Journal of Equity in Science and Sustainable Development

Vol. 3(2):32-40
Article Number: JESSD19.10.2018
ISSN 2523-1901(Online)
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URL:http://jessd.mwu.edu.et/index.php/jessd
Email: jessd@mwu.edu.et

A Review

The Essence of Hydrogen Fuel in Harmonizing Energy Supply and Environmental Safety

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Received October 19, 2018 Accepted February 19, 2019 Published June, 2019

Abstract

In this article, the essence of hydrogen fuel in harmonizing energy supply and environmental safety is reviewed. It is found that, currently, hydrogen is produced globally about 50% through steam reforming of natural gas, 30% through oil/naphtha reforming, 18% through coal gasification, 3.9% through water electrolysis, and 0.1% through other sources and methods. That is, globally, 4% of H_2 is producing from renewable and sustainable sources with no environmental pollution. In most cases production of H_2 in large scale from renewable and sustainable sources with no environmental pollution is not matured and widespread. However, H_2 is a globally accepted clean and sustainable fuel when it is produced from renewable sources such as biomass and water through processes with no environmental pollution. Mainly H_2 is clean fuel for all end user applications since its application in fuel cells and combustion engines never release green house gases.

Key words: Energy supply, environmental safety, hydrogen fuel, hydrogen production

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Introduction

As the world's demand for energy increases, scientists are researching new energy source and alternative fuels, including hydrogen (Chevron Corporation, 2009). As an additional problem the current source of energy like fossil fuels causes green house effect that degrades the beauty of environment. In addition, fossil fuels are not renewable source for sustainable energy supply. Today, the world requires a unique method of reducing dependency on fossil fuel and increasing the contribution of clean, sustainable and efficient renewable energy sources. Now a days, there is an increasing interest in hydrogen as an energy carrier because it creates almost no pollution as in fuel cells which employ hydrogen as a fuel. It is a clean fuel with no green house gas emissions.

Hydrogen is a tasteless, odorless, colorless and lightest gas. It is the most abundant element in the universe (70%). However, it is not found freely in nature rather in trace amount. Water, biomass and fossil fuels are the major sources of hydrogen. Hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times more than an average hydrocarbon fuel (Caio, 2007). The major problem in utilizing of hydrogen gas as a fuel is its non-availability in enough amount in free state and the need for inexpensive production methods as well as storage in small volume. However, energy has to be consumed in order to separate it from hydrocarbons or water. Source of the energy used in hydrogen production is also crucial issue. This energy can be renewable such as either solar or wind energy. If so, it is possible to produce hydrogen using a non-polluting process. Hence, method and source for hydrogen production are the decisive parameters for both environmental and energy supply issues. There is huge range of possibility to provide H_2 from different primary sources. However, renewable sources of hydrogen such as ethanol are best alternatives in most aspects.

Ethanol can be produced renewably from several biomass sources. It has many advantages related to its natural availability, storage and handling than fossil fuel derived sources. It has low toxicity and volatility nature which makes it easier and safer to store and transport it. In addition, the CO_2 released during steam reforming of ethanol is consumed in biomass growth. Hence, steam reforming of ethanol is nearly CO_2 neutral, thus offering a nearly closed carbon loop while the use of methanol and gasoline adds to CO_2 emission (Caio, 2007). The most effective process for H_2 production from ethanol is the steam reforming reaction (**Reaction 1**).

$C_2H_5OH(l) + 3H_2O(l) \rightarrow 6H_2(g) + 2CO_2(g)$; $\Delta H^0_{298K} = +157\ kJ\ mol^{-1}$ …….**Reaction 1**

Indeed, hydrogen can be produced through various processes such as natural gas reforming, biomass and coal gasification, electrolytic water splitting using a variety of energy resources, and photolytic splitting of water using sunlight through biological and electrochemical materials (Funk, 2000; Schultz, 2003; Balat *et al.*, 2010; Kalamaras *et al.*, 2013).

