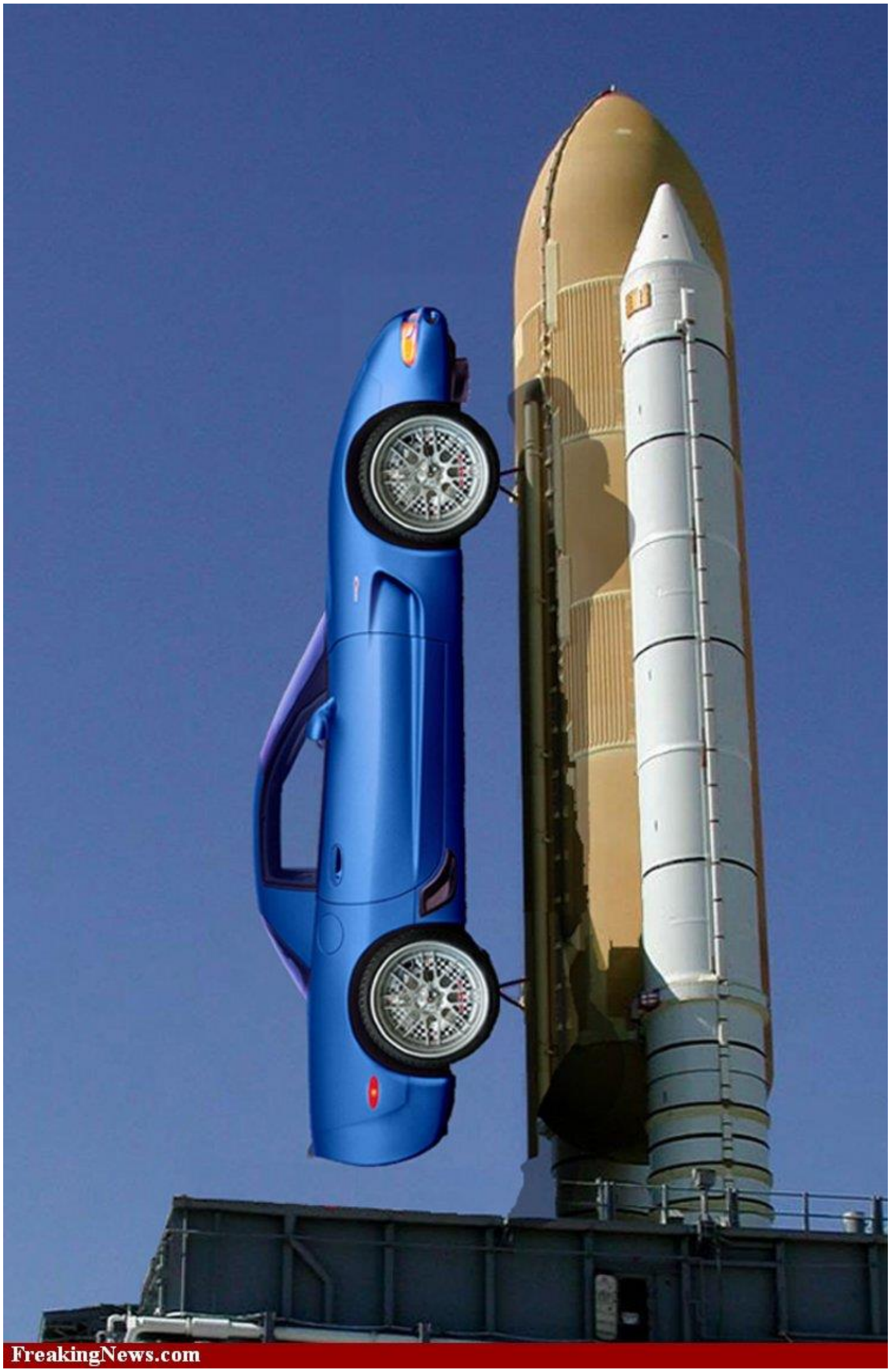
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Hydrogen Fuel?

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A new baby boom is about to happen in the automotive industry with hydrogen fuel cell vehicles. More and more car makers have announced new hydrogen powered cars: BMW, Chevrolet, Chrysler, Ford, Honda, Hyundai, Mazda, Nissan, you name it. Toyota, for example announced mass production in 2015. The promised price is in the range of $50,000 – $100,000.

Is it really the future?

There are a lot of materials, websites and even serious papers about advantages of “new” hydrogen car fuel. The most frequently mentioned advantages are:

1. Readily available – hydrogen is the most abundant element in the universe.
2. No harmful emissions– just water.
3. Environment friendly – non-toxic.
4. Very powerful – three times more powerful than gasoline.
5. Renewable.

