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Last Updated: January 15 2020

Hydrogen Energy

Overview of hydrogen energy technologies

Basic definitions

Hydrogen energy is one of the important and promising areas of modern industry. So, today it is unthinkable to create an ecologically perfect motor fuel without the use of hydrogen, the large-scale development of renewable energy is inextricably linked with hydrogen-based storage systems, the utilization of industrial waste by gasification methods leads to the production of synthesis gas, which is based on hydrogen, etc. The pinnacle of energy improvement - the creation of controlled thermonuclear fusion - is also ultimately associated with hydrogen, or rather its isotopes. Hydrogen is the lightest element in the periodic system, the most common in the Universe, and has the lowest liquefaction temperature among industrial gases, excluding inert ones. Hydrogen is very active and has long found a pair on the Earth, first of all having formed it with oxygen in the form of water, and with carbon in the form of oil and natural gas, which are familiar in the energy sector.

In practice, hydrogen exists in liquid and gaseous states (in theory and in solid) and various conversion units are used to measure it in the following ratio at a standard pressure of 1.013 bar:

1 Nm^3 gas = 0.08988 kg = 1.2699 litres

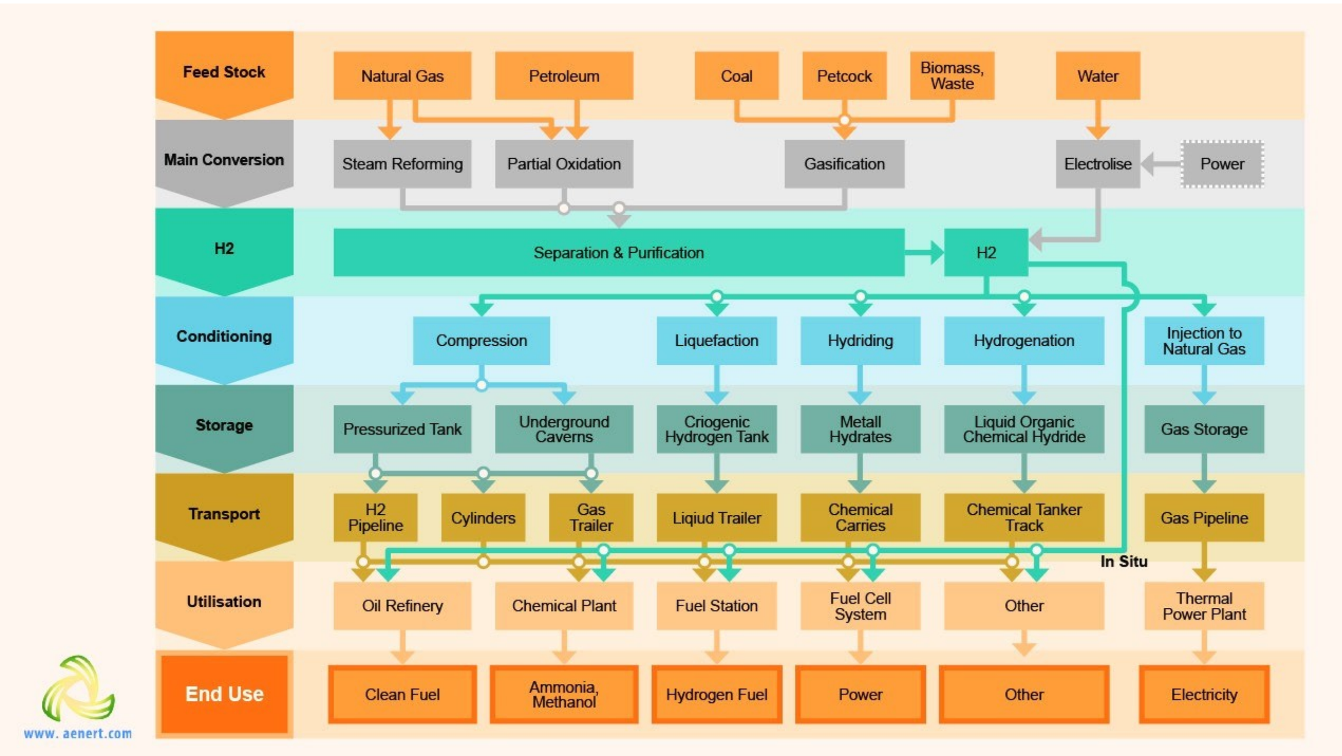
For more details on the physical and technological properties of hydrogen, conversion procedures, and other characteristics, see [1,2].

Various technologies are used in industry to produce hydrogen - primarily Steam reforming, Partial oxidation and Auto-Thermal Reforming. In addition, gasification of coal or biomass and electrolysis are often used. Natural gas, to a lesser extent oil and coal, as well as water during electrolysis operations, dominates as a raw material for producing hydrogen.

The main use of hydrogen in modern energy is associated with the production of high-quality fuel in oil refineries as a result of processes such as, for example, hydrocracking or hydrodesulfurization. In recent years, the use of hydrogen as a fuel, in particular in the USA, Japan and Western Europe, as well as the proliferation of fuel cells, has gained more and more intensive development. Synthetic gas, which always contains hydrogen, is used to produce methanol and its derivatives.

The general scheme of modern production and use of hydrogen is shown in Fig. 1.

Figure 1. Main hydrogen production & use



A serious limiting factor in the development of hydrogen energy is the imperfection of storage and transportation technologies, especially on a large scale and over long distances. The experience accumulated in recent years in storing hydrogen in underground salt caves, as well as projects for transporting hydrogen in the form of organic compounds, can help solve these problems and open the way for even more widespread use of hydrogen in the energy sector, in particular as a means of storing energy in batch and renewable power plants resources (wind and solar stations).

Hydrogen Resources

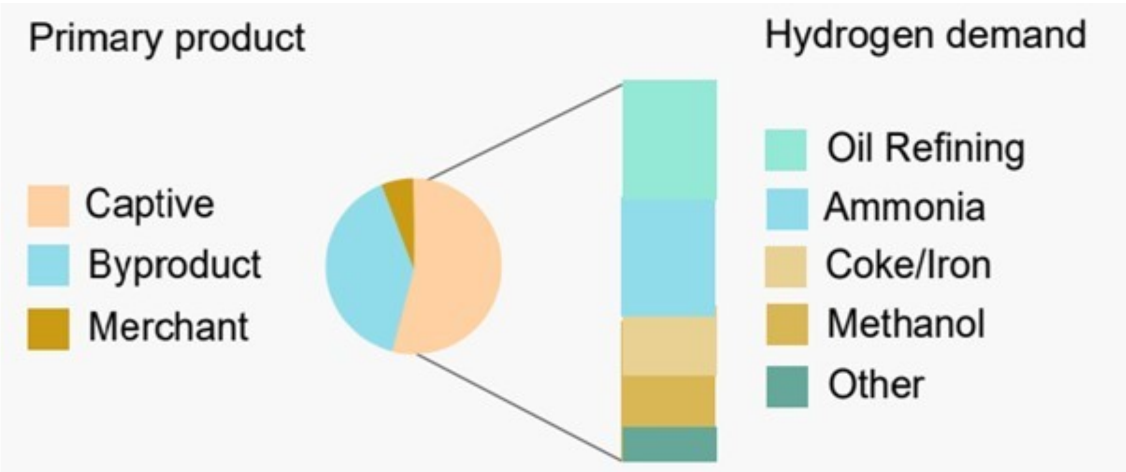
As previously mentioned, the main raw material for the production of hydrogen is natural gas, and its share in the total production volume is steadily increasing. Thus, according to [2] in 2009, 48% of hydrogen was produced from natural gas, 30% from oil, 18% from coal, and 4% by electrolysis. The same data are given in [3]. However, in one of the last fundamental works on hydrogen energy [4], completely different data are presented. Here, the share of natural gas for targeted production of hydrogen is estimated at more than 70% and coal a little more than 28%. The rest is oil, electrolysis and other less significant technologies. Moreover, an increase in the share of natural gas use occurs simultaneously with an increase in hydrogen production both for direct use and as a part of mixed gases. Today, for example, in the United States, 95% of hydrogen is produced by steam reforming from natural gas [3]. The largest amount of hydrogen from coal is produced in China. Obviously, against the background of growth in consumption and, accordingly, hydrogen production by these giants, the share of other technologies, for example, based on electrolysis, is becoming less noticeable, despite the physical increase in production.

Data on hydrogen consumption is very controversial. Thus, according to [4], in recent years the share of the main hydrogen consumer in the energy sector, oil refining, has grown significantly, which today seems to be ahead of another large-scale consumer - ammonia chemical plants. Moreover, for example, in 2010, according to [2], the ratio between them was 46.3% by 44.5% in favour of ammonium. In [6] (2016), the ratio in hydrogen consumption between oil refining and ammonia production is indicated to be approximately the same. On the other hand, in [3] based on FCH JU, 2016, the ratio between ammonium and oil refining is indicated as 65% to 25% of total consumption.

A comparative analysis of various estimates of the production and consumption of hydrogen in the world is given in work [4]. These estimates range from 65 to 100 million tons per year of hydrogen production worldwide, of which about 70 million tons per year of "on-purpose" hydrogen (Fig.2).

Figure 2. Hydrogen production and demand

Hydrogen production and demand
The range for global hydrogen production 65–100 MMT per year. Growth since 2005 by about 50%. The US share in world hydrogen production is 12-16%. In the US 95% of hydrogen is produced by steam reforming

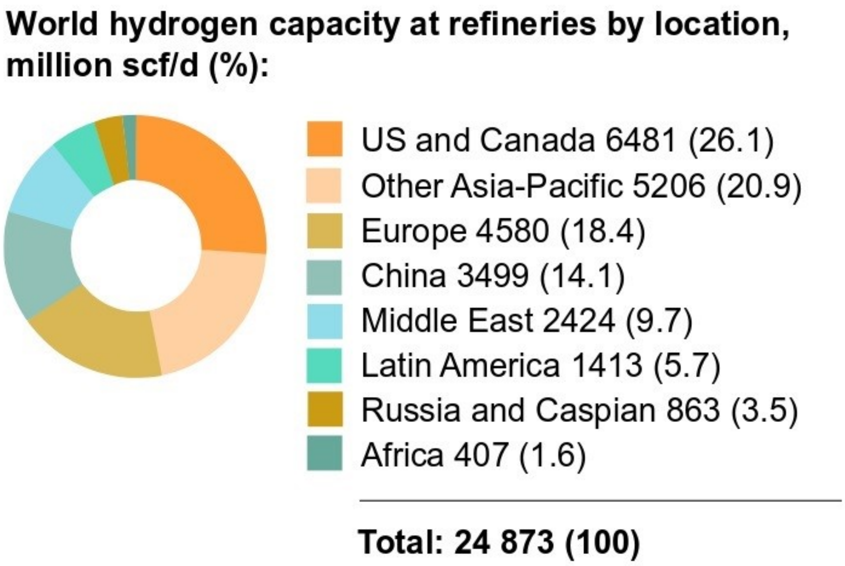


Source: Based on [5,6,7]

Mainstream technologies

The main producers of hydrogen for the needs of the energy sector are oil refineries through internal technological processes, as well as specialized enterprises producing commercial hydrogen (merchant producers). The total capacity for hydrogen production at oil refineries in various regions of the world is presented in Figure 3.

