Estimation of possibility to implement fuel cell technology for decentralized energy supply in Russia

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Abstract

Subject: “Estimation of possibility to implement fuel cell technology for decentralized energy supply in Russia”. Master thesis work, contains 66 pages, 12 tables, 43 figures, 40 references. Supervisor: Professor Vladimir Koutcherov, co-supervisor: Valery Bessel.

Industrial power generation is an ever-changing practice. After the steam turbine was invented energy production developed with accelerated tempo. Coal replaced wood, oil replaced coal and after natural gas started being used as an energy source, no one could even imagine better and cleaner energy technologies. But in the 21st century renewable energy started its development. The western world decided to develop green, environmentally friendlier technologies with a strong desire to become independent form oil and gas exporters. Hydrogen energy and fuel cell technology are two of the most promising fields of energy study. The European Union and the USA regularly invest a lot of money for research in this area and rapidly develop an energy economy that is free from CO₂ emissions.

In this scientific report, the situation of hydrogen energy systems in the world but also with a large focus on Russia has been investigated. The main focus was made on successful international projects which have been created within last decades. Moreover, hydrogen production methods and fuel cell technology were described in detail. The cost to produce 1 kg of hydrogen gas based off of Russian economic figures and using water electrolysis and steam reforming process was estimated. Solid oxide and polymer electrolyte membrane fuel cells were considered in the analysis. The next step was to estimate effectiveness of combined technology with electrical power of 1 kW and economic feasibility of using such technology as stand-alone power generation system in the regions with decentralized electricity.
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Introduction

“In the twenty-first century, hydrogen might become an energy carrier of importance comparable to electricity. This is a very important mid- to long range research area.”

-U.S. President’s committee of Advisors on Science and Technology, 1997[23]

“Now analysts say that natural gas, lighter still in carbon, may be entering its heyday, and that the day of hydrogen – providing a fuel with no carbon at all, by definition – might at last be about to dawn.”

-New York Times, 1999[23]

“This study shows that FCEVs [Fuel Cell Electric Vehicles] are technologically ready and can be produced at much lower cost for an early commercial market over the next five years. The next logical step is therefore to develop a comprehensive and coordinated EU market launch plan study for the deployment of FCEVs and hydrogen infrastructure in Europe.”

-McKinsey study, 2010[23]

The world’s energy committees have revised their energetic strategy at the beginning of the new century. The European Union created a new energy strategy where they plan to increase the share of renewable in energy production to 20% and decrease the CO₂ emissions by 20% by the end of 2020. Many developed countries invest large sums into hydrogen energy development and fuel cells technology. In 2010, American Congress decided to invest about 300 billion USD into hydrogen and fuel cell research work. Particularly, the USA focused on hydrogen transport technologies and provides necessary funding for it. The United States is not the only country which has accelerated hydrogen energy development, as some countries in Europe and Asia have announced their projects in this area. In 2011, a new project called “Hydrogen moves Scandinavia” was established, which aimed to be a demonstration of fuel cell (FC) vehicles’ safety and simplicity. Many automobile corporations supported the project and provided their own FC transport models. (Mercedes, Alfa Romeo, Tank, Toyota) [22]. Another interesting project was developed in Iceland. In 1999, Icelandic government together with energy companies of the island created the organization “Iceland New Energy”. The objective of it was to become a main hydrogen-producing base of Europe. This project clearly shows that Europe started to develop a hydrogen infrastructure and strives to limit or even eliminate fossil fuel energy sources in the nearest future.

Japan is ahead of Europe in terms of hydrogen technologies. The twelve biggest Japanese automobile companies had a meeting on the 4th of August 2011 to propose a plan of hydrogen fuel station development in the region. By 2015, Japan plans to build 100 hydrogen fuel stations, by 2020 one thousand and by 2030 five thousand. In 2010, South Korea announced at symposium that there nine hydrogen fuel stations were built and that there will be four more constructed in 2011. China is also planning to operate a 100 million car market where 4.4 million will be hydrogen cars [23].

In other words, countries with limited access to fossil fuels are rapidly overcoming their energy dependency on oil and gas exporters. Another factor that has an effect on such behavior is worsening ecological situation in the world and the global warming danger. Russia being one of the main exporters of oil and gas to Europe should reconsider all geopolitical changes and start to prepare new energy strategy with the focus on renewable energy development.