Hydrogen Production Technologies

With respect to the energy required, it is easy to remove hydrogen from substances that are at a higher energy state, such as fossil fuels. This process releases energy, reduces the amount of process energy required. It takes more energy to extract hydrogen from compounds that are at a lower energy state, such as water, as energy has to be added to the process (Caio, 2007). There is huge range of possibility to provide H_2 from different primary sources. Nowadays, the estimated annual production of hydrogen reaches 55 million tons and its consumption is increasing by approximately 6% per year (Kalamaras *et al.*, 2013). Up-to-date, the methods for H_2 production are mainly based on nonrenewable fossil fuels (Chevron Corporation, 2009; Umegaki *et al.*, 2009). Currently, hydrogen is produced globally about 50% through steam reforming of natural gas, 30% through oil/naphtha reforming, 18% through coal gasification, 3.9% through water electrolysis, and 0.1% through other sources and methods (Balat *et al.*, 2010; Kalamaras *et al.*, 2013). However, technologies which use renewable feed stock and having safe friendship with environment are very attractive and acceptable. Renewable sources such as solar and biomass have attracted much attention as H_2 resource to achieve the full environmental benefit for generating power with H_2 fuel cells (Braden, 2005; Umegaki *et al.*, 2009).

From the renewable source and environmental safety point of view, feed stocks derived from biomass, and water is the best sources of hydrogen. For instance, 3/4th of our universe is covered by water. And if inexpensive technology is developed to produce hydrogen from water; more than enough, sustainable and clean energy can be obtained. Methane, methanol, ethanol, ammonia, gasoline, natural gas and other hydrocarbons can be possible feedstock's of hydrogen production. Ethanol is preferable than others as H_2 source. This is because ethanol can be easily produced from biomass by fermentation (Umegaki *et al*., 2009). In addition, ethanol is easier to reform than gasoline or natural gas with lower energy input (Braden, 2005). As the U.S. Department of Energy (2008) report, Steam–Methane Reforming requires 700-1000°C whereas steam ethanol reforming requires 500 ^{0}C in average. Some chemical species like methanol and ammonia have toxic nature and, ammonia can be source of oxides of nitrogen (Caio, 2007). Generally, the technologies for producing H_2 fall into four broad categories: photo-biological, photo-electrochemical, electro-chemical and thermo-chemical (Ruggiero, 2006).

Photo-biological Technology

Photo-biological systems generally use the natural photosynthetic activity of bacteria and green algae to produce H_2. One major limitation of this technology is the relatively slow production rate (Ruggiero, 2006). Even though this process has low environmental impact, it is difficult to produce hydrogen in large scale as other technologies.

Photo-electrochemical Technology

Photo-electrochemical process is a process which produces H_2 from water by illuminating a water-immersed semiconductor with sunlight. In this system, the semiconductor uses light energy to directly dissociate water molecules into hydrogen and oxygen. Different semiconductor materials work at particular wavelengths of light and energies. Photo-electrochemical water splitting is not matured technology at this time. Some of the major obstacles of this process are; poor matching of the semiconductor band gap with the solar spectra, instability of the semiconductor materials in the aqueous phase, difference between the semiconductor band edges and the electrochemical reactions, and poor kinetics of the H_2 generation reaction (Ruggiero, 2006).

Electrochemical Technology

Water electrolysis process which involves decomposition of water into hydrogen and oxygen using electricity. Water Electrolysis is energy-intensive and to decompose it, an energy input equal to an enthalpy change of 286 kJ/mol is required (**Reaction 2**).

$$H_2O\ (l) \rightarrow H_2\ (g) + 1/2O_2\ (g);\ \Delta H^0_{298K} = +286\ \text{kJ/mol}\ldots\ldots\ldots(\textbf{Reaction 2})$$

Electrolysis process is performed with the help of an electrolyzer. An electrolyzer is a series of cells each with a positive and negative electrode. The electrodes are immersed in water that has been made electrically conductive. It requires the input of large amounts of electrical energy (Caio, 2007; Ruggiero, 2006). As Ruggiero (2006) stated in his literature, energy requirement of current electrolysis system ranges from 53.4 to 70.1 kWh/kg of H_2 produced. Water electrolysis has been used for some time as an industrial process to produce hydrogen and is especially attractive in areas where electricity is abundant and inexpensive (Funk, 2000).