There are only a few known processes for hydrogen energy utilization:

- Internal combustion engine – no major difference from ordinary car engine. Gasoline is replaced with hydrogen and the engine is modified to accommodate the new fuel.
- Fuel cell technology – hydrogen is used for direct electricity generation.
- Direct hydrogen burning for jet-propelled vehicles.

There are no new technologies involved which make hydrogen powered motors available these days. All technologies have been well known for a long period of time. Let's take a brief look at the history:

1. History

Internal Combustion Engine:

- 1806 – Francois Isaac de Rivaz (born in Paris, December 19, 1752; Died in Sion, July 30, 1828) was a Swiss inventor, credited with inventing and constructing the first successful internal combustion engine in 1806. The engine was powered by a mixture of hydrogen and oxygen. A year later, Isaac de Rivaz built one of the first automobiles – of course, powered by his new engine. NOTE: Gasoline was not used for internal combustion engines until 1870.
- 1908 – Hydrogen powered car was released for sale for $950. (After 19 years of production price dropped to $280)
- 1991 – Mazda HR-X Hydrogen Wankel Rotary
- 2002 – BMW 750hl
- 2006 – Ford F-250

Fuel Cell:

There is no principal difference between a fuel cell and a battery; both use a chemical reaction to generate electricity. A Battery contains a certain amount of chemical components and when all components are consumed, the battery needs to be either re-charged or disposed-of, depending on the battery type. If we add a few pipes to the battery: some for supplying reagents for the chemical reaction and some for the removal of reaction products, then we have a fuel cell.

- 1801 – Humphry Davy demonstrates the principle of what became the fuel cell
- 1839 – William Grove invents the "gas battery", the first fuel cell

- 1889 – Charles Langer and Ludwig Mond develop Grove's invention and name the fuel cell
- 1912 – Battery powered electric car mass production for $1950
- 1935 – Inventor Henry Garrett patented a electrolytic carburetor and let a car run on tap water
- 1950 – General Electric invents the proton exchange membrane fuel cell
- 1959 – Francis Bacon demonstrates a 5kW alkaline fuel cell
- 1960 – NASA first uses fuel cell in space mission.

Now let's take a closer look at the advantages of the hydrogen as a fuel.

2. **Hydrogen is three times as powerful as gasoline**.

That is true at first glance. Hydrogen combustion energy is 141.8 MJ/kg, while for gasoline it is 47.3. Three times indeed! The only problem is that a car's fuel tank does not contain any "kilos"; it contains liters. Let's calculate the energy content of a 100 liter tank:

- Gasoline – 3384 MJ
- Hydrogen – 992 MJ

What a surprise! Fuel your car with hydrogen and you will have three times less distance (assuming zero losses, which will be discussed later). The above calculation was done for liquid hydrogen. To keep hydrogen as a liquid in the fuel tank requires 1/3 of its energy content, and the real number will be 600 MJ, or 5.5 times less! There is no surprise for those who are familiar with liquid hydrogen properties: one cubic meter (1000 liters) of gasoline weighs 703 kg, while the same volume of liquid hydrogen weighs only 71 kg! Using gaseous hydrogen significantly reduces energy content numbers unless the internal pressure is extremely high.

Now let's analyze 2 different types of engines working on "mighty" hydrogen.

2.1. **Internal combustion engine.**

The principle is very simple: fuel (gasoline or hydrogen) is ignited in the presence of oxygen and the products of the reaction expand doing some mechanical work. In the year 1823, the theoretical thermodynamic cycle was proposed by Nikolas Leonard Sadi Carnot and it was proved that Carnot cycle is the most efficient cycle for converting thermal energy to work. Any real engine has efficiency less than this theoretical cycle. The formula for Carnot cycle efficiency is extremely simple and could be written as:

$$\eta = \frac{T_H - T_C}{T_H}$$

Where T_H and T_C are hot and cold temperatures

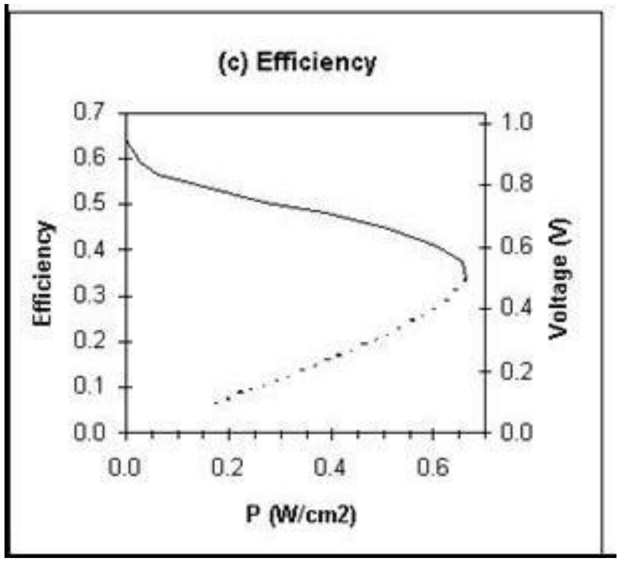
Theoretically, the efficiency limit is 100%. The only limitation here is how high we can increase the temperature. The choice of materials for building an internal combustion engine is very complicated. Material should not degrade at working temperatures; thermal expansion coefficient will affect all gaps and limits the compression ratio, etc. Modern internal combustion engines have an efficiency of about 40%.

There are some additional losses when hydrogen is used as a fuel; hydrogen should be pressurized during fueling. Simple calculations show that 5% of the energy content will be lost due to pressurization.

2.2. **Fuel Cells.**

There is much contradiction in the data about fuel cell efficiency. Most articles about fuel cells refer to the efficiency for internal combustion engines of 20%. Some papers indicate efficiency up to 80%.

This is not true – the theoretical limit for H2/O2 fuel cell is 64% at light loads as shown in many theoretical papers:



Careful analysis of the paper articles shows that 80% is the expected value when additional heat will be utilized in some near future. It is not possible to find out what kind of technology is used by automakers for their fuel cells, but most common working temperatures for hydrogen fuel cells are about 100°C to 200°C. Proposed new types which are still under development require working temperatures of up to 1000°C in some cases.

It is not clear how this additional heat will be utilized. A lot of such heat recovery systems are used for the purpose of heating and cooling houses. The efficiency is pretty good, but what are these systems doing? Most commonly, they heat or cool water, or preheat incoming air using high temperature exhaust air. It is difficult to imagine significant savings on car heating or air conditioning. It is an electric car, and all it needs to run more effectively is additional electrical energy.

The simplest way to converting heat to electricity is via the Seeback effect. Everybody is familiar with thermocouples – and that’s what it is, a technologically-advanced thermocouple. Today's efficiency of the conversion is 6% and a lot of well-funded research has promised 10% in the near future. The math is simple: theoretical waste is 40% and we are going to save 10% from this. Overall efficiency will rise from 60% to 64%.

The most efficient fuel cells available on the market today have efficiency of 24%.

3. **Readily Available.**

It is absolutely correct that hydrogen is the most abundant element in the universe, but mankind is still living on Earth and not in the universe. The Earth's atmosphere contains 0.000055% of hydrogen and extraction is extremely expensive. Currently, the dominant technology for hydrogen production involves extracting it from hydrocarbons (fossil fuel, mostly natural gas, which is 95% methane). Water electrolysis is under consideration by the hydrogen car manufacturers as an alternative means of production.

3.1. **Electrolysis.**

It sounds very ridiculous to produce hydrogen by electrolysis. Hydrogen as a fuel contains a certain amount of energy, absolutely the same amount required for water electrolysis. The scenario is as follows:

- We are getting electricity from somewhere
- Instead of putting this electricity into a battery with pretty high efficiency, we are using the same electricity to produce some amount of hydrogen (with losses of course) and then using said hydrogen with 25% efficiency.

There is some objection in the press – "who cares about efficiency if the technology is green?" This will be discussed later.

Another question – where to get the electricity in the first place? (Chicken or egg?). The answer from green enthusiasts is simple – we should produce electricity using “clean” electricity sources (solar, for example). And indeed, Honda announced just such a fueling station for personal use:

The specification said that the station will produce 0.5 kg of hydrogen overnight. What kind of car it is targeted? An Average car requires, let’s say, 60 liters of gasoline per week or roughly 8 liters per day. The energy content of those 8 liters is equal to 270 MJ and that 0.5 kg of hydrogen will produce 70.9 MJ or 3.8 times less! Let’s just downsize our gasoline cars, and I am pretty sure the pollution problem will be gone in a more inexpensive way.

Let’s estimate how much electricity one needs for a hydrogen-fueled car with the power capabilities close to these same 8 liters per day. We are considering charging once a day. The solar panel will collect sunlight during the day. The efficiency of current modern solar panels does not exceed 15%. The energy is equal to power times time:

$$E = P * t$$

The Longest day in California is 15 hours; let's assume 10 hours per average day. The power required to produce 270 MJ of energy will be 7.5kW. The solar power in the open space in Earth proximity (above atmosphere) is equal to 1200W per square meter. Below atmosphere in California, the number will be 800W per square meter or 120W per square meter taking efficiency into account. The aforementioned car requires 62.5 square meters of solar panel! (670 square feet) For Canada, that number will be even higher due to less sunlight.