By the end of 1980s, the USSR was one of the leading countries in hydrogen energy. One of the first automobiles as well as the first plane running on hydrogen was developed there. But the Soviet Union collapse and economic crisis caused significant slowdown of progress in this area [10]. Today, there are few successful commercial products based on fuel cell technology and hydrogen produced by water electrolysis is used only for special industrial purposes such as military equipment, medicine and space industry.
The relevance of work

Rapid hydrogen economy development hardly can be related to Russia despite the fact that 25 years ago USSR was one of the leading countries in hydrogen research. Today Russia is far away from leaders in this area and need to reconsider energy policies for next decades. Natural gas as an energy carrier does not attract European countries anymore and many of them will try to become fossil fuel free by 2020. One of the ways to save the European export market for Russia is to replace natural gas with hydrogen which can be produced with much lower cost than in Europe. However, European policies may not allow using hydrogen which was produced from fossil fuels and thus complicates this problem. In addition, hydrogen can be used as alternative fuel for stand-alone power generation systems on Russian territory where no centralized electrification is available. In the case of solar and wind power development hydrogen can be used as storage media and thus solve the problem of seasonal character of mentioned energy sources.

More than 60% of Russian territory does not have centralized energy supply. In such regions diesel and gasoline electro generators are used with total power of 5 GW and total fuel consumption of 8 M tones. Replacement of at least half of them would help to safe 1-2 M tones of fuel per year [12].

On the graph below there is comparison of main economic parameters in several regions and world. Relation between GDP and energy production in Russia is almost one to one while in regions such as Europe and the USA this relation is much higher. It means that Russian economy strongly depends on energy production and this industry in Russia is represented only by conventional energy carriers. Renewable energy development would cause development of chemical processes and production of more expensive and useful products which will positively effect on GDP.

[Figure 1– Comparison of main economic indicators of World, Europe, China and Russia [23], [25]]
The main goal of work:

Make an overview of the world hydrogen economy and project the best experience on Russian economy. Choose the best method of hydrogen production and fuel cell technology to produce electricity. Estimate the cost of hydrogen production and the economic feasibility of the chosen technology.

Main tasks:

1. Analyze hydrogen properties as energy carrier
2. Analyze world hydrogen market
3. Describe all production methods
4. Describe all ways of power generation from hydrogen
5. Choose the most appropriate technology and calculate efficiency
6. Calculate economic feasibility of the technology
7. Make a conclusion regarding hydrogen economy perspectives
Chapter 1. Market overview

1.1. Hydrogen as energy source

Hydrogen is invisible, tasteless, odorless, the most widespread chemical element on Earth. It has just one electron spinning around the core which makes it very reactive. Hydrogen as an energy carrier has many advantages compared with other fuels. The most important of them is large heat of combustion – 121 MJ/kg [10]. Methane has a lower heating value (LHV) of only about 50 MJ/kg which is 2.5 times smaller [10]. That makes hydrogen very attractive fuel from energetic point of view. In addition, it is considered to be green energy carrier, because water is the only byproduct if hydrogen is combusted. It can be used as storage media for such energy technologies as solar and wind. Hydrogen can be produced from different feedstock, starting from coal and hydrocarbons and going through biomass and water.

But even with such advantages, it remains exotic type of energy carrier and still has not found implementation in power generation in industrial scale. Main reason is that hydrogen has to be synthesized before it can be used which dramatically increase investment cost and makes technology out of competition. Moreover, energy stored in 1 m$^3$ of hydrogen is way less than in 1m$^3$ of methane or other hydrocarbon gases. Thus hydrogen has to be compressed or even liquefied to increase concentration of stored energy in limited space. High diffusion coefficient and broad diapason of detonation concentration with air also causes some problems in storage.

Absence of well-developed hydrogen infrastructure causes slow technology development in this field. Nevertheless, in Russia transport and storage systems for hydrogen were developed since 60s years of last century. Construction of cryogenic equipment for liquid hydrogen storage and transport over railways and roads was caused by need of hydrogen for space rocket systems. The leader in cryogenic technologies in Russia is “Cryogenmash” company. It has sufficient scientific potential, rich experience and necessary basement for production of hydrogen equipment [5].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>High combustion heat per kg =121MJ/kg</td>
<td>Low combustion heat per m$^3$ =10,8 MJ/m$^3$</td>
</tr>
<tr>
<td>Unlimited amount on a planet, different feedstock</td>
<td>Present only in associated state, extra cost for production</td>
</tr>
<tr>
<td>Environmentally friendly, and water is the only combustion byproduct</td>
<td>Wide range of detonation concentration with oxygen</td>
</tr>
<tr>
<td>Storage media for seasonal energy sources</td>
<td>Highly volatile and diffusive which cause transport and storage losses</td>
</tr>
<tr>
<td>Non-toxic</td>
<td>Absence of hydrogen infrastructure</td>
</tr>
</tbody>
</table>
1.2. World hydrogen market