Figure 3. Hydrogen production capacities at refineries in various regions of the world



Sources: OPEC, World Oil Outlook 2017.

The hydrogen content in off gases in various oil refining processes can be very significant and reach 60-85% (for example, catalytic reforming), but in most cases this is not enough to satisfy the ever-increasing needs for hydrogen. Hydrogen is used in refining to remove sulfur from feedstock or final products and is also used as process gas in basic processes. In recent years, especially in the USA, where the hydrogen transport infrastructure is well developed, refineries prefer to purchase hydrogen on the free market. So according to [8] between 2008 and 2014, the share of commercial hydrogen in US refining increased by 135% with a slight increase (less than 1%) of its own production.

Table 1. Top 10 companies by hydrogen capacity at refineries as of January 1, 2018 in United States

Status	Country	Name	Hydrogen Capacity, MMscfd
Company	US	Valero Energy Corporation	597
Company	US	Chevron Corporation	488
Company	US	WRB Refining LP	281
Company	US	Andeavor	239
Company	US	Phillips 66 Company	219
Company	NL/GB	Royal Dutch/Shell Group	193
Company	US	Koch Industries Incorporated	189
Company	US	PBF Energy Co LLC	155
Company	US	BP plc	137
Company	US	CHS Incorporated	112
Rest of the companies	n/a	n/a	387

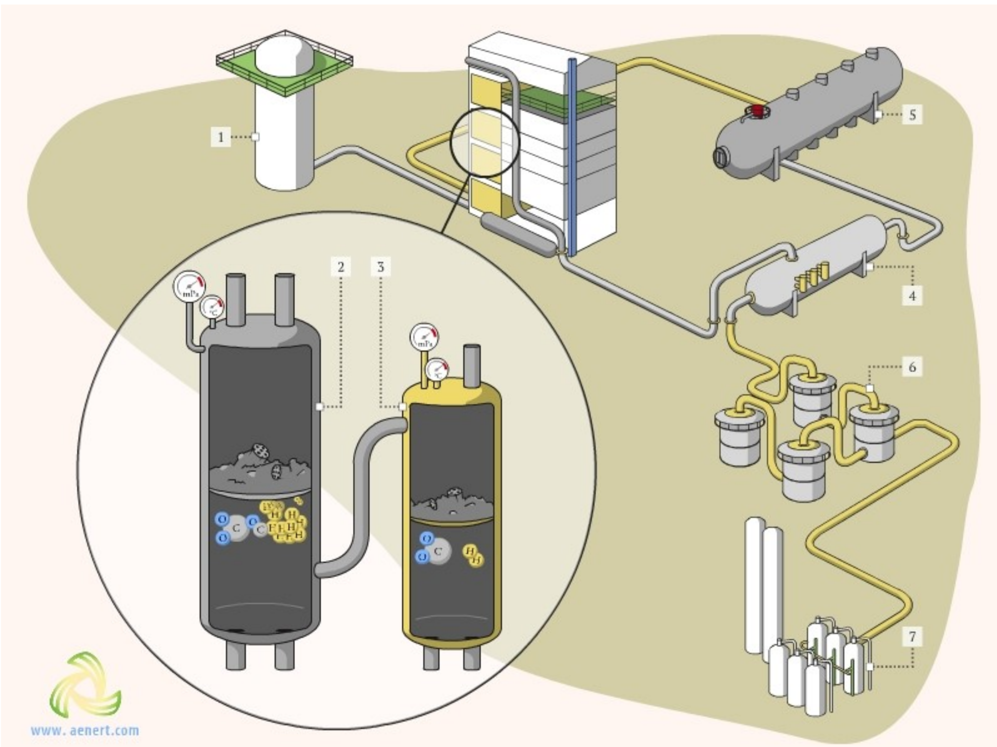
Source: U.S. Energy Information Administration (Refinery Capacity Report, June 2018)

An increase in the supply of heavy and sour crude oil to refineries, as well as the flexible production of various fuels, create additional barriers to their sustainable supply of hydrogen without specialized production or external supplies. Therefore, most modern refineries have specialized units for the production of hydrogen, part of which, in turn, is supplied to the free market, for example, to provide hydrogen gas stations.

Figure 4 - 5. Storage tanks for industrial gases in oil refineries. Left – Suncor Refinary, Edmonton, Canada. Right – Antwerp Refinery, ExxonMobil, Belgium

The most common method for producing commercial hydrogen is steam reforming of hydrocarbons, primarily steam methane reforming, which allows one to obtain synthesis gas with a high hydrogen content. For example, AIR LIQUIDE's steam reforming plants make it possible to obtain a final product with an H_2 / CO ratio in the range of 2.6 to 4.2 [9]. According to [10], 95% of hydrogen is produced in the United States via steam reforming. A simplified diagram of this process is shown in Fig. 6.

Figure 6. Hydrogen production as a part of synthesis gas through steam reforming in combination with the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen



1. *Feed pretreatment*

2. *Steam reformer 850°C*

3. *CO-shift conversion 350°C*

4. *Gas cooler*

5. *Steam drum*

6. *Pressure swing adsorption (PSA)*

7. *Desulphurization*

After feed pretreatment (hydrodesulfurization), the heated gas mixture of methane and water vapor is passed through a tubular reactor, usually with a nickel catalyst, at a temperature of 700–1100°C and with a relatively low pressure of 3–25 bar [10] and decomposes into hydrogen and carbon monoxide in compliance with a strong endothermic reaction:

$CH_4 + H_2O = CO + 3 H_2$

Specific parameters are determined by the developers of the process, the feedstock, and the requirements for the final product, for example, steam methane reforming at AIR LIQUIDE technologies have the following performance characteristics: temperature - 800 to 940°C, pressure - from 15 to 45 bar [9]. At the second stage, to increase the efficiency of hydrogen production, a water-gas shift reaction or CO-shift conversion is implemented, as a result of which carbon monoxide interacts with water vapor to produce heat by reaction:

$CO + H_2O = H_2 + CO_2$

and in the temperature range 200–450°C (400°F and 900°F) [11]. In the low-temperature version of the process, CuO -based metal oxide catalysts are used, and in the high-temperature - Fe_2O_3-based catalysts [12].

When using a limited amount of oxygen instead of water vapor, hydrogen can be obtained by partial oxidation by the following reaction [10]:

$CH_4 + ½O_2 = CO + 2H_2$

The main process parameters are the outlet temperature of 950-1100°C, pressure - up to 100 bar. This technology allows the production of synthesis gas with flexible variation in the ratio of hydrogen to carbon monoxide [13].

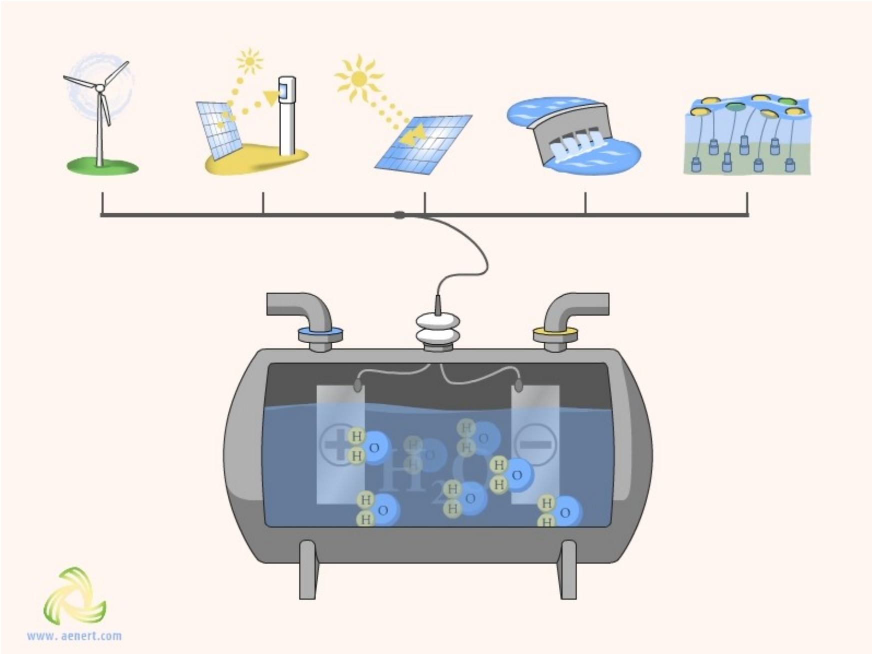
In addition to the aforementioned AIR LIQUIDE, hydrogen refineries are available from several companies, including TechnipFMC, whose asset is Largest single-train plant for 224,000 Nm^3 / h (200 MMSCFD) hydrogen; Haldor Topsoe, whose SynCOR ™ technology is low cost; Linde group, supplying the market with modular plants with capacities from 150 to 12000 Nm^3 / h [14 - 16].

In the production of ammonia, especially in China, coal gasification has been widely used for the production of hydrogen. Certain prospects are also assigned to the biomass gasification. The standard gasification process, as in the case of steam methane reforming, is the conversion of carbon-containing substances into syngas in a special reactor by exposing the feedstock to high temperature and pressure along with the supply of oxygen or air and water vapor. Process parameters are highly dependent on the characteristics of the feedstock. For lumps of 5–30 mm in size, Fixed - or moving-bed gasifiers are used [17, 18, 19]. For fine-grained raw materials - gasifiers with a fluidized bed (fluidized bed), and for pulverized - gasifiers with an entrained flow. To process each type of raw material, a certain temperature and time are required. So for a fluidised bed, the process time is up to 100 s at a temperature of 800-1050°C, for entrained-flow - up to 5 s at a temperature up to 1600°C [17, 19].

