy Road Map (NHERM)

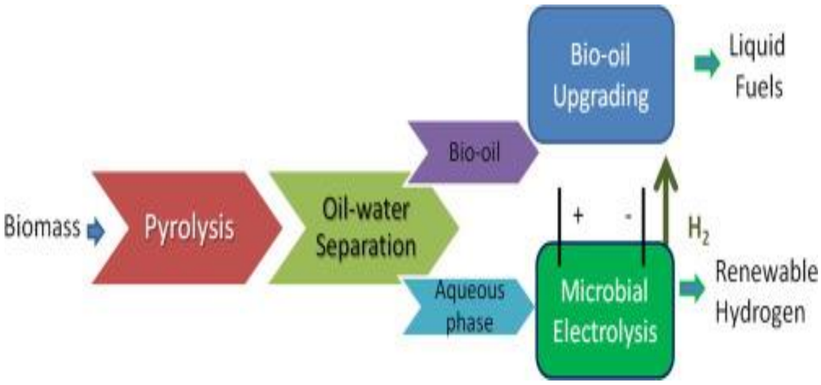
With a view to accelerate development of hydrogen energy sector in India, a National Hydrogen Energy Road Map (NHERM) was prepared and adopted by the National Hydrogen Energy Board in January, 2006 for implementation. The main objective of NHERM was to identify the pathways, which will lead to gradual introduction of hydrogen energy, accelerate commercialization efforts and facilitate the creation of hydrogen energy infrastructure in the country. NHERM covered all aspects of hydrogen energy development in India including its production, storage, transport, delivery, application, codes & standards, public awareness and capacity building. NHERM formed the basis for implementation of Hydrogen Energy Progamme in the country from 2006 - 07 onwards. NHERM suggested modifying and upgrading it later based on field experience in the country and new developments worldwide. Accordingly, a Steering Committee on Hydrogen Energy and Fuel Cells was constituted by the Ministry of New and Renewable Energy (MNRE) which has submitted its report - *Hydrogen energy and Fuel Cells in India—A way forward.*

The Ministry of New and Renewable Energy also supports research, development and demonstration projects on various aspects of hydrogen energy including its production, storage and use as a fuel for generation of mechanical/thermal/electrical energy. As a result, Hydrogen fueled small power generating sets, two wheeler (motor cycles), three wheeler, catalytic combustion systems for residential and industrial sectors and fuel cell buses have also been developed and demonstrated.

Hydrogen might be the most abundant element on earth but it can be found rarely in its pure form.

Practically, this fact means that in order to produce hydrogen, it needs to be extracted from its compound.

Of course, this extraction process needs energy but hydrogen can be produced or extracted using virtually any primary source of energy, be it fossil or renewable. Characteristically, hydrogen can be produced using diverse resources including fossil fuels, such as natural gas and coal, biomass, non-food crops, nuclear energy and renewable energy sources, such as wind, solar, geothermal, and hydroelectric power to split water. This diversity of potential supply sources is THE most important reason why hydrogen is such a promising energy carrier.