Thermo-chemical Processes

Some thermal processes use the energy in various resources, such as natural gas, coal, or biomass, to release hydrogen. In other processes, heat, in combination with closed-chemical cycles, produces hydrogen from feedstocks such as water - these are known as "thermo-chemical" processes (U.S. Department of Energy, 2009).

Gasification

Gasification is a type of thermo-chemical process used in hydrogen production. Hydrogen can be produced from a range of hydrocarbon fuels by gasification process. Gasification and pyrolysis processes are used when the feedstocks are solids (such as coal, wood, and other biomass) or semisolid (such as heavy or residual oils) (Ruggiero, 2006; Caio, 2007;). In gasification process, the hydrocarbon fuel is reacted with oxygen (in a less than stoichiometric ratio), and steam yielding a mixture of CO and hydrogen at 1200°C to 1350°C. The gasifier uses steam and air to partially oxidize sources like coal into gaseous product, and make use of the exothermic gasification reactions to produce heat. While these systems are less mature than steam reforming, these are also relatively well established (Caio, 2007). Pyrolysis is thermochemical decomposition (gasification) of organic material (biomass) at elevated temperatures in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430°C.

I) Coal Gasification: Chemically, coal (non-renewable) 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 reacting coal with oxygen and steam under high pressure and temperature to form synthesis gas (U.S. Department of Energy, 2009). Coal gasification reaction (**Reaction 3**).

$CH_{0.8}(s) + O_2(g) + H_2O(g) \rightarrow C_{0.5}O(g) + C_{0.5}O_2(g) + 0.8H_2(g)$ + other species (like S_X and N_X)….**Reaction 3**

Water-gas shift reaction (**Reaction 4**).

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ (+small amount of heat)…..**Reaction 4**

As the coal gasification reaction indicates, almost the same amount of carbon dioxide and hydrogen are produced even though the main purpose is to produce hydrogen. From the environmental safety point of view, it is possible to say getting energy from coal gasification means polluting the environment equivalently.

II) Biomass Gasification: Biomass, a renewable organic resource, includes agriculture crop residues, forest residues, municipal organic solid waste, and animal waste. Converting biomass into hydrogen is possible by applying heat under pressure in the presence of steam and a controlled amount of oxygen (in a unit called gasifier) (U.S. Department of Energy, 2008). Biomass gasification reaction (**Reaction 5**).

$C_6H_{12}O_6(s) + O_2(g) + H_2O(g) \rightarrow CO(g) + CO_2(g) + H_2(g)$ + other species…..**Reaction 5**

Water-gas shift reaction (**Reaction 6**).

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ (+ small amount of heat)…..**Reaction 6**

The biomass resources used in biomass gasification consume carbon dioxide in the atmosphere as part of their natural growth process, which means that biomass gasification results in a near-zero net release of greenhouse gases. Biomass can provide a major contribution in clean energy supply. However, biomass cannot meet the entire world's energy demand.

Thermo-chemical Cycles

Thermo-chemical Cycles for Hydrogen Production from water operate at high temperature ranging from 500°C to 2000°C (U.S. Department of Energy, 2009). Thermo-chemical cycles are better than direct thermolysis of water which requires temperature of above 2500 ^{0}C (Funk, Chemicals used in thermo-chemical cycle process are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen. The High-Temperature Water Splitting process is subdivided into different partial reactions according to the chemicals involved. Zinc/Zinc Oxide cycle and Sulfur-iodine cycle are types of thermo-chemical water splitting cycles.

I) Zinc/Zinc Oxide Cycle: In this cycle zinc oxide powder passes through a reactor operating at about 1,900°C. At this temperature, the zinc oxide dissociates to zinc and oxygen gas. The zinc cools, separates, and reacts with water to form hydrogen gas and solid zinc oxide at 427°C exothermically. The net result is hydrogen and oxygen, produced from water. The hydrogen can be separated and purified. The zinc oxide can be recycled and reused to create more hydrogen through this process. The heat released at the exothermic step is recycled and supplied to the reactor where ZnO dissociates.