Coal gasifiers of AIR LIQUIDE (Lurgi Fixed-bed), GE and ECUST companies [20, 21, 22] are very popular on the market, and Valmet, Tarpo and EQTEC [23, 24, 25] for gasification of biomass. The largest enterprises of this type are Yinchuan CTL Plant, China, 9300 and Sasol Synfuels II (West), South Africa, 7048 MWth. High hopes for the production of hydrogen are placed on electrolysis. This is primarily due to the significantly lower environmental impact of this technology on the environment compared to steam reforming and gasification, which are characterized by a high level of harmful emissions and also use of fossil fuels as raw materials. Another major advantage of electrolysis is that the raw material for the production of hydrogen in this case is water, and the final products are hydrogen and oxygen, released respectively at the cathode and anode. Such indicators are most significant for renewable energy, where energy storage is one of the primary problems, and the production of hydrogen due to the electricity generated by solar or wind power plants can solve this problem. Electrolysis as a physicochemical reaction proceeds under the influence of an electric current, as a result of which water is divided into hydrogen and oxygen molecules (Fig. 4).

To increase the efficiency of the process, water heating and various electrolytes are used. Depending on the amount of characteristic minerals in the water, alkaline or acid solutions are distinguished. Currently, the processes most widely used are alkaline water electrolysis, Proton exchange membrane (PEM) electrolysis and Solid Oxide Electrolysis (SOE). Alkaline water electrolysis is usually carried out at the temperature range of 50-120°C, pressure up to 60 bar using KOH or NaOH as an electrolyte and a nickel catalyst. For PEM, the typical temperature range of the

Figure 7. Hydrogen production by water electrolysis



electrolysis process is 60-100°C at a pressure of 30 - 80 bar and the use of platinum-iridium (platinum / iridium) catalysts, for SOE - 650-1000°C (water is in a vaporous state) [4,26,27]. The electrical efficiency of the processes ranges from 56 - 81%, with lower values characteristic of PEM electrolytic cells, and large values for SOE [4]. The Norwegian company NEL is one of the oldest and largest among manufacturers of various types of electrolyzers since 1927. The main activity of the company is aimed at the use of hydrogen obtained by electrolysis in renewable energy. Alkaline electrolyzers of the series A company can produce more than 8 tons of hydrogen per day, and, for example, PAM electrolyzers of the M series can produce hydrogen with a purity of 99.9998% [28].More detailed information on electrolysis technologies and their application in renewable energy can be obtained in [29].

A list of the main operations for processing the hydrogen obtained during various technological processes is shown in Figure 1. The first step is separation and purification, which is traditional for all industrial gases. Most often in the production of hydrogen, adsorption methods, low-temperature condensation, and membrane technologies are used.

Figure 8-9. Air Liquide & Praxair along with Air Products are the largest producers of commercial hydrogen in the world. Air Liquide has the longest network of hydrogen pipelines of about 2,000 km. Praxair is the leader in the production of liquefied hydrogen - more than 60,000 Nm^3 / hr

The next technological stage is conditioning, which includes technologies for bringing finished products to a condition to ensure the delivery of hydrogen to the final consumer and its storage. Regarding hydrogen, compression and liquefaction are most widely used. The technology of physical adsorption of some solid materials (metals and alloys, composites, graphene, etc.), as well as hydrogenation, that is, the creation of a compound of hydrogen and a suitable organic substance are under development. Compressing with a total capacity of about 11 million Nm^3 / hr occupies a dominant position in the hydrogen market. Moreover, all the hydrogen liquefaction capacities in the world do not exceed 200 thousand Nm^3 / hr [1].

The compression of hydrogen for its storage and transportation is due to the fact that for storage of 1 kg of hydrogen under normal conditions (100 kPa and 25°C) requires a tank with a volume of more than 12 m^3, and after compression to 350 bar the volume of the fuel is reduced by more than 99%. The standard pressure during storage of compressed hydrogen in cars is agreed at 700 bar. [thirty]. The largest enterprises for the production of merchant compressed hydrogen plants are located in the US states of Texas and Louisiana - Air Products Baytown, TX, USA, 139 542 Nm^3 / hr and Praxair Geismar, LA, USA, 106 387 Nm^3 / hr [1]. Pressurized tanks are most often used to store compressed hydrogen. However, the storage of hydrogen in underground salt caverns, as well as in depleted fields, natural gas aquifer storages, has great prospects. A detailed review of technologies and other data on the underground storage of hydrogen can be found in [31]. The three largest operating underground hydrogen storage facilities are located in the US, Texas - Air Liquide Beaumont; Conoco Phillips Clemens, Lake Jackson; Praxair Moss Bluff [31, 32]. In Europe and especially in Germany, the technology of storing and transporting hydrogen using natural gas networks that blend hydrogen and natural gas, are gaining great popularity [35]. The most important element of the economic feasibility of such a technology is the use of existing infrastructure, which avoids additional and very significant capital costs. However, a noticeable difference in the density of hydrogen and natural gas, as well as in the conditions of their interaction with atmospheric oxygen during combustion create serious engineering difficulties in the large-scale implementation of this technology [4]. The use of liquefied hydrogen is primarily due to the requirement to provide the highest possible energy content per unit volume, therefore the aerospace industry was the first consumers of such hydrogen. However, taking into account the fact that the temperature of the transition of hydrogen to a liquid state is around – 253°C, such a process is extremely expensive [1,30,33,34]. Nevertheless, the accumulated engineering experience in hydrogen liquefaction allowed us to create technologies for its use in the modern automotive industry. The largest enterprises for the production of liquefied hydrogen are concentrated in the USA, Canada and Japan. The largest of them are Air Products New Orleans, LA, USA with a capacity of 29 415 Nm^3 / hr and Praxair Niagara Falls, NY, USA, 25 118 Nm^3 / hr [1].

The transportation and distribution of hydrogen between consumers is currently carried out mainly in the following ways - by means of (hydrogen pipeline, Gas or liquid trailer. The total pipeline network of hydrogen pipelines in the world exceeds 4500 km. The largest hydrogen pipeline in the world is located in the USA - Texas-Louisiana, 2223 km long [1]. Pipelines are used both for transportation over relatively large distances, and between separate production units of one enterprise. Nevertheless, despite the progress in this area, gas or liquid trailer remain the main transport units for the distribution of commercial hydrogen between small and medium-sized consumers in the hydrogen production area.

Figure 10-11. Air Liquide's hydrogen infrastructure is one of the most extensive in the world

An undoubtedly significant breakthrough in the development of hydrogen infrastructure would be the development of safe and economically viable technologies for long-distance transmission of hydrogen, including by sea. Today, several suitable options are being considered. Among them, first of all, it is necessary to mention hydrogen to ammonia conversion and the creation of LOHC or liquid organic hydrogen carrier. The advantages and disadvantages of each method are discussed in detail in [4]. In the case of ammonium, we can mention the Togliatti (Russia) -Odessa (Ukraine) pipeline, which has a long and successful history. The liquid organic hydrogen carrier option is actively promoted by the Japanese company Chiyoda Corporation [36]. The technology includes hydrogenation of hydrogen to methylcyclohexane by combining it with toluene, storing a liquid organic carrier and its transportation, followed by dehydrogenation at the delivery site with the formation of the starting products - hydrogen and toluene. According to the developers, organic chemical hydride has the best combination of volumetric density and gravimetric density compared to other hydrogen storage options, including liquefaction. According to the company's press release, hydrogen will be produced in Brunei by steam reforming followed by hydrogenation. Then, hydrogen in methylcyclohexane will be transported by sea to Kawasaki in Japan, where the construction of a dehydrogenation complex is planned with the subsequent distribution of pure hydrogen to consumers [37]. The completion of the necessary facilities is scheduled for the end of 2019, commissioning in January 2020. According to [4], transportation of hydrogen via pipelines, as a rule, is the cheapest option, however, for large distances, transportation in the form of ammonium or LOHC can also be cost-effective.

Additional information on the storage and transportation of hydrogen is to be found in [38–39]. The use of hydrogen in modern energy has several applications. The most widespread application, as noted above, is in the oil refining industry. Among other important areas - the use of hydrogen as a clean fuel, as well as a means of storing energy with subsequent production of electricity through fuel cells.

Currently, Japan has the largest number of hydrogen refueling stations, where their number exceeds one hundred, followed by the United States, Germany and the United Kingdom. In total, about 30 countries are involved in this process, and the total number of existing refueling stations in the world is close to 500.

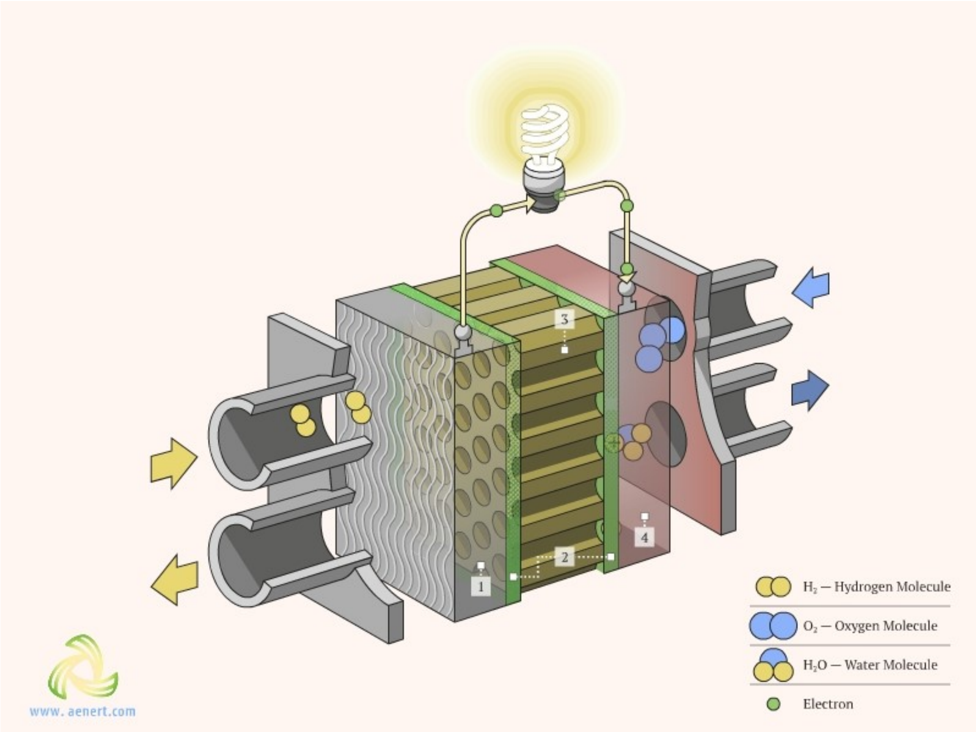
Figure 12-13. hydrogen refueling stations – are an integral part of the hydrogen infrastructure. Left - Belgium, right - Dennmark

Essentially, all of this infrastructure has been built over the past 10 years. In addition to Japan, a large number of hydrogen refueling stations exist in California and Germany with the countries adjacent to it. Many countries have programs to promote the development of hydrogen infrastructure, including hydrogen refueling stations.