On the 25th of March 2014 conference “Hydrogen 2014” was held in Moscow. A comparison of world and Russian hydrogen market was presented. In 2013 about 55-58 M tones of hydrogen were produced around the world [3]. 25% of it belongs to USA, 22% to China, 13% of hydrogen was produced in Europe, Russia has 8%, Japan-5%, South Korea-2% (Figure 2).

USA remains the main hydrogen producer – about 25% from world production. 67% of it goes for refining processes, 22% for ammonia production and 2% - methanol production. Last 8% includes power generation and transport [23].

The most popular feedstock for hydrogen production – natural gas, it takes about 48% of total amount. Water electrolysis provides just 4% of hydrogen [3].

![Figure 2– World leaders in hydrogen production, 2013 (3)](image)

![Figure 3– Main types of feedstock for hydrogen production, 2013 (3)](image)
Most of the produced hydrogen goes to refining processes, ammonia and methanol production. Some small parts are necessary for such industries as food production, medicine, space crafts and military equipment. Power generation and automobile industries still consume very small amount of hydrogen – about 0,1%. But in many countries new technologies and research work are welcomed by the government which makes hydrogen technologies very attractive for development. In 2008 about 5,6 B USD were spent around the world for research work [15]. It is expected to have a benefit from hydrogen economy from 3 to 9 B USD by the end of 2015 [15]. Fuel cell technology is one of the most perspective fields of study which could bring the biggest income. In 2009 hydrogen industry had about 40,000 employees and this value will grow till 700000 by the end of 2019 [15].

According to WETO (World Energy Technology Outlook) H2 project in 2010 2 TWh of the world’s electricity were produced from hydrogen. By 2030 it is expected to grow till 39 TWh and by 2050 till 811 TWh [15]. Main source for production will be renewable energy by 2050, followed by coal gasification [15].

<table>
<thead>
<tr>
<th>Electricity Production (TWh)</th>
<th>2001</th>
<th>2010</th>
<th>2030</th>
<th>2050</th>
<th>Annual % change</th>
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<tbody>
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<td>Thermal, of which :</td>
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<tr>
<td>Coal, lignite</td>
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<td>of which advanced coal</td>
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<td>Gas</td>
<td></td>
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<td>of which combined cycle</td>
<td></td>
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<tr>
<td>of which cogeneration (industry)</td>
<td>5.06</td>
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<tr>
<td>Oil</td>
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<td>Biomass</td>
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<td>Nuclear</td>
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<td>of which new design</td>
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<td>Hydro (large)</td>
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<td>Hydro (small)</td>
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<tr>
<td>Wind</td>
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<tr>
<td>Solar</td>
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<tr>
<td>Hydrogen</td>
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<table>
<thead>
<tr>
<th>WORLD</th>
<th>2001/10</th>
<th>2010/30</th>
<th>2030/50</th>
</tr>
</thead>
</table>

Table 2- World electricity production methods [38]

It is expected that by 2050 about 55% of hydrogen will be produced from renewable energy sources, 30% from coal, 10% from nuclear power and only 5% from natural gas [38].
1.3. Successful international projects

1.3.1. "H₂ moves Scandinavia"

In 2008 public-private partnership Fuel Cell and Hydrogen Joint Undertaking (FCH JU) funded a new and unusual project which was acknowledged by European Union. This project had the goal to increase popularity of hydrogen energy in Europe, broad diversity of energy sources, increase renewable energy share in European energy industry and reduce greenhouse gas emissions to the environment. Total project cost is estimated to 7.7 M Euros[22]. Four automobile companies joined the project and offered their fuel cell models for test: Daimler, Honda, Toyota, and Hyundai. The idea of the project was that local auto drivers would use fuel cell transport for 1-2 years every day going to work and charging cars on special hydrogen fuel cell station. To realize this project Oslo was chosen as the main place for test. It was chosen due to many factors. Over 95% of electricity in Norway is produced from hydro energy [22]. Norwegians are very open for green technologies and support the government in this area. Government also tries to make green transport more attractive for citizens by lowering taxes, providing free charging fuel stations and parking area. In Norway electrical charging stations are already existed before start of the project. In addition cold Norwegian climate is suitable for testing of cold start characteristics. 8 out of 10 Mercedes Benz cars on Daimler fuel cells were given to clients and two cars were left for fuel station testing. By the end of the project all participants were satisfied with engine operation and none of them had any problem with charging the car on fuel station, cold start features and driving on the streets [22].