II) Sulfur-Iodine cycle: Iodine-sulfur (IS) process is of considerable potential which is 40 – 50% efficient in hydrogen production from water. It consists of three steps; two endothermic and one exothermic process. The net result is hydrogen and oxygen, produced from water. The sulfuric acid and iodine are recycled and used to repeat the process (Schultz, 2003). The high-temperature heat needed can be supplied from nuclear reactors (up to about 1000°C) or by using sunlight with solar concentrators (up to about 2000°C). Solar- and nuclear-driven high-temperature thermo-chemical water splitting cycles produce hydrogen with near-zero greenhouse gas emissions. A solar concentrator uses mirrors and a reflective or refractive lens to capture and focus sunlight to produce temperatures up to 2,000°C. However, it is not a mature technology for it has many limitations. Also nuclear reactors that can supply 800°C-1,000°C for high-temperature thermo-chemical water splitting cycles are under development (**Figure 1** and **Figure 2**).

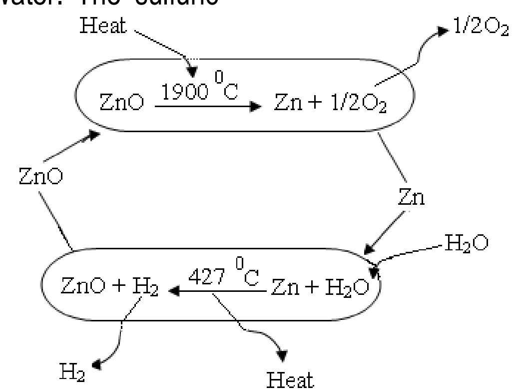


Figure 1. Zinc/Zinc Oxide thermochemical water-splitting cycle in hydrogen production from water.

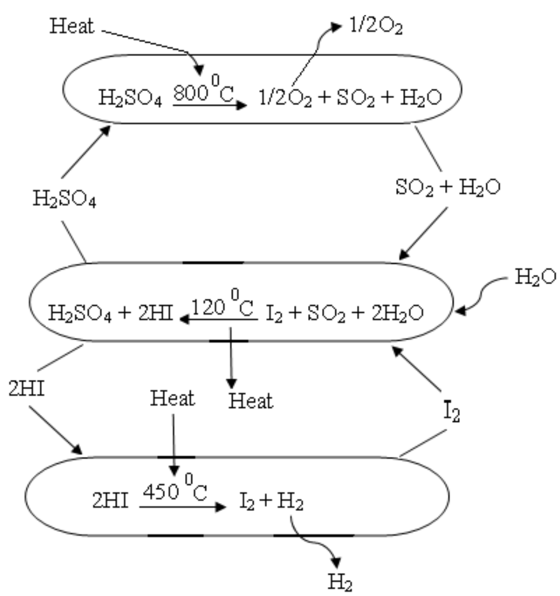


Figure 2. Sulfur-Iodine thermochemical Water-Splitting Cycle in hydrogen production from water.

Steam Reforming

Reforming is a chemical process where hydrogen containing fuels in the presence of steam, oxygen, or both are changed into hydrogen-rich syngas (Caio, 2007). Steam reforming is the most widely used thermo-chemical process to produce H_2 from raw materials such as natural gas, coal, methanol, ethanol, or gasoline. Currently, the steam reforming of natural gas, which contains methane, covers almost 50% of the world feedstock for H_2 production (Ruggiero, 2006).

I) Steam-Methane Reforming

Hydrogen production via steam-methane reforming in United States comprises 95%. Steam reforming is endothermic that is, heat must be supplied to the process for the reaction to proceed. Hence, high-temperature steam (700°C–1000°C) is used to produce hydrogen from natural gas. In addition 3–25 bar pressure (1 bar = 14.5 psi) is required to react methane with steam in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane or even gasoline. Steam reforming reactions (**Reaction 7** and **Reaction 8**):