Detailed information on the distribution infrastructure of hydrogen fuel can be found here [40-43].

Fuel cells are one of the most promising areas for utilizing hydrogen to generate electricity. The advantage of a fuel cell as a converter of one type of energy into another is primarily in the efficiency of the conversion process. Compared to most traditional technologies, fuel cells convert the chemical energy of the starting elements or substances (for example, hydrogen and oxygen) into electrical energy as a result of direct redox reactions without any intermediate steps, for example, combustion. The simplified design of the fuel cell is shown in Fig. 14.

Figure 14. Simplified fuel cell design and principle of operation



1. *Anode (Gas diffusion electrode)*

2. *Catalyst*

3. *Membrane (Proton exchange)*

4. *Cathode (Gas diffusion electrode)*

The composition of the fuel cells always includes the anode, cathode and electrolyte. At the anode, with the participation of the catalyst, oxidation occurs, i.e. the interaction of fuel with oxygen, resulting in the formation of positively charged ions and electrons. Ions move in the electrolyte to the cathode, and electrons move to the cathode through an external circuit, doing useful work. The final product of the operation of the fuel cell is most often water, which predetermines the second important advantage of fuel cells - the environmental cleanliness of the energy conversion process, although carbon dioxide can also be emitted when using certain types of fuel.

There are a fairly large number of different designs of fuel cells. The most commonly mentioned are proton-exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cell (PAFC), solid acid fuel cell (SAFC), alkaline fuel cell (AFC), as well as high temperature fuel cells - solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC). Each of the noted options has its own characteristics, for example, the type of electrolyte or membrane, the type of catalyst, etc., however, the general principle of operation of any fuel remains unchanged. They also distinguish between stationary, transport and portable fuel cells, the principal of difference of which follows from their name. There is a huge amount of excellent specialized information on this topic, see, for example, [1, 44 - 53].

The main technical characteristics of these types of fuel cells are grouped in table 2.

Over the past 10 years, the total capacity of installed fuel cells has grown many times, approaching 3,000 MW in 2017 [45], mainly due to transport and stationary options. The most popular types of fuel cells are proton-exchange membrane fuel cells and solid oxide fuel cell. The largest stationary fuel cell power plant is the Korean Hanwha Energy Seosan with a capacity of 50 MW.

Table 2. Main technical characteristics of various types of fuel cells

Types of Fuel Cells	Proton Exchange Membrane Fuel Cell (PEMFC)	Direct Methanol Fuel Cell (DMFC)	Alkaline Fuel Cell (AFC)	Phosphoric Acid Fuel Cell (PAFC)	Molten Carbonate Fuel Cell (MCFC)	Solid oxide fuel cell (SOFC)
Electrolyte	Solid Polymer Membrane	Solid Polymer Membrane	Potassium Hydroxide Solution in Water	Liquid Phosphoric Acid Ceramic in a Lithium Aluminium Oxide Matrix	Typically Consists of Alkali (Na & K) Carbonates Retained in a Ceramic Matrix of LiHO2	Solid Oxide Material
Catalyst	Platinum is the most active catalyst for low-temperature fuel cells	Platinum is the most common	Can use a variety of non-precious metal catalysts	Carbon-supported platinum catalyst	High MCFC operating temperature permits the use of lower-cost, non-platinum group catalysts	High SOFC operating temperature permits the use of lower-cost, non-platinum group catalysts
Operating Temperature,C°	<120	Around 50-120	<100	150-200	Around 650 (600-700)	500-1100
Fuel	H_2	CH_3OH	H_2	H_2	H_2&CO	H_2&CO
Electrical Efficiency, %	40-60	Up to 40	60-70	36-42	50-60	60
Power	1 W – 500 kW	100 mW – 1 kW	10 – 100 kW	< 10 MW	100 MW	< 100 MW
Applications	Transport, Stationary, Backup and Remote Power	Backup and Remote Power	Transport	Stationary	Large Stationary Systems	Stationary, Backup and Remote Power
Shipments(1000Units)/ Megawatts, 2017	45,5/486,8	2,8/0,3	0,1/0,5	0,2/81	0/24,7	24/76,4
Major Companies	Ballard Power Systems, Hydrogenics, Plug Power, Proton Motor GmbH, ENEOS CellTech, US FuelCell, SymbioFC, Acta S.p.A., Horizon Fuel Cell Technologies	Oorja Protonics, Oorja Fuel Cells, SFC Energy	AFC Energy, Apollo Energy Systems, Inc.	Doosan Fuel Cell, Fuji Electric	FuelCell Energy, Fuji Electric	Bloom Energy U.S., Ceramic Fuel Cells Ltd., Elcore GmbH, Acumentrics

Sources: US Department of Energy (June 2019); E4Tech, The Fuel Cell Industry Review 2017

Advantages and disadvantages

The main promising direction of the use of hydrogen in modern energy, excluding oil refining, is its use as environmentally friendly fuel for the production of useful energy, which can come to replace fossil fuels in the form of oil, natural gas and coal. Fossil energy sources, in fact, are a gift from nature to humanity, because it has a number of unique properties - it has limited, but large-scale reserves, it produces useful energy when interacting with oxygen in the air, without which it can be stored for a long time, can be transported over long distances and used in any region of the world, they are relatively safe, well studied and mastered; with an existing global infrastructure. However, fossil fuels have several significant disadvantages - they produce greenhouse gases during combustion; have limited and extremely unevenly distributed deposits, as a result of which some states are donors of energy resources and others are consumers, which is often the cause of political manipulation and conflict; during the extraction, transportation and processing of fossil energy resources, various technological disasters are inevitable, which leads to environmental pollution. Can hydrogen become a substitute for such a competitor? For now it is impossible to get a definite answer to this question.

The advantages and disadvantages of hydrogen as a competitive energy carrier are well identified both at the level of its physical and chemical properties, and at the stages of technological transitions. First of all, it is worth highlighting the unique Heat of combustion ability of hydrogen, which is approximately two and a half times greater than that of methane, three and a half times higher than that of oil and almost five times higher than that of coal. Hydrogen is a very light and non-toxic element that can be stored in isolated containers for a long time without loss of productive properties. Hydrogen has a low viscosity, and therefore can be easily transported through pipelines of even small diameters. When burned, hydrogen does not form harmful emissions.
On the other hand, hydrogen is explosive and flammable gas. At a certain ratio with oxygen (2:1) and even with air, Oxyhydrogen is formed, which has a large combustible and detonation potential. Given that hydrogen is able to diffuse relatively easily in metals (for example, penetrate through the walls of metal vessels), has no smell and colour, but has very high thermal conductivity, the problem of ensuring safe interaction with hydrogen inevitably leads to the use of a large number of complex technical devices and technologies. To liquefy hydrogen, a very low

temperature close to absolute zero is required, which dramatically reduces the benefits of liquid hydrogen for storage and transportation. The hydrogen density at 20°C pressure in 1 atmosphere is only 0.0838 kg / m^3 versus 0.668 kg / m^3 for methane [1] or about eight times less, which determines its low energy density, ie amount of energy per unit of volume. Since today the production of hydrogen is carried out mainly from natural gas and coal, and is accompanied by a significant amount of harmful emissions, its advantage as an environmentally friendly gas is devalued. The production of hydrogen from energy from renewable sources is currently expensive and cannot economically compete with the above methods.

Figure 15-16. Not all hydrogen projects are successful. On the left is Shell's closed hydrogen fueling station, on the right is a decommissioned fuel cell bus, Iceland

The universality of hydrogen as an energy resource, which simultaneously has the ability to accumulate energy, to act as fuel for electricity production and for vehicles has not yet been realized on an industrial scale and forecasts of such a perspective are still theoretical. The large-scale use of hydrogen for energy needs is severely limited by the lack of developed infrastructure, despite significant progress in this direction in recent years. For example, the delivery and storage of hydrogen for gas stations or fuel cell power plants are the main constraints to the development of this energy sector. In [4], the existing legal regulatory restrictions in force in many countries are indicated as an additional barrier to the development of the hydrogen industry.

Obviously, despite the above problems, the hydrogen industry has accumulated rich engineering experience in solving many technical problems and is steadily increasing production volumes. However, for the use of hydrogen in clean energy, it is first necessary to solve one fundamental problem - to ensure the competitive production of hydrogen by clean methods, bypassing the use of fossil fuels, as well as efficient delivery to consumers. The current prices of hydrogen production by steam reforming from natural gas are in the range of 1–2.5 USD / KgH_2 depending on the region, and the main costs are determined by the cost of natural gas, which is especially typical for Europe and China [4]. In renewable energy, as an alternative way to produce hydrogen, wind power and solar energy applications are considered, followed by electrolysis. According to calculations [4], the prices for hydrogen obtained by electrolysis in comparison with hydrogen obtained from natural gas can be comparable at an electric power cost of 40-10 USD / MWh, provided that the electrolysis capacity factor is at least 50% and CCUS (carbon capture, utilization and storage) process is included. Moreover, with a decrease in the cost of CCUS, the equivalent cost of the produced hydrogen will shift towards lower values of the cost of electricity for electrolysis. However, the cost of electricity from renewable sources below 40 USD / MWh is episodic and can be realized mainly due to hydro and geothermal energy [54]. Thus, at present, an economically viable scheme for the production of hydrogen via electrolysis is possible only through network connections. Moreover, there are several additional barriers: the cost of hydrogen production by electrolysis substantially depends on the duration of the electrolyser and the time of day the electricity is consumed from the network; large-scale production of hydrogen will require a significant amount of fresh water, while the use of sea water will require additional energy costs for desalination; with an emphasis on the production of electricity from renewable sources, excluding hydropower, additional and significant capacities are needed [4].