Figure 5 – H₂ moves Scandinavia project, map of participants [22]

In May, 2011 Hyundai joined the project and offered its models. Copenhagen and Oslo were chosen as the place for testing.

Other automobile companies mentioned above took the part in driving tour over 5 countries and 9 cities which was finished in 1 month. During this tour participants demonstrated their models and new technologies in this area on seminars, exhibitions and conferences [22].
For the project purposes a stationary hydrogen fuel station was constructed in Oslo. This station produces 20 kg of hydrogen per day by electrolysis of water. However, the maximum production is estimated to 200 kg per day. This hydrogen fuel station is still functioning in Oslo.

![Hydrogen fuel station in Oslo](image)

To provide the fuel for cars during demonstration tour around 5 countries several mobile fuel stations were developed. Fuel cell modules were fixed inside the tracks and when it achieved destination construction works took 2 days. Such mobile fuel stations were installed in 4 countries and 6 cities in total. During all demonstration tour no emergency situation happened. It proves reliability of hydrogen as alternative energy source.

“H₂ moves Scandinavia” was finished in 2012 and showed feasibility of hydrogen transport development. Nevertheless, to start fuel cells car implementation into auto market many problems should be solved. Hydrogen used in fuel cells must be very clean which can be achieved only by electrolysis of water. However, electrolysis is very expensive way of hydrogen production. It can be afforded only by such countries as Norway, Sweden and Denmark where electricity prices are lower than fossil fuel prices. In Germany electricity remains relatively expensive and other more economic hydrogen production methods should be developed. In addition hydrogen infrastructure is not enough developed yet to convince people buying fuel cell cars. Amount of hydrogen fuel station in Scandinavia is quite small which forces drivers to plan their route and time for charging in advance and reject long distances trips [22].

### 1.3.2. “myFC”

“myFC” is a Swedish innovation company which develops new green technologies in the field of portable electronics. Nowadays, the main achievement of the company is charging device that can work not just through a Li-ion battery but also through a fuel cell system without access to regular electricity. This product is already available on the market and any person can buy it just for 150 euros. Capacity of 1400 mAh or 5.15 Wh, power 6.5 W and charging can be done through USB port [28].

The main principle of the device is based on electricity generation by means of an electrochemical reaction. NaBH₄ and water are used to produce the hydrogen gas. The hydrogen dissociates into protons and electrons. Hydrogen protons migrate through the Nafion electrolytic membrane which divides the cathode-anode space and reacts with the air's oxygen. This process causes a water byproduct and electricity generation.
Accurate and smart marketing allowed this device to occupy some space in the European market of portable devices. The price of such charging system remains higher compared with the price of a cell phone, which should use it but nevertheless, it is a big step in development of portable green technologies [28].

1.3.3. “Iceland New Energy”

Even though Iceland is not a member of the EU it actively participates in many European projects. In 1999 Icelandic government decided to create new organization “Iceland New Energy” which will deal with new transport industry development free from fossil fuels. This organization focused all strength on hydrogen infrastructure development in Iceland and it should replace all fossil fuel market in the nearest future.

Of course such project for a country with population of 300 thousand people is more than ambitious. Therefore, the European Union actively supports it providing all necessary technical equipment, transport models and qualified human resources. Iceland from its side provide outstanding platform for project realization – geothermal energy sources make this country very attractive object for funding new green technologies.

During 2003-2007 three fuel cell buses operated in Reykjavik. Every day they were charged at a hydrogen fuel station combined with a gasoline station. It produces about 60 m³ of hydrogen per day which is enough to charge three busses. One charge of 20-25 kg of hydrogen is enough to drive 15-200 km for one bus. The station also has an option to charge cars with capacity of 2-5 kg. Hydrogen price on such station is 1390 Icelandic crowns (króna) or 14 euro per kg. Apart from busses there are 13 automobiles on fuel cells or hydrogen internal combustion engine. The Daimler A-class engine model for Mercedes Benz requires charge every 25 miles with battery capacity 35 kWh [25].