$CH_4\,(g) + H_2O\,(g)\,(+heat) \rightarrow CO(g) + 3H_2(g)$…….**Reaction 7**

$C_3H_8\,(g) + 3H_2O(g)\,(+heat) \rightarrow 3CO(g) + 7H_2(g)$…….**Reaction 8**

Gasoline (using iso-octane and toluene as example compounds from the hundred or more compounds present in gasoline), (**Reaction 9** and **Reaction 10).**

$C_8H_{18}\,(g) + 8H_2O(g)\,(+heat) \rightarrow 8CO(g) + 17H_2(g)$…….**Reaction 9**

$C_7H_8\,(g) + 7H_2O\,(g)\,(+heat) \rightarrow 7CO(g) + 11H_2(g)$…….**Reaction 10**

Water-gas shift reaction 11

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ (+ small amount of heat)…..**Reaction 11**

So the steam reforming of fuels derived from fossil fuels like natural gas require high temperature and emits large amount of green house gases through combustion. The main advantage of reforming fossil fuels is that it is a mature technology that uses existing fuel infrastructures. It also reduces the need to transport and store hydrogen and it becomes less expensive process than other hydrogen production methods.

II) Steam-Ethanol Reforming

Hydrogen production through steam reforming of ethanol is not matured technology. In the last few years, researchers were tried to explore alternative ways of safe and sustainable energy supply in the globe. This is because to reduce global warming and to assure sustainable energy supply as well as to make continue the outweighed system of environmental features. Currently, there are very exiting reports that indicate the possible technology of hydrogen fuel production from renewable sources such as ethanol. The energy that irradiated from the sun is partially trapped by plants through photosynthesis (**Reaction 12**).

$6CO_2\,(g) + 6H_2O\,(l) + light \rightarrow C_6H_{12}O_6\,(s) + 6O_2(g)$……**Reaction 12**

Approximately 114 kilocalories of free energy are stored in plant biomass for every mole of CO_2 fixed during photosynthesis. So today, since biomass is a renewable resource, methods of production of fuels from biomass are helpful in reducing the dependency on fossil fuel derived energy supply. Through biological process, biomass wastes for instance wood waste in the paper and pulp industries and bagasse from the sugar-cane industry can be converted into very useful fuels such as ethanol. The biomass wastes contain cellulose, $(C_6H_{12}O_5)$-n that is polymer of glucose.

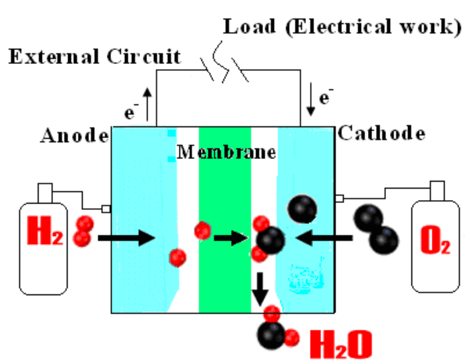
Cellulose, a main component of plant cell walls, can be hydrolyzed by either enzymatic or acid hydrolysis in to glucose. Enzymatic processes are however preferable owing to drawbacks of the acid hydrolysis process. The glucose is then fermented into ethanol. Then using suitable catalyst, ethanol can be transformed into hydrogen fuel at around 500°C and at atmospheric pressure. The maximum theoretical producible hydrogen from ethanol is six times the ethanol fed (Therdthianwong *et al.,* 2001; Basile *et al.,* 2008; Yakimova *et al.,* 2008; Umegaki *et al.*, 2009). The main possible reactions proposed which can describe steam reforming of ethanol are (Therdthianwong *et al.,* 2001; Basile *et al.,* 2008) (**Reaction 13**).