A detailed analysis of the cost of hydrogen produced through basic industrial technologies was carried out in [55]. Based on the Energy Information Administration data, the author calculated the cost of producing one kilogram of hydrogen (Estimated Hydrogen Production Costs), which was 1.4 USD / KgH_2 and 2.63 USD / KgH_2 for steam reforming, including distribution, for coal gasification - 1.21 and 1.82 (with CCUS) USD / KgH_2, for gasification of biomass - 1.44 USD / KgH_2, distributed electrolysis - 6.75 USD / KgH_2, wind electrolysis - 3.82 USD / KgH_2, distributed wind electrolysis - 7.26 USD / KgH_2. The data demonstrate the competitive cost of hydrogen produced by biomass gasification and indicate the prospects of this direction, as well as the economic issues of electrolysis.

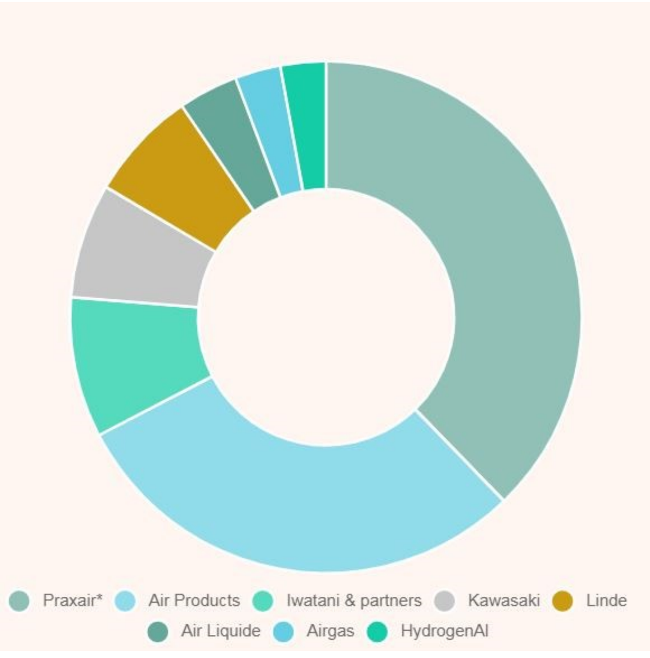
Production Cost of Hydrogen is also estimated in [56]. Here, the cost of producing one Nm3 by various renewable energy technologies and electrolysis is set in the range between 22 cent / Nm^3 and more than 50 cent / Nm^3 depending on the region and method of production, and the best values are typical for hydropower in countries with a high level of development, and worst for wind energy and photovoltaics. At the same time, the cost of producing hydrogen from fossil sources for almost all the regions considered in this work is determined below 22-23 cent / Nm^3. In [3], interesting data is presented on the levelised cost of hydrogen by comparing extreme options - with a high share of wind generation (in Denmark) and off-grid dedicated facilities. With low load factors, the levelised cost of hydrogen remains very high, at mid-range load factors are significantly reduced and equalized at a level of 6 to slightly below 4 USD / KgH_2. The target values of selling prices for hydrogen for different countries, including for the USA - 5 USD / KgH_2, for Japan, the cost of hydrogen at refueling stations is supposed to be reduced from the current 10 to 3 USD / KgH_2 by 2030, for Europe it is planned to reach 3-7 USD / KgH_2.

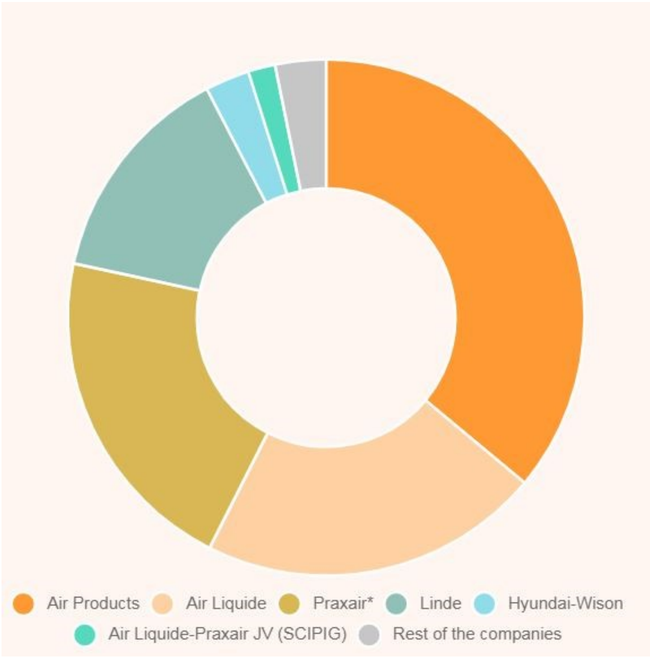
The current situation with the development of hydrogen energy outwardly strongly resembles the starting period of the development of renewable energy, when it seemed that this area would never be able to achieve a competitive state with fossil fuels. Nevertheless, as a result of a gradual increase or scaling up of production, state support and numerous engineering solutions, it was possible to ensure a significant reduction of the electricity prices. Currently, we can say that at least photovoltaics and wind energy have entered a phase of direct competition with fossil fuels. Obviously, hydrogen energy will have to undergo the same transition, but it seems that it will not be so painful, since, as mentioned above, nowadays, the production of hydrogen and its use is a long-established and highly developed industry, albeit not yet aimed at creating world-wide clean fuel infrastructure.

Hydrogen energy statistics

This section provides some important statistics regarding hydrogen production and elements of the hydrogen infrastructure.The distribution of capacities for the production of liquefied and compressed hydrogen between the leading world manufacturers is presented in Fig. 17-18.

Figure 17 - 18. Left - Cryogenic Liquid Hydrogen Production Capacity by Company, Nm^3/hr. To the right - Compressed Gas Hydrogen Production Capacity by Company, Nm^3/hr

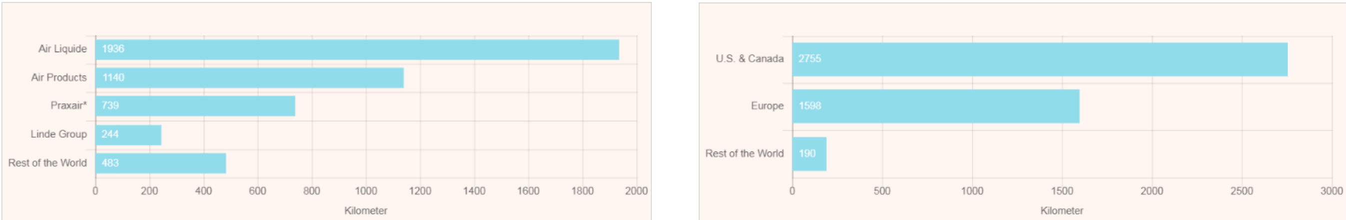




Sources: Pacific Northwest National Laboratory with funding from the U.S. DOE Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office

The distribution of hydrogen pipelines by region as well as the share of companies in this infrastructure are shown in Figures 19-20.

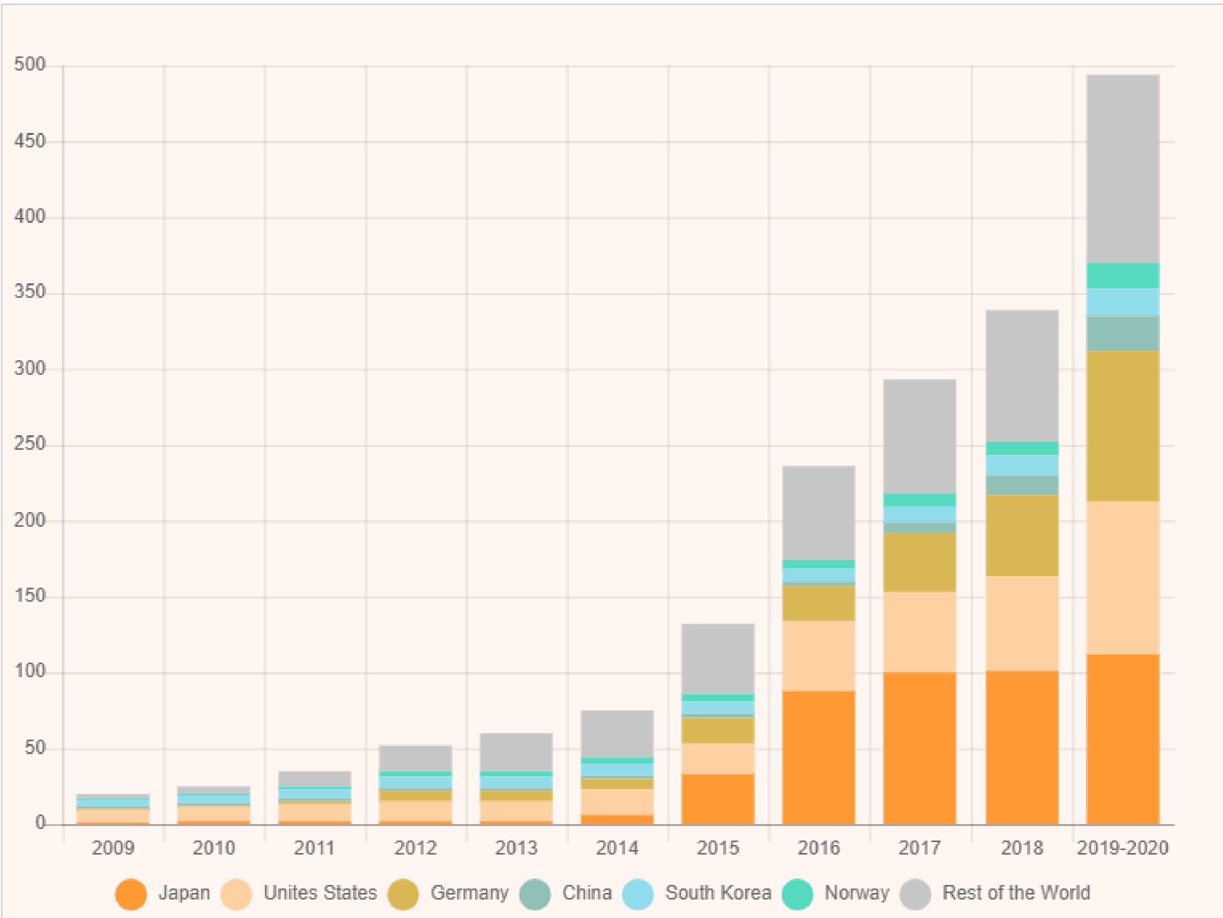
Figure 19 - 20. Left - Share of the World's Leading Companies in the length of a Hydrogen Pipelines. To the right - The proportion of parts of the world in the length of hydrogen pipelines



**In 2018 Praxair merged with Linde AG to form Linde plc.*
Source: Pacific Northwest National Laboratory with funding from the U.S. DOE Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office

The development of hydrogen transport infrastructure is largely determined by the number of hydrogen refuelling stations. The increase in their number in the world over the past 10 years is shown in Figure 21.