Toyota provided a car with internal combustion engine on hydrogen. Such models are less successful requiring charge every 165 km. Every 1 kg of hydrogen holds enough energy for 60-80 km [25].
Ford also implemented 15 cars on Iceland’s roads. Ford models used proton exchange membrane fuel cells with compressed to 34 MPa hydrogen. Ford Focus FCV has best mileage per day between other fuel cells models – about 2250 km and charging every 240-320 km [25].

The most impressive project realized in Iceland is the sea boat Elding that runs on fuel technology.

![Figure 8–Boat powered by fuel cell in Iceland [25]](image)

“Iceland New Energy” continues to set ambitious goals by constantly increasing number of green transport on the roads.

### 1.4. Hydrogen market in Russia

In the world, main share of produced hydrogen is used for refining processes. However, hydrogen consumption in Russia differs from the world’s. Russia produces about 8% of world hydrogen which is about 4.5 M tones. 55% of it goes for ammonia production, 22% for refining processes and 13% for methanol production [3]. Almost all hydrogen is consumed at the same place where it was produced. Present demands of liquid hydrogen in Russia are relatively low even though infrastructure for its production, storage and transportation has already been developed. The space-rocket industry plans to develop modern starting blocks for space constructions which will use liquid hydrogen as a fuel. Thus in 2015 fly testing events are planned for new oxygen-hydrogen starting block РБ КВТК (RB KVTK) [3].

A new project between “Linde” and “Kuibishev Nitrogen” about hydrogen production was discussed in 2013. The start of production is set in 2016 with power load of 120 thousand m³/h and 1340 tones of ammonia per day. Investment cost of the project is about 11 M rub. [3].

“Air Liquide Gas AB” company has 3 plants of hydrogen production in Russia. Two of them produce hydrogen for glass industry and the third for open usage. Foster Wheeler representatives develop new natural gas steam reforming reactors which will have smaller sizes and relatively low investment cost[3].

Many chemical companies experienced a problem with Sulphur content in hydrocarbon fuels after new policies were established. Therefore hydrogen is necessary to reduce Sulphur and increase quality of fuels. In 2014 new membrane reactor Medal was started by “Air Liquide Gas AB”. “Haldor Topsoe” also presented their unit of natural gas steam reforming which will start exploitation in 2016 [3]. “UralKriomash” is working on railway tankers for liquid hydrogen transportation improving old technologies by loss reduction and size increasing.

In 2005-2009 The Russian Federal Nuclear Center (VNIIEF) created pilot stand-alone power generation system based on polymer electrolyte fuel cell technology which can be used on cathode protection stations
of pipeline transport system. Such stand-alone pilot plant has no analogs in the world. It uses import fuel cell stacks produced by “Morphil Exergy” (Italy) with power load of 6 kW [8].

Main characteristics of the pilot plant:

- **Fuel**: natural gas
- **Oxygenation agent**: air
- **Electrical power**: 1-3.5 kW
- **Voltage**: 220 V
- **Electrical efficiency**: 24%
- **Lifetime**: 40000 hours
- **Time to achieve operating mode**: 2 hours
- **Toxic exhaust gases**: CO, NOx within ppm scale
- **Noise**: less than 60 Db
- **Construction scheme**: 3 modules (electro technical section, electrochemical generator, fuel cell processor), gabarites 4.6x2.3x2.5 m [8].

*Figure 9 – Pilot plant’s stand-alone power generation system made by “Rosatom” [8]*
Chapter 2. Production of hydrogen

2.1. Water destruction

2.1.1. Electrolysis

Electrolysis of water was first performed in 1800 by English scientist William Nicolson:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2 \]

Iogan Ritter first collected electrolysis products separately after 1 month after the invention. In industry electrolysis found application only in XX century. In 1927 the Norwegian company “Norsk Hydro electrolysers” constructed first alkaline electrolyser for ammonia production [10].

The maximum efficiency of the electrolyser is the relation between hydrogen combustion heating value and the changing of Gibbs energy during the process. Experimental works showed that for water destruction it is necessary to attach 1.48V of electricity. With growing pressure this value is growing and it causes efficiency reduction. Nevertheless, further compression of hydrogen for better transportation and storage make it economically reasonable to perform electrolysis under 2-3 MPa. The influence of temperature is the opposite – with growing temperature voltage is decreasing and efficiency is growing [10].