$C_2H_5OH(l) + H_2O(l) \rightarrow CH_4(g) + CO_2(g) + 2H_2(g)$; $\Delta H^0 298K = -8.0$ kJ mol^{-1}
$CH_4(g) + H_2O(l) \rightarrow CO(g) + 3H_2(g)$; $\Delta H^0 298K = +206.1$ kJ mol^{-1}
$CO(g) + H_2O(l) \rightarrow CO_2(g) + H_2(g)$ (water gas shift reaction); $\Delta H^0 298K = -41.2$ kJ mol^{-1}

$C_2H_5OH(l) + 3H_2O(l) \rightarrow 2CO_2(g) + 6H_2(g)$; $\Delta H^0 298K = +157$ kJ mol^{-1}……..**Reaction 13**

Application of Hydrogen in Fuel Cells

H_2 is a globally accepted clean fuel (Umegaki *et al.,* 2009). It is the key to lightest energy carrier in a future sustainable energy economy. And it provides a unique method of reducing today's dependency on fossil fuels and increasing the contribution of renewable energies or nuclear and solar energies. H_2 is used in fuel cells, where it is efficient and intrinsically clean for all end user applications. It can also be used in advanced combustion engines in vehicles and in gas turbines for small co-generation and for medium to large scale electricity production. H_2 offers the best energy to weight ratio than any fuel and is capable of supplying the high energy needs in future. When hydrogen is used as energy carrier in a fuel cell, water is released, which can then be electrolyzed to make more H_2 which means that its waste product supplies more fuel. As a result it provides high electrical energy, cost effective solutions to reduce green house gas emission, improve air quality, diversify energy supply and reduce noise pollution. Figure 3 shows the working principle of a proton exchange membrane fuel cell type (**Figure 3**).



Anodic reaction: $2H_2(g) \rightarrow 4H^+(g) + 4e^-$
Cathodic reaction: $O_2(g) + 4e^- \rightarrow 2O^{-2}(g)$
$4H^+(g) + 2O^{-2}(g) \rightarrow 2H_2O(l)$

Over all reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Figure 3. The electrochemistry of a $H_2 – O_2$ fuel cell.

Thermodynamic analysis

The enetropy of the gas decreases by 48.7 kJ mol^{-1} in the process of combination since the number of water molecules is less than the number of H_2 and O_2 molecules combining. Since the total entropy will not decrease in the reaction, the excess entropy in the amount $T\Delta S$ must be expelled to the environment as heat at temperature T. The amount of energy per mole of H_2 which can be provided as electrical energy is the change in Gibbs energy (**Reaction 14**).

$$\Delta G = \Delta H - T\Delta S = -285.83 \text{ kJ mol}^{-1} + 48.7 \text{ kJ mol}^{-1} = -237.1 \text{ kJ mol}^{-1}$$ …….**Reaction 14**

For this ideal case, the fuel energy is converted to electrical energy at an efficiency of 237.1/285.8 x100% = 83%. This is far greater than the ideal efficiency of a generating facility which burned the H_2 and used the heat to power a generator. Although real fuel cells do not approch that ideal efficiency, they are still much more efficient than any electric power plant which burns a fue (**Table 1**)l.

Table 1. Few thermodynamic properties of the reacting species to form water at 298 K and 1 bar.

Quantity	$H_2(g)$	$0.5O_2(g)$	$H_2O(l)$	Change
Enthalpy (kJ mol^{-1})	0	0	-285.83	ΔH = -285.83 $kJmol^{-1}$
Entropy (J K^{-1} mol^{-1})	130.68	0.5x205.14	69.91	$T\Delta S$ = - 48.7 $kJmol^{-1}$

Conclusions

The dependence of energy supply on fossil fuel derived sources causes environmental pollution and its consequences in addition to its none-sustainability. The one way that reduces the dependence on fossil fuel in the future can be hydrogen fuel. This is because, first, hydrogen fuel is clean energy carrier. There are also many renewable sources of hydrogen and it can be produced by none- polluting methods. Second, it can be used in transportation system as well as stationary energy supply. Third, Efficiency of fuel cells is approximately three times than combusting engines.

Countries that follow agricultural based economy can easily provide hydrogen renewable sources such as ethanol. Both the technologies of ethanol production and the reforming of ethanol into hydrogen are not more challenging technologies rather they can adopt them. Therefore, since the energy demands of the globe is still increasing and not has safe energy provision, alternative energy supply such as hydrogen fuel should be developed. The transition from none-renewable fossil fuel into hydrogen based energy supply should be facilitated. In addition, researches concerning hydrogen fuel should be motivated.

Conflict of Interest

The author didn't declare any conflict of interest regarding to this review.

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