3.2. **Extraction from Hydrocarbons.**

Toyota, along with the promises to mass-produce a hydrogen car, announced that 86 hydrogen fueling stations will be available in the next couple of years in California. All stations will produce hydrogen from natural gas. We'll take a closer look at hydrogen generation in the environmental section.

4. **Hydrogen is Environment Friendly.**

This is not about emission. The claim is that hydrogen itself is not toxic and some leakage is good for nature.

Every country paid a billion dollars in the past when fluorocarbons (used in aerosols) were banned. The idea was to prevent ozone layer depletion.

Ozone is an extremely active substance, and it will react with almost anything to produce the oxides. Oxides themselves are the only things which are don't react with ozone. As shown in many papers starting from 1904, hydrogen is accelerating ozone depletion, and hydrogen is much worse when compared to fluorocarbons. The lightest fluorocarbon is Tetrafluoromethane (CF_4). It has an atomic weight of 88! The average atomic weight of the air is 27; anything heavier will sink, anything lighter will float. How could such substance be delivered to the upper atmosphere? All other members of this family have an even greater atomic weight. Hydrogen, with an atomic weight of 4, will deliver itself to the ozone layer in self-propelled way.

Hydrogen is the smallest known molecule. It has been widely used for a long time as a power plant turbine cooling agent. A well-known problem when dealing with hydrogen is its very high diffusivity. It passes through plastic; it passes through metal; it passes through everything! Under extreme pressure conditions in the car tank and systems (Nissan reported 10,000 psi or 680 atm.!), the diffusivity will be extremely high. People should expect the accumulation of some hydrogen under the hood or under the roof (smokers beware!).

An Important safety issue with hydrogen is its high flammability. Here is a quote from a paper:

> Hydrogen is very flammable, but so is gasoline. Moreover, hydrogen is not inherently explosive, and where there are no ignition sources, it is highly unlikely that hydrogen will ignite in the open atmosphere. While petrol will self ignite at temperatures between 228-501°C, the self ignition temperature for hydrogen is 550°C. In principle, for an explosion to occur, hydrogen would first have to accumulate and reach a four percent concentration in air in a closed space and then an ignition source would have to be triggered. With proper safety systems in place, this is unlikely to ever happen. Hydrogen is lighter than air and dissipates rapidly, so the risk of a hydrogen fire or explosion in an open area is also much lower than that of gasoline.

Looks good, doesn't it? The self-ignition temperature is a function of pressure. Self-ignition temperature of hydrogen at 1000 psi is about 400°C and will be much lower at higher pressure.

The minimal ignition energy (spark from your finger) is 0.24 mJ for gasoline and 0.017 mJ for hydrogen! Some incidents of hydrogen explosion have been reported, where all obvious sources of ignition had been excluded and self-ignition had been blamed. The propensity of hydrogen to ignite in this fashion for no apparent reason has been reported several times previously, by Reider (1965), Lees, (1991), Anon

(1922), and Fenning and Cotton (1930). In these incidents, no specific cause for ignition was identified.

Brearley and Tolson (1995) measured power levels and contact loads required to ignite flammable gas mixtures by a 25 mm cube of stainless steel frictionally heated through rubbing against a stainless steel wheel at circumferential velocities of 5 and 20 m/s. In these tests, a contact load of 750 N was required to ignite hydrogen. This equates to a dissipated power of approximately 2 kW and a power density of approximately 0.5 W/mm^2. No electricity involved! Brake or not to brake?

Joule-Thomson effect: When gas passes through small nozzle or valve it will expand and cool upon expansion. There are only few exceptions: helium, neon and **hydrogen** – they **warm** upon expansion. Theoretically, even a small leakage could produce self-ignition temperature depending on the pressure and size of the hole.

Another well-known property of hydrogen is its ability to embrittle metals, which should be accounted for safe operation.

The flame of burning hydrogen has a very high temperature of 2210°C compared to 1026°C for gasoline. This is the temperature at the core of the flame; it will be colder further from the core. For reference: the self-ignition temperature of steel is around 900°C depending on alloy composition. In case of fire – it will be one of a kind!

5. No harmful emissions

In order to validate this statement, we should consider the whole cycle starting from hydrogen production. As was mentioned above, all Toyota charging stations will produce oxygen from pipe-fed natural gas.

One more thing to mention about that: there are fuel cells on the market which accept natural gas as a fuel! Why should it be more complicated?