Water-gas shift reaction
$CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

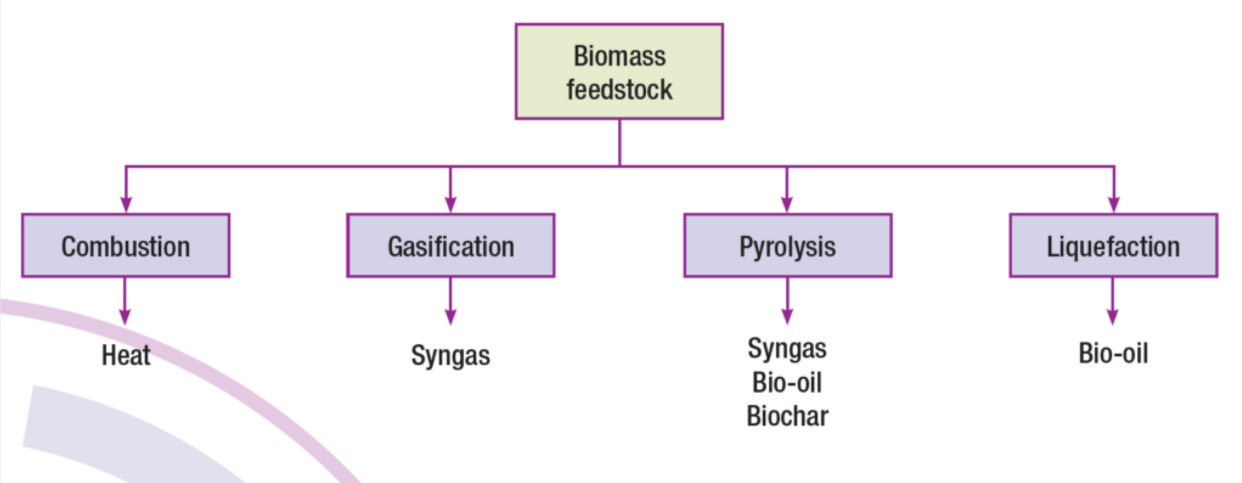
Pyrolysis is the gasification of biomass in the absence of oxygen. In general, biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier; this is especially true when no oxygen is used. As a result, typically an extra step must be taken to reform these hydrocarbons with a catalyst to yield a clean syngas mixture of hydrogen, carbon monoxide, and carbon dioxide. Then, just as in the gasification process for hydrogen production, a shift reaction step (with steam) converts the carbon monoxide to carbon dioxide. The hydrogen produced is then separated and purified.

Gasification

Gasification is the partial oxidation of biomass at high temperatures (over 700°C) in the presence of a gasification agent, which can be steam, oxygen, air or a combination of these. The resulting gas mixture is called syngas or producer gas, and can be used in various processes to produce liquid fuels such as methanol, ethanol and Fischer-Tropsch diesel, and gaseous fuels, such as hydrogen and methane.

Syngas is comprised mainly of hydrogen and carbon monoxide, but could also contain methane, carbon dioxide, light hydrocarbons (e.g. ethane and propane) and heavy hydrocarbons (e.g. tars). Undesirable gases, such as hydrogen sulfide may also be present. The composition of the syngas depends on the type of biomass, the gasifier, the gasification agent, and on the temperature used in the process. Generally, when the biomass has high content of carbon and oxygen, the syngas produced via gasification is rich in carbon monoxide and carbon dioxide.

The most common biomass feedstocks used in the gasification process to produce biofuels are different kinds of wood, forestry wastes and agricultural residues. The heat for the high temperature gasification process can be supplied either directly by oxidation of part of the biomass in the gasifier, or indirectly by transferring energy to the gasifier externally.



Thermochemical conversion processes and the energy carriers produced.

Pyrolysis

Pyrolysis is the thermal decomposition of biomass to liquid, solid and gaseous fractions at high temperatures in the absence of oxygen in order to avoid significant levels of combustion. The liquid fraction is called bio-oil or bio-crude; a dark brown, viscous liquid with a high density, composed by a mixture of oxygen-containing organic compounds. Due to its high oxygen content, bio-oil is not suitable for direct use as a drop-in transportation fuel. However, it can be easily transported and stored, and after upgrading it has the potential to substitute crude oil, which makes it the most interesting product of pyrolysis. The solid fraction obtained from pyrolysis is called biochar, i.e. charcoal made from biomass, and the gasous fraction is syngas. The relative proportions of these fractions depend on the type of reactor employed and the feedstock used. It is controlled by varying the temperature, the heating rate and the residence time of the material in the reactor.