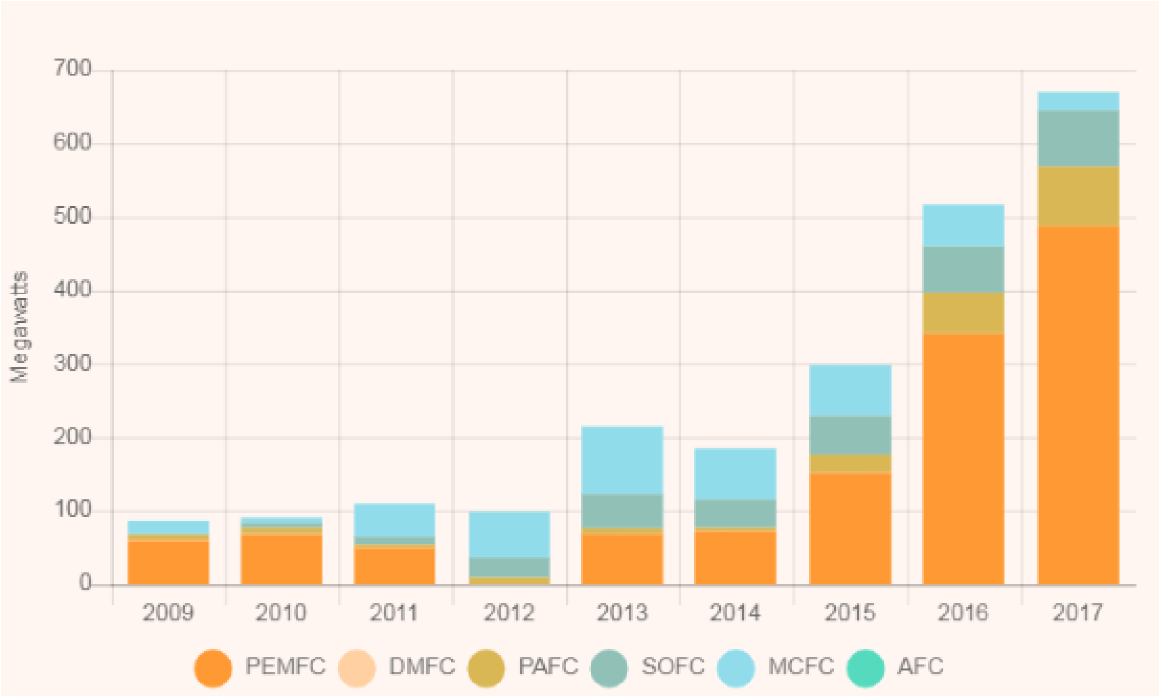
Figure 21. The growth rate of the number of hydrogen filling stations in the world in 2009-2018



Sources: Pacific Northwest National Laboratory with funding from the U.S. DOE Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office.; Alternative Fuels Data Center, US Department of Energy

Another important indicator of the development of hydrogen technology is the use of fuel cells. The annual increase in new fuel cell capacities between 2009 and 2017 is shown in Figure 22.

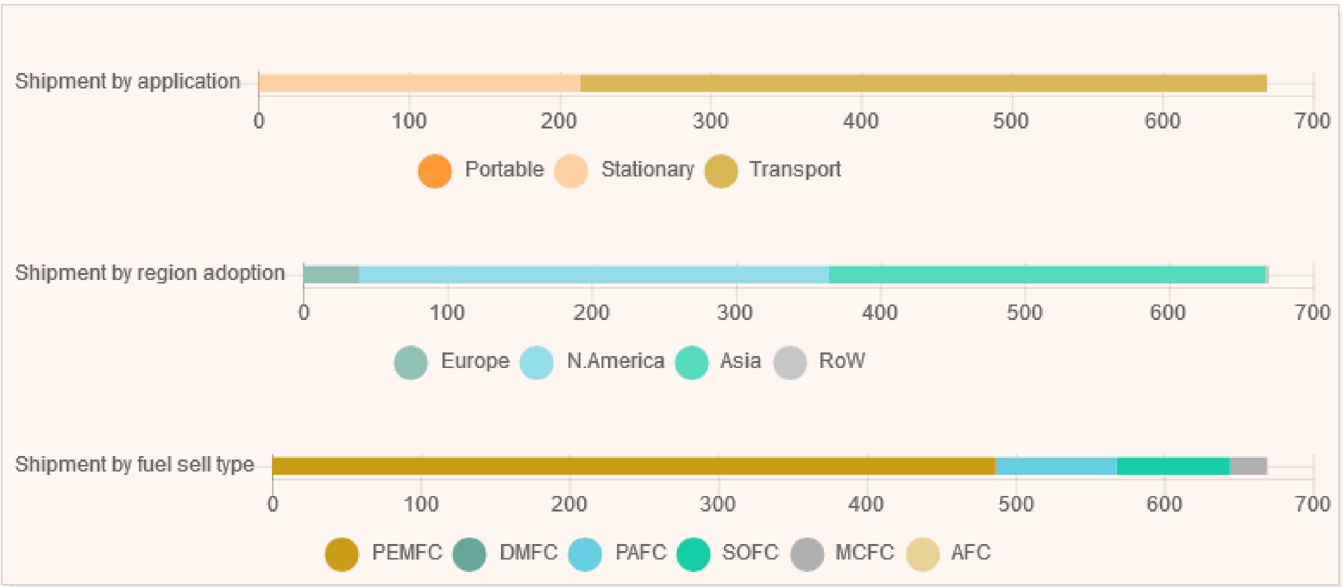
Figure 22. The growth rate of shipments by fuel cell type in the world in 2009-2017, MW



Sources: E4Tech, The Fuel Cell Industry Review 2017

The total distribution of fuel cells by regions as well as by their types and categories of destination in 2017 is shown in Figure 23.

Figure 23. Data shipment by application, region and fuel sell type in 2017, MW

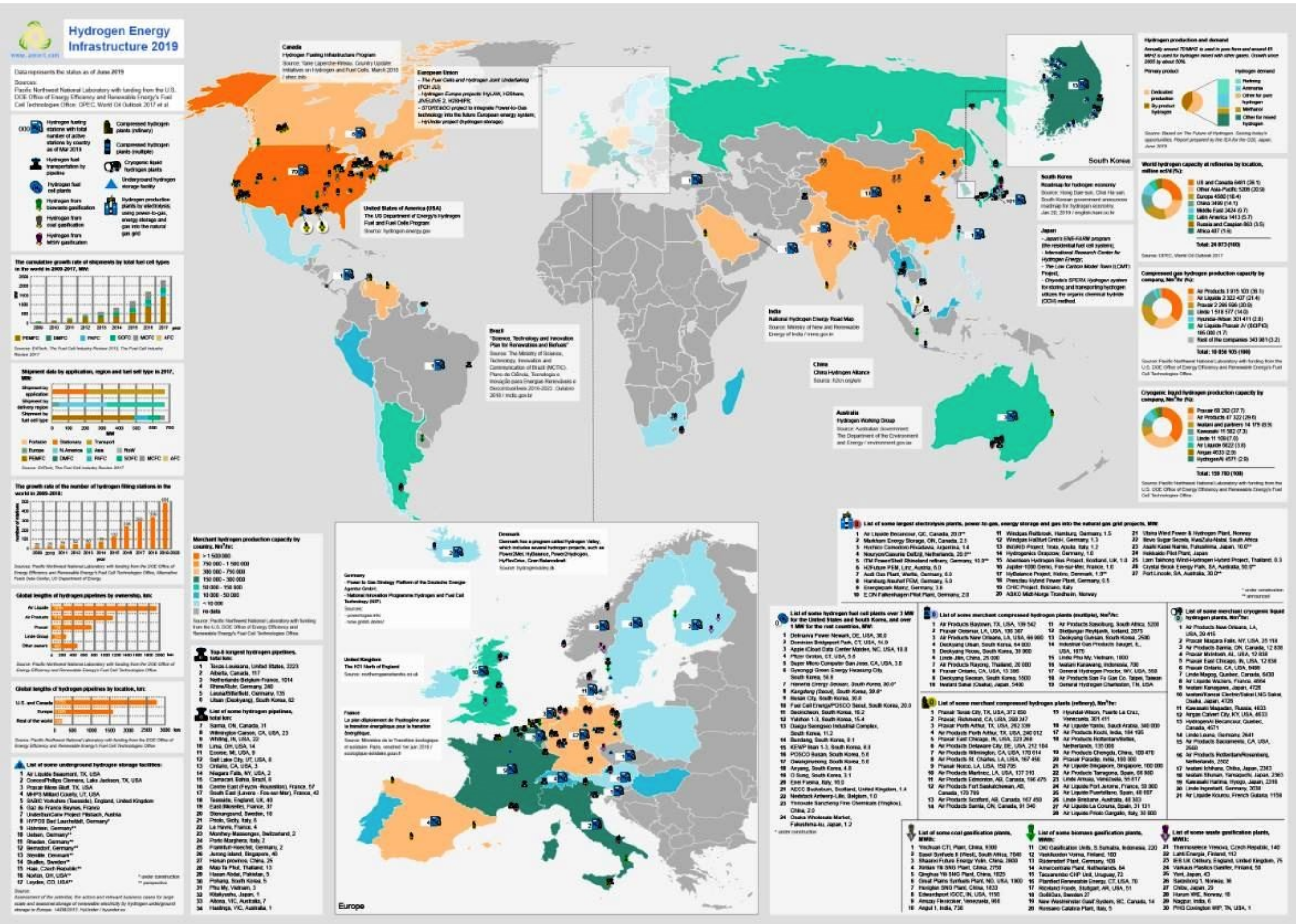


Sources: E4Tech, The Fuel Cell Industry Review 2017

Hydrogen energy infrastructure

Modern hydrogen energy infrastructure is characterized by a large number of various objects - enterprises for the production, storage and transportation, as well as the use of hydrogen. In addition, the units are ranked by type of technology , by their capacity and other characteristics. For obvious reasons, it is almost impossible to display all this information in any visual format. Therefore, the following option is proposed in the form of a world map, which displays only the basic facilities of the hydrogen infrastructure, including the main large projects, important statistical data on certain thematic areas and other related information. The contents of the map on hydrogen energy infrastructure included: data on the total capacity for the production of commercial hydrogen in various countries of the world (to the extent that it was possible to be reliable based on the indicated sources of information); data on the number of hydrogen refuelling stations in the countries of the world (without their geographic location); a list of hydrogen pipelines in the world with an indication of their length and location; list of underground hydrogen storage facilities, including prospective ones, and their location; lists of the largest facilities for the production of commercial liquefied and compressed hydrogen, indicating the production capacity and location of facilities; a list of the largest stationary fuel cell stations indicating the capacity, status and location of facilities; list of the largest installations for the gasification of coal, biomass and municipal waste, specializing in including in the production of hydrogen indicating the power and location of objects; list of the largest electrolysers, power-to gas facilities, renewable energy enterprises with hydrogen storage systems, indicating the capacity and their location; list of various programs for the development of hydrogen energy in some countries of the world; related statistics. Location of objects is indicated approximately.