Figure 10 - Electrolyser working principle

For alkaline and polymer electrolyte membrane electrolysers efficiency varies between 75 and 85%. They can be used for gas chromatograph production, in metallurgy, heavy water and hydrogen isotopes production.

Types of electrolysers

The most popular types of electrolyser are alkaline and polymer electrolyte membrane electrolysers. In alkaline electrolyser water solutions of KOH or NaOH (up to 40%) are used as electrolyte. Reduction of water with hydrogen generation happens on cathode. Oxidation of alkaline hydroxyl ions with oxygen generation happens on anode:
K: \(2\text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-\)

A: \(2\text{OH}^- - 2e \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}\)

Electrical potential \(E_o = 1.229\ \text{B}\)

As a material for electrodes steel lattice cover with Ni is used. Porous diaphragm which separates cathode-anode area can be prepared from asbestos.

The main advantages of alkaline electrolyser are cheap materials and components of the process. But the quality and purity of hydrogen produced is relatively low. Energy consumption in such electrolyser is about 4.5 kWh/m³ with electrical density 0.2-0.3 A/sm². With growing electrical density energy consumption is growing. World leader in electrolyser production is Norsk Hydro Electrolyser. Their production ratio – 495 m³/h and energy consumption – 4.1-4.3 kWh/ m³ under working temperature of 80 °C and atmospheric pressure. The hydrogen purity is 99.9% [10]. The removal of O₂ and water vapor requires catalytic DeOxo and a dryer for subsequent removing of water contaminants [33].

Polymer electrolyte membrane electrolysers are considered the safest and the most effective for hydrogen production. First such electrolysers came out in 1966 by General Electric and were applied for space crafts.

Destruction of water and generation of oxygen happens on anode and hydrogen ions migrate through ion-exchange membrane and pure hydrogen generates on cathode.

A: \(\text{H}_2\text{O} - 2e \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+\)

K: \(2\text{H}^+ + 2e \rightarrow \text{H}_2\)

The membrane represents elastic transparent film with thickness of several hundred microns which was made from tetrafluoroethylene with substituted sulphur-groups. If the membrane contacts with water it swells and dissociation of components starts. Thus hydrogen ions are able to migrate through the membrane. Such type of electrolyser is safe under high pressures, has smaller size and provides hydrogen with purity 99.99%. Energy consumption is 3.9 kWh/m³ with electrical density 0.5-1 A/sm³. Production ratio is up to 26 m³/h. As disadvantages high cost, short lifetime of membrane and usage of rare metals can be considered [10].

The third type – ceramic electrolyte electrolysers. Water reduces till hydrogen on cathode and oxygen ions migrate to anode with further oxygen generation.

K: \(\text{H}_2\text{O} + 2e \rightarrow \text{O}^{2-} + \text{H}_2\)

A: \(2\text{O}^{2-} - 2e \rightarrow \text{O}_2\)

Solid oxide electrolysers work under 800-1000 °C. Dioxide of Zr stabilized with Ir and Sc oxides is used as electrolyte. Cathode and anode materials are placed on both surfaces of electrolyte. Metalokeramic alloy based on Ni and Zr is a cathode material and doped Pt is an anode material. Such electrolyser has unique technology of water and carbon dioxide destruction with oxygen production which can be used as a life support system in space. Energy consumption is just 2.3-3 kWh/m³ but the problem of construction material is still actual [10].
The need for electrolysers:

- Automobile hydrogen station (100-1000 m³/h)
- Standalone renewable energy installations (10-100 m³/h)
- Electronic industry (10000-15000 m³/h)
- Metallurgy (8000 m³/h)
- Glass production (5000 m³/h)
- Food production (2000 m³/h)
- Energy production (1000 m³/h)
- Production of heavy water and hydrogen isotopes
- War technique [10]