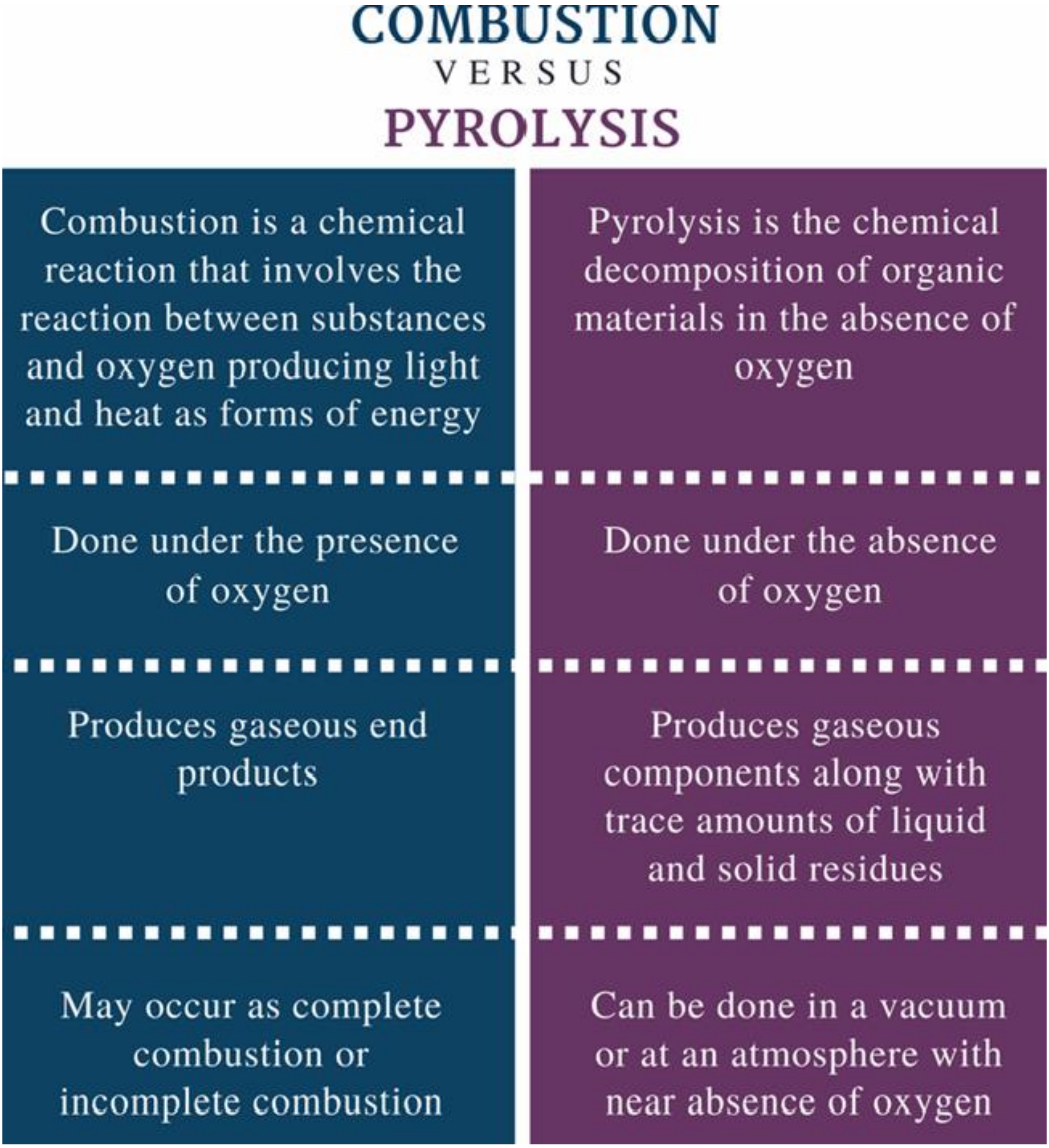
Depending on the heating rate employed, there are three main types of pyrolysis processes: slow, fast and flash pyrolysis. Slow pyrolysis has been used for thousands of years for the production of solid fuel. It is a decomposition process at relatively low temperatures (up to 500°C) and low heating rates (below 10°C/min), which takes several hours to complete, and results in solid biochar as the main product.

Fast pyrolysis is currently the most widely used process. It occurs at controlled temperature of around 500°C employing relatively high heating rates and only takes a few seconds to complete. The key product from fast pyrolysis is bio-oil (60-75%). In addition, biochar (15-25%) and syngas (10-20%) are also produced.