Figure 24. Hydrogen energy infrastructure around the world



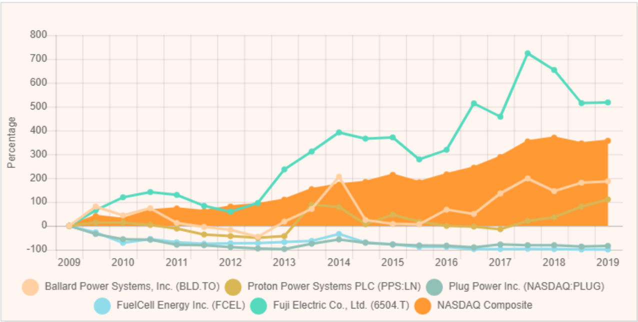
[Hydrogen energy infrastructure 2020.pdf [1.9 MB]]()

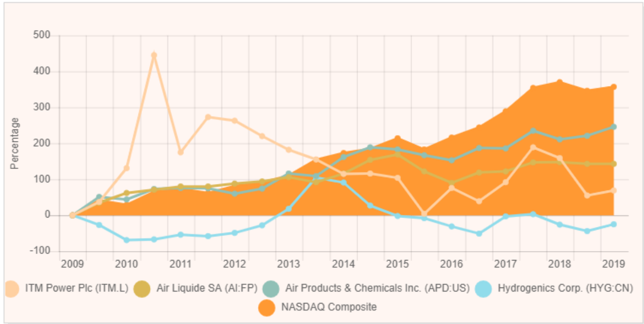
More information on the hydrogen infrastructure, in addition to the sources indicated on the map, can be found in [19, 40–43, 45, 48–53, 57–59].

Major companies

In the field of hydrogen energy there are a large number of different companies - hydrogen producers and consumers, equipment creators and technology developers, designers and service companies. Some of them are public, which allows us to assess their positioning on the stock market. Below, we display charts of changes of shares value of some companies, in which a significant share in their business activity is occupied by the production of hydrogen or related equipment, starting in 2009, when the value of the shares was conditionally equated to zero.

Figure 25 - 26. Left - Price change in relative units for public companies in the field Fuel Cell. To the right - Price change in relative units for public companies in the field Hydrogen Energy





Sources: Yahoo Finance, Bloomberg

As follows from the diagrams presented, most companies have positive trends on the market, in particular Air Product, Air Liquide, Ballard Power Systems, Proton Power Systems, whose stock prices have increased by more than 100% over the reviewed period.

Below are the key manufacturers, working the main areas of the hydrogen industry, as well as other companies associated with the hydrogen production. Company names are provided for convenience with hyperlinks to the home pages of their websites.

Manufacturers of hydrogen and equipment for its production, developers and owners of hydrogen technologies:

Air Products and Chemicals, Inc.

Air Liquide

Praxair

Linde Group

Sichuan Air Separation Group

TechnipFMC

AirGas Inc.

Showa Denko

Shenhua Group

Messer Group

Taiyo Nippon Sanso

Kaimeite Gas

Basf

Iwatani International Corp.

Caloric Anlagebau GMBH

Haldor Topsoe

Hebei Jiheng Chemical

Valmet

Tarpo

EQTEC

Chiyoda Corporation

Nel

Deokyang

Sasol

Siemens

ITM Power

GE

GreenHydrogen

Sunfire

Proton OnSite

McPhy

Key manufacturers, suppliers and consumers of fuel cells:

Bloom Energy

Ballard Power Systems

Doosan Fuel Cell America

FuelCell Energy

Fuji Electric

Hydrogenics

Proton Motor GMBH

Ceramic Fuel Cells Ltd.

Hanwha Energy

Gyeonggi Green Energy

Key fuel cell car manufacturers:

Hyundai

Kia

Toyota

Honda

BMW

Audi

Mitsubishi

Nissan

Lexus

Mercedes

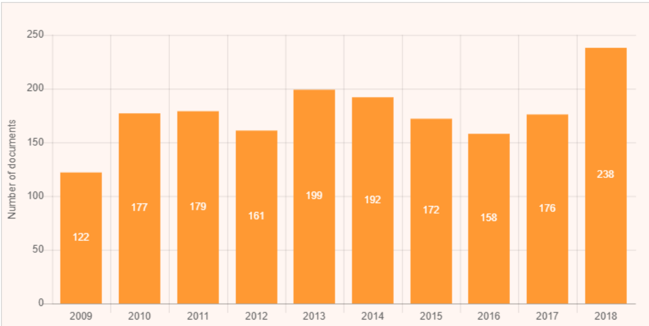
A more detailed list of companies operating in the hydrogen industry can be found on the page “List of companies”.

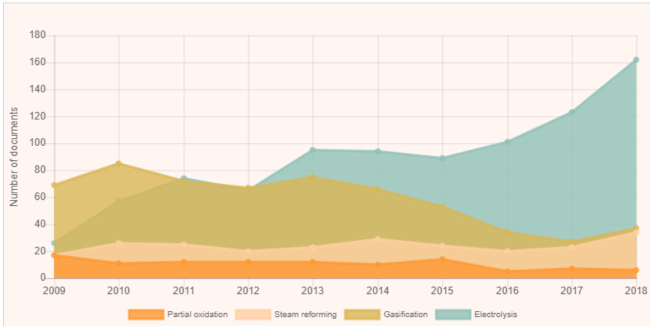
Research and innovations

One of the most affordable options for assessing research and inventive activity in modern technology is provided by the database of patent applications of the World Intellectual Property Organization (WIPO) [60]. A brief overview of patent applications published by WIPO from 2009 to 2018 on topics related to the production of hydrogen and fuel cells is presented below. The following search code was used to search for applications regarding hydrogen production (Searchquery): DP:[2009 TO 2018] ANDOF:WOAND ((IC:C01B3* ANDFP:("STEAM REFORM*" OR "STEAM METHANE REFORM*" OR "PARTIAL OXIDAT*" ORPOX)) ORFP:(gasif* AND (syngas OR "syngas" OR "synthesis gas" OR "synthetic gas" OR (hydrogen AND "carbon monoxide"))) ORIC:(C25B1/04)).

The main results of the analysis are shown in Figures 27-28.

Figure 27-28. Left - Number of patent applications registered within WIPO according to keywords of hydrogen energy. To the right - Distribution of registered patent applications within WIPO in recent years on topics related to hydrogen energy

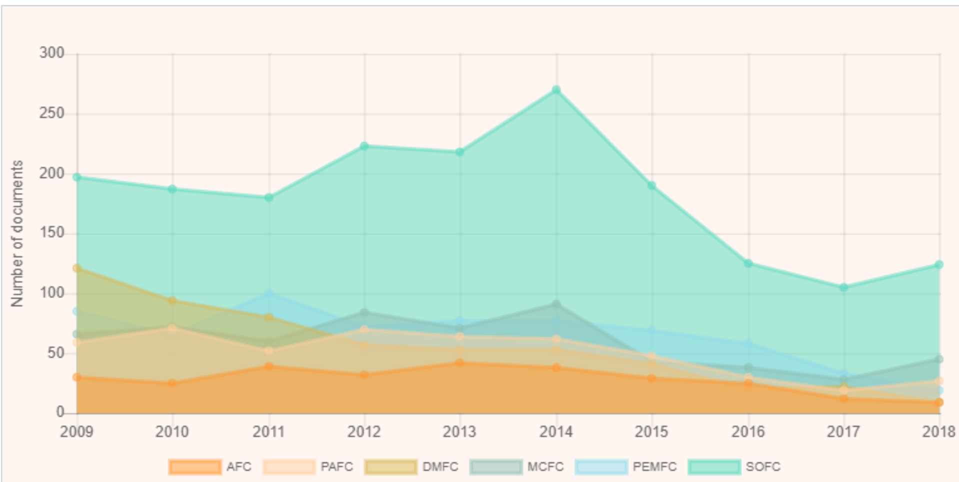




Source: World Intellectual Property Organization, search words used steam reforming"; "partial oxidation"; "gasification"; "electrolysis"; update 18.06.2019

As follows from the diagrams presented, interest in hydrogen production over the past 10 years has a slight upward trend. On average, more than 150 applications for inventions are registered annually. The greatest interest of the inventors is related to electrolysis technologies, and the topics following it related to steam reforming and gasification are rather few. Since 2009, the annual number of patent applications in the WIPO system on this subject has increased from less than 30 to 160. This is certainly a clear demonstration of the growing interest of developers in solving the problem of producing hydrogen using environmentally-friendly methods, which noticeably coincides in time with the growth of hydrogen refuelling capacities as well as fuel cells. When analysing verbal expressions in patent documents it was found that, in addition to traditional and general technological words and expressions, the word WATER was used in 13.9% of cases, GASIFICATION in 13.5%, ELECTROLYSIS in 11%, and CELL in 10.3%. At the same time, for example, STEAM and REFORMING were used much less frequently - in 7 and 5.5% of cases. A diagram of the distribution of the number of patent applications when using the key phrase fuel cells is presented in Figure 29.