These days, the controlled emissions from gasoline engine are:

- Carbon dioxide (CO_2)
- Carbon monoxide (CO)
- Nitrogen oxides (NO_X)
- Hydrocarbons

The hydrocarbons and carbon monoxide are produced because not all fuel was burnt. In theory, this could be eliminated by fine adjustment.

Nitrogen oxides: nitrogen reacts with oxygen at elevated temperatures. With fuel cells' tendency for increasing temperatures, (some fuel cells require 1000°C), the content of nitrogen oxides will be increased.

Now the most interesting thing – hydrogen generation from natural gas:

Generating hydrogen from natural gas does not require as much energy as the electrolytic method because natural gas already contains a certain amount of energy. This method, of course, is more attractive for manufacturers – you get the same, but spend less.

This process is called Steam Reforming. 95% of natural gas is methane (CH_4) and the final reaction looks like:

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

The gasoline combustion (mostly octane) formula is:

$$2C_8H_{18} + 25O_2 = 16CO_2 + 18H_2O$$

5.1. How much carbon dioxide will be released if we burn one liter of gasoline? It could be easily calculated from the reaction above – 1203 liters under normal condition (25°C, 1 atm.).

5.2. How much hydrogen do we need to provide energy content equal to one liter of gasoline? The answer after calculations is 277.2 grams.

5.3. How much carbon dioxide will be released based on the steam reforming reaction? After calculation we have 839.3 liters. If we are taking into account that the reaction requires some additional heat, this number should be increased by 25%, making it 1049 liters.

5.4. How close this number is to the real life? The annual report from a hydrogen producing factory by steam reforming said the following:

- Hydrogen production – 120500 kg/day
- CO_2 emission – 1366 tons/day

Recalculating this to our amount of hydrogen, the carbon dioxide emission is 1746 liters, 1.7 times more! There is no wonder, the process is very complicated and consists of a lot of stages, some of them requiring additional heating (methane burning).

5.5. Is it GREEN? Definitely not, although the theoretical portion looks good at first. Some big cheating happens very often at the hydrogen production stage. A lot of papers mentioned that we are disturbing carbon balance only if we are releasing carbon dioxide in the atmosphere – “let’s not do it!” they dictate. But they are pumping the resulting carbon dioxide into the oil reservoirs. Clever? Nobody even mentions what is going to happen to this carbon dioxide when it’s time to pump the oil out.

5.6. We have several numbers for carbon dioxide emission, all for energy content equivalent to one liter of gasoline:

- Gasoline – 1203 liters.
- Hydrogen production from methane (theoretical) – 1049 liters.
- Hydrogen production from methane (practical) – 1746 liters.
- What if we are going to burn methane directly, instead of making hydrogen? After calculations, the amount of emitted carbon dioxide will be 857 liters! Surprisingly, just feeding combustion engine with methane will produce less carbon dioxide than the complicated hydrogen cycle.

6. Renewable

This is a very questionable claim, since methane is definitely not renewable, and no paper provides a well-defined answer. In short – if we are using electrolysis and a “renewable” energy source, then the resulting hydrogen will be “renewable”.

7. Price Analysis

The following table shows different fuels prices. The energy content of each fuel is equal to one liter of gasoline energy.

Fuel	Price
Gasoline	$1.20
Natural Gas	$0.097
Hydrogen	$0.32 (manufacturing cost)
Electricity	$0.61

The calculation was based on the following assumptions:

- Gasoline price – $1.20 per liter
- Natural gas price – $0.12 per m^3 as per Enbridge
- Hydrogen price is not consumer price, it is manufacturing cost. Purchase of natural gas ($4.0/MMBtu) accounts for 55% of this price, capital equipment charges are 28% and operating and maintenance accounts for 17% of costs. Capturing of CO_2 emission will increase cost by 35%.
- Electricity price – $0.067 per kW*h as per Ontario Energy Board
- No efficiencies were taken into accounts, they are 40% for internal combustion, 24% for fuel cell and 75% for battery (a lot of battery manufacturers claim an efficiency of 98%, but they use a little trick here. Battery efficiency is defined as real efficiency divided by theoretical efficiency. If we want to know how much electricity we can we get back compared to what amount we putted in, then the term is “Coulomb efficiency” and it is not provided anywhere)

There is another concern nobody mentioned – fiscal. A huge part of gasoline prices are federal and provincial taxes. Imagine that all cars on the market are electrical or hydrogen. No more gasoline taxes and the budget will never be done. We should expect similar taxes either on electricity or on hydrogen. In such case the price of those alternative fuels should be increased at least twice.

8. The End

Buying a hydrogen car? I am not.