When heating rates and reaction temperatures are even higher, and the reaction time is shorter than that of fast pyrolysis, the process can be described as flash pyrolysis. Flash pyrolysis can result in a high yield of bio-oil and high conversion efficiencies (up to 70-75%).

Liquefaction

Hydrothermal liquefaction is the conversion of biomass to bio-oil in the presence of water, with or without a catalyst. During hydrothermal liquefaction, large compounds in the biomass are broken down into unstable shorter molecules that in turn reattach to each other and form bio-oil. In contrast to pyrolysis and gasification, the liquefaction process does not require the use of dry biomass, which reduces the cost of drying. The resulting bio-oil has lower oxygen content than the bio-oil obtained from pyrolysis, and therefore, it requires less upgrading prior to utilization as a transportation fuel.



NOTE:Pyro = heat. Lysis = break down.

Geothermal resources are generally **classified** according to reservoir temperature as low temperature (<90°C), intermediate temperature (90°C–150°C), and high temperature (>150°C) (Dickson and Fanelli, 1990).

Pyrolysis is a **process** of chemically decomposing organic materials at elevated temperatures in the absence of oxygen. The **process** typically occurs at temperatures above 430 °C (800 °F) and under pressure. ... The word **pyrolysis** is coined from the Greek words "pyro" which means fire and "lysis" which means separating.

Photolysis, chemical **process** by which molecules are broken down into smaller units through the absorption of light.

THE BENEFITS OF HYDROGEN WILL HELP MOVE US TO A SUSTAINABLE ENERGY ECONOMY.

To better understand hydrogen's benefits, we can first review some of the present concerns with the structure of the existing energy economy.

Four realities suggest that the current energy economy is not sustainable:

1. The demand for energy is growing and the raw materials for the fossil fuel economy are diminishing. Oil, coal, and natural gas supplies are not replenished as it is consumed, so an alternative must be found.
2. Most of the people who consume fossil fuels don't live where fuels are extracted. This situation creates enormous economic motivation for the consuming nations to try to exert control over the regions that supply the fuels. For many people and governments in the world, the resulting conflicts are unacceptable.
3. Emissions from fossil fuel usage significantly degrade air quality all over the world, especially in Northeastern United States. The resulting carbon byproducts are substantially changing the world's climate. For many people and governments in the world the resulting health and climate impacts are unacceptable.
4. Third world economies are especially susceptible when developing energy systems needed to improve their economies. The fossil fuel economy puts people and nations under the undue influence of energy suppliers. This lack of economic independence is unacceptable to many businesses and governments.

Hydrogen has three basic benefits that address these concerns.

1. **The use of hydrogen greatly reduces pollution.** When hydrogen is combined with oxygen in a fuel cell, energy in the form of electricity is produced. This electricity can be used to power vehicles, as a heat source and for many other uses. The advantage of using hydrogen as an energy carrier is that when it combines with oxygen the only byproducts are water and heat. No greenhouse gasses or other particulates are produced by the use of hydrogen fuel cells.
2. **Hydrogen can be produced locally from numerous sources.** Hydrogen can be produced either centrally, and then distributed, or onsite where it will be used. Hydrogen gas can be produced from methane, gasoline, biomass, coal or water. Each of these sources brings with it different amounts of pollution, technical challenges, and energy requirements.
3. **If hydrogen is produced from water we have a sustainable production system** . Electrolysis is the method of separating water into hydrogen and oxygen. Renewable energy can be used to power electrolyzers to produce the hydrogen from water. Using renewable energy provides a sustainable system that is independent of petroleum products and is nonpolluting. Some of the renewable sources used to power electrolyzers are wind, hydro, solar and tidal energy. After the hydrogen is produced in an electrolyzer it can be used in a fuel cell to produce electricity. The byproducts of the

fuel cell process are water and heat. If fuel cells operate at high temperatures the system can be set up as a co-generator, with the waste energy used for heating.