Economic aspects of electrolysis

Despite relatively high efficiency of the process the cost of hydrogen produced by electrolysis of water remains high due to significant electricity consumption. Calculation of hydrogen cost depends on such factors as cost of equipment, electricity tariffs, electrolyte, salary for employees, reconstruction and repair of installed details. Life cycle of alkaline and polymer electrolyte membrane electrolysers before overhaul are about 5-8 years. After 5000 hours of operation time cost of hydrogen depends on electricity prices on 65-70%. Mitsubishi announced production of polymer electrolyte membrane electrolysers under 7nMPa with cost of 720000 rub/m³ of hydrogen. Russian alkaline electrolysers models cost about 260000-500000 rub/m³ of hydrogen. Estimated price for 1 kg of hydrogen is 3-4 USD which is 2 times more expensive than production from fossil fuels. Polymer electrolyte membrane electrolysers have the lowest electricity demands but overall efficiency remains 20-30% lower because of thermal losses [10].
2.1.2. Water thermolysis and thermochemical cycles

Hydrogen and oxygen can be produced by thermochemical destruction of water under 3000°C where 10% of water is destructed and the rest can be recycled. However, there are some methods with milder conditions which are called thermochemical cycles.

Mark-1

In 1969 de Beni offered first 4 steps cycle working with Hg, Ca and Br compounds:

\[ [730 \, ^\circ C] \quad CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr \]
\[ [250\, ^\circ C] \quad Hg + 2HBr \rightarrow HgBr_2 + 2H_2 \]
\[ [200\, ^\circ C] \quad HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + HgO + H_2O \]
\[ [600\, ^\circ C] \quad HgO \rightarrow Hg + 1/2O_2 \]

This method did not find application due to toxic components used.

As another example sulphur/iodine cycle can be described:

\[ [850\, ^\circ C] \quad H_2SO_4 \rightarrow SO_2 + H_2O + 0,5 O_2 \]
\[ [120\, ^\circ C] \quad I_2 + SO_2 + H_2O \rightarrow H_2SO_4 + 2HI \]
\[ [450\, ^\circ C] \quad 2HI \rightarrow I_2 + H_2 \]

SUM: \quad H_2O \rightarrow H_2 + 0,5 O_2

Efficiency of such processes depends on amount of steps, reaction complicity, heat losses and energy cost for reagents transfer. Development of such technologies is restrained by complicity, absence of high temperature energy sources and strong corrosion. Nevertheless, efficiency and productivity of some of them make process development perspective [10].

2.2. Production of hydrogen from fossil fuels

2.2.1. Natural gas

There are many different types of feed which can be used for hydrogen production: natural gas, liquefied natural gas (LNG), mixture of gasoline fractions, methanol, heavy duty oil fractions, coal, municipal solid waste and biomass. Almost in every case the main product of the process – synthesis gas which contains of carbon monoxide and hydrogen in different proportions.

Hydrogen can currently be produced from natural gas by means of three different chemical processes:

1. Steam methane reforming (SMR)
2. Partial oxidation (POX)
3. Autothermal reforming (ATR)

Although several new production concepts have been developed none of them is close to commercialization.

Steam reforming of methane is the most popular method of hydrogen production in industry. It involves methane and water vapor endothermic conversion into hydrogen and carbon monoxide:

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]
As an oxidiser oxygen or carbon dioxide can be used:

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]

The main products of reaction are synthesis gas, carbon dioxide and unconverted reactants.

With increased temperature and decreased pressure process conversion is growing. It is close to 100% at 800-900 °C. However, to increase reaction ratio one should deliver high pressures and use catalyst. As a catalyst Ni on Al₂O₃ support can be used. Thus typical reaction parameters are 700-850 °C and 0,3-2,5 MPa [30]. Addition of carbon dioxide allowed regulation of CO/H₂ ratio which is used for different purposes and different chemical reactions. Efficiency of the process is the highest between other hydrogen production methods – 70-80%. This caused by high energy intensity and productivity of the process.

The product gas contains approximately 12% of CO, which can be further converted to CO₂ and H₂ through the water-gas shift reaction:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

If water is used as oxidiser reformation is divided in two steps: 1st under 350-400 °C with Fe-Cr catalyst and 2nd under 200-250 °C with Zn-Cr catalyst.

![Figure 12– Technological scheme of natural gas steam reforming combined with FC stack.][11]

Steam reforming provides syngas with hydrogen content about 75% at elevated pressure. Pressure swing adsorption (PSA) can produce purified hydrogen with typical purity of 99,99%. Non-hydrogen gases are adsorbed by activated carbon or molecular sieves. By expanding the adsorber vessel to almost atmospheric pressure these gases are desorbed and returned to the reformer as auxiliary fuel [33].