Figure 29. Number of patent applications registered within WIPO according to keywords of fuel cells

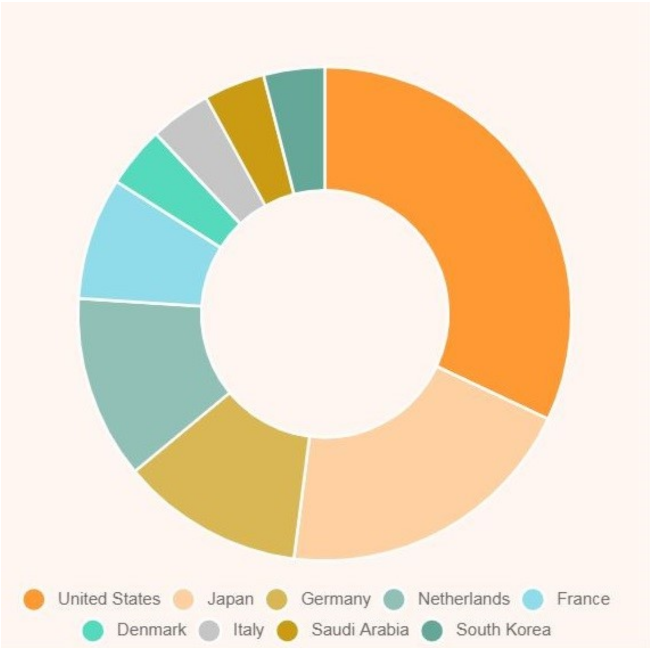


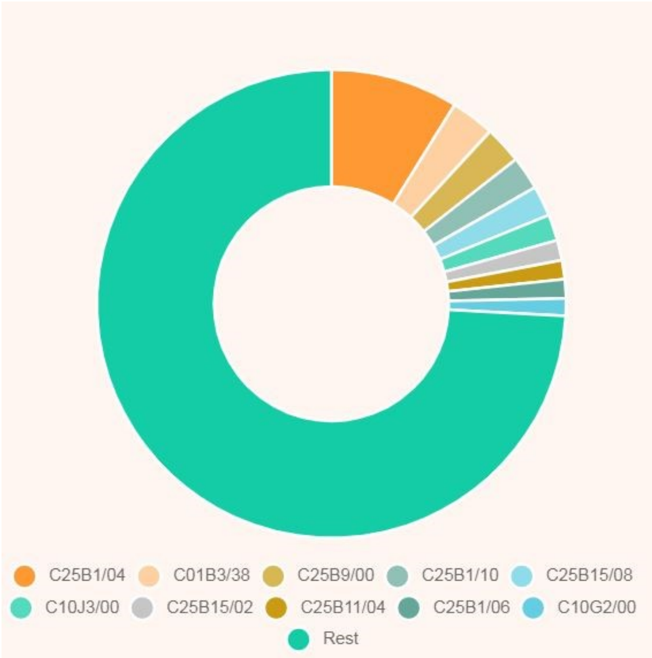
Sources: World Intellectual Property Organization, search words used "Proton Exchange Membrane Fuel Cell"; "PEMFC"; "Direct Methanol Fuel Cell*"; "DMFC"; "Alkaline Fuel Cell*"; "AFC"; "Phosphoric Acid Fuel Cell*"; "PAFC"; "Molten Carbonate Fuel Cell*"; "MCFC"; "Solid oxide fuel cell*"; "SOFC" update 19.06.2019*

In this case, in contrast to the above charts, there is a clear decrease in patent activity, at least in this patent office. The main interest of the inventors is focused on the Solid oxide fuel cell.

Figure 30 shows a distribution chart of the share of participation in the patenting process of various countries, the residents of which registered patent applications for the said time period, from among the top 25 applicants. Figure 31 shows the distribution diagram of the most common subgroups of the international patent classification identified in the examined patent documents.

Figure. 30 - 31. Left - The proportion of countries in the world in terms of the activity of their residents among the top 25 applicants. To the right—The most frequently mentioned subgroups of the IPC, (% of total)





Source: World Intellectual Property Organization, search words used "steam methane reform"; "partial oxidat"; "syngas"; "hydrogen"; "carbon monoxide"

The top five leaders among countries included the USA, Japan, Germany, the Netherlands and France, whose residents showed the highest patent activity.

These are the top 10 most commonly used IPC subgroups according to WIPO terminology -C25B1/04 - by electrolysis of water; C01B3/38 - using catalysts;C25B9/00 - Cells or assemblies of cells; Constructional parts of cells; Assemblies of constructional parts, e.g. electrode-diaphragm assemblies; C25B1/10 - in diaphragm cells; C25B15/08 - Supplying or removing reactants or electrolytes; Regeneration of electrolytes; C10J3/00 - Production of gases containing carbon monoxide and hydrogen, e.g. synthesis gas or town gas, from solid carbonaceous materials by partial oxidation processes involving oxygen or steam; C25B15/02 - Process control or regulation; C25B11/04 - characterized by the material; C25B1/06 - in cells with flat or plate-like electrodes; C10G2/00 - Production of liquid hydrocarbon mixtures of undefined composition from oxides of carbon.

Subgroup C25B1 / 04 - by electrolysis of water was much more common than others - in 8.8% of cases.

Table 3 shows the top 10 applicants who submitted the largest number of applications to WIPO during the said time period.

Table 3. Top 10 applicants in the collection of WIPO patent applications in the field of technologies, 2008-2017. (A total of 1,774 documents submitted by 2,446 applicants were processed)

Applicant	Country	No. of applications	Share of applications, %
Commissariat À L'Énergie Atomique Et Aux Énergies Alternatives	France	46	2.59
Siemens Aktiengesellschaft	Germany	42	2.37
L'Air Liquide, Société Anonyme Pour L'Etude Et L'Exploitation Des Procédés	France	30	1.69
Shell Internationale Research Maatschappij B.V.	Netherlands	29	1.63
Linde Aktiengesellschaft	Germany	28	1.58
Haldor Topsøe A/S	Denmark	24	1.35
Greatpoint Energy, Inc.	United States	22	1.24
Shell Oil Company	United States	21	1.18
Kabushiki Kaisha Toshiba	Japan	20	1.13
Praxair Technology, Inc.	United States	19	1.07

Source: World Intellectual Property Organization

The largest number of applications was submitted by Commissariat À L'ÉnergieAtomique Et Aux Énergies Alternatives (France) and the company Siemens Aktiengesellschaft (Germany). The total share of the first ten companies in the number of applications was about 16%.

Trend of development

There are many forecasts of the development of the hydrogen industry in the medium and long term up to 2050, among them there are estimates of the potential of hydrogen as a mean to reduce CO_2 emissions and boost the renewable energy.

In [61], in the framework of The Global Pathways Analysis Tool (GPAT), hydrogen demand was estimated up to 2050 for eight major countries — France, Germany, Norway, Spain, Sweden, Denmark, Japan, and the United States, as well as individual cases for some other countries. For each country, the demand for hydrogen was calculated based on assumptions about future market shares of hydrogen vehicles. The costs of hydrogen production were estimated based on regional data on raw materials available for hydrogen production by type, cost, quantity, etc. The analysis was carried out according to several scenarios based on the dominance of individual indicators. The study determined that by 2050 the general demand for hydrogen will be approximately 35 billion kg / year, while the main share of the United States. Among other consumers, Germany, Japan, Spain and France will stand out. It was also established that hydrogen production will rely on natural gas as the main raw material, and it will still be difficult for other technologies to compete with steam reforming. Insignificant competition for this method will be provided by gasification of coal and biomass and wind energy. However, for example, when doubling the price of natural gas, biomass will play a dominant role in the production of hydrogen. The taxation of CO_2 emissions can also play an important role, and this is especially sensitive to coal gasification. Also in [61], hydrogen production was estimated for the countries where the number of technological variations is much more diverse.

Sources [62–64] provide excerpts from hydrogen industry development programs for the main countries involved in this process, as well as options for Broad Hydrogen Production Portfolio in different time ranges. In the medium term, it is planned to develop biomass gasification, electrolysis through the use of electricity from wind energy and photovoltaics. In the long run, biohydrogen production is possible; renewable electrolysis; photoelectrochemical solar breakdown of water; solar high temperature thermochemical cycles.

Detailed estimates of the use of hydrogen in order to reduce CO_2 emissions at national and global levels in 2030 and 2050 are given in [65]. According to the authors, by 2050 the hydrogen industry will provide up to 20% of the global reduction in CO_2 emissions. This can be achieved primarily due to hydrogen power generation, hydrogen transport, hydrogen energy industry as well as building heating and power with hydrogen. Thus, it is assumed that by 2030 between 10 and 15 million passenger vehicles and 500,000 trucks will run on hydrogen. By 2050, even more impressive indicators are forecasted - up to 25% passenger vehicles, about 30% trucks and more than 25% of buses will operate on hydrogen. By 2030, there will be more than 5000 hydrogen refuelling stations in the world, according to the announced investments in different countries, summarized as a result of [65]. This process will be most actively developed in the United States, Germany, Denmark, France, Netherlands, Norway, Spain, Sweden, the United Kingdom, China, Japan, and South Korea. Also it is assumed that by 2030 the demand for hydrogen will increase by 4 million tons, and in 2050 12% of the global energy demand will be determined by hydrogen [65]. According to [66], there will be a significant increase in the consumption of mixed hydrogen by private households. According to the forecasts, 8% of the world's energy consumption in buildings will also be provided by hydrogen by 2050.

The analysis of the potential for future hydrogen demand in oil refining is presented in [4]. In accordance with current trends, it is predicted that the total demand for hydrogen at refineries will increase by 7% by 2030, followed by a slowdown. In this paper, as in [61], it is assumed that steam reforming, even in combination with CO_2 capture technologies, will remain the cheapest way to produce hydrogen. According to [4], hydrogen production in the chemical sector by 2030 will develop quite actively - 1.7% per year for ammonium and 3.6% per year for methanol. Regarding the use of hydrogen for vehicles in [4], it predicts a possible increase in the fleet of hydrogen vehicles - more than 50% for cars and noticeably less for trucks and buses by 2030. Prospects for the use of hydrogen in buildings for heating according to [4] are possible both as an option of mixing it with natural gas and in the form of pure hydrogen, however, this will largely depend on the price of the supplied hydrogen. There is also a table of demand and indicative prices for hydrogen for some countries of the world provided in [4].

A forecast of hydrogen demand in Asia-Pacific Economic Cooperation (APEC) countries up to 2050 is presented in [56]. It is assumed here that in 2040 the total demand for hydrogen in the region will exceed 450 billion Nm^3, and by 2050 - more than 1350 billion Nm^3. In both cases, China is the leader in demand, with a significant margin in relation to other countries, including the United States. Among other large consumers of hydrogen, in addition to, for example, the traditionally mentioned Japan, Thailand and Vietnam are mentioned. The leader in the field of the transport sector is the United States, and in the sector of power generation and industrial industry - China.

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