In case of partial oxidation no additional heat is required for process acceleration because of methane combustion with oxygen in exothermic reaction:
\[ \text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]

Thus more compact reactor design is possible as there is no need of any external heating of reactor. Temperature can reach 1400 °C and pressure 5-6 MPa. Synthesis gas after partial oxidation also goes for second step of the process – water gas shift reaction. Due to redundant heat efficiency of partial oxidation process can reach 90%. However to produce pure oxygen one should spend a lot of extra energy which reduce the overall efficiency of such method.

![Figure 13- Simplified process flow sheet for steam reforming process [33]](image)

The combination of two processes listed above represents auto thermal reforming. The heat produced from combusted methane is used for steam reforming with Ni catalyst. The total reaction is exothermic, and so it releases heat. The outlet temperature from reactor is in a range of 950 to 1100°C and the gas pressure can be as high as 10 MPa [30]. Such method is attractive because other types of feed such as heavy duty oils can be used.

<table>
<thead>
<tr>
<th>Technology</th>
<th>SMR</th>
<th>ATR or POX</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benefits</strong></td>
<td>Higher efficiency</td>
<td>Smaller size</td>
</tr>
<tr>
<td></td>
<td>Costs for large units</td>
<td>Simple system</td>
</tr>
<tr>
<td></td>
<td>Lower emissions</td>
<td>Costs for small units</td>
</tr>
<tr>
<td><strong>Challenges</strong></td>
<td>Complex system</td>
<td>Emissions/flaring</td>
</tr>
<tr>
<td></td>
<td>Sensitive for feed quality</td>
<td>Lower efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{H}_2 ) purification</td>
</tr>
</tbody>
</table>

In Western countries hydrogen is often produced from methanol. Temperature of the process is just 200-300 °C and conversion is carried in 1 step with direct production of hydrogen and carbon dioxide. Disadvantage of the process is production of methane as a byproduct. To suppress side products
formation such catalysts as Cu and Zn can be used. Methanol is popular hydrogen source in automobile industry, often converter with it is installed directly in automobile which is very continent and provide quick source of hydrogen for fuel cell.

One more method for hydrogen production is pyrolysis of methane or any others hydrocarbons.

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

Essential conditions are metallic catalyst and temperature of 800 °C. Carbon is another product of the process apart from hydrogen. It can be used in production of resins, graphite, electrodes and plastics. But the efficiency of such process is relatively low – just 55% because methanol energy potential is used not totally.

### 2.2.2. Production from coal and solid hydrocarbons

Hydrogen can be produced by gasification of solid hydrocarbons. The main difference from conversion of organic compounds is that the feed has solid state. That defines reaction kinetics features. Gasification needs special preparation of the feed and elimination of slag. The most popular solid material used is coal, but sometimes it can be peat, oil shale, biomass or municipal solid waste. The main product of gasification is carbon monoxide. Hydrogen comes mainly after second step of the process – steam reforming. The main disadvantage of the process is increased carbon dioxide yield which is greenhouse gas.

Only 1% of world’s hydrogen is produced by gasification of coal. It can be performed be two ways: in the reactor or underground. Second type is gasification of coal right in the deposits where produced synthesis gas is extracted through special channels back on surface. Apart from synthesis gas there are many side products such as nitrogen, methane, nitrogen and sulfate oxides. Increasing temperature above 950 °C reduces side products formation until 5% and replaces equilibrium to the synthesis gas formation side. Pressure affects the process on the opposite direction [32].

![Typical coal gasification process](image)

**Figure 14** – Typical coal gasification process [32]

Hydrogen produced from coal is the cheapest one. The price varies around 2$ per kg. But carbon dioxide production is much higher comparing with other processes and counts about 1-1,4 kg/m³ [10].
Capture and storage of CO₂

Carbon dioxide is a major exhaust in all production of hydrogen from fossil fuels. The amount of CO₂ varies with respect to the hydrogen content in the feedstock. By capturing and storing carbon dioxide exhaust energy industry goes in a way of sustainability with respect to ecological situation on the world.

There are three main types of decarbonization used in combustion processes:

1. Post-combustion
   In conventional gas turbine power plant CO₂ from exhaust gas can be captured by monoethanolamin or its homologies. Exhaust gas after burner goes through absorber where CO₂ forms salt with MEA. Second step of the process is regeneration of MEA.

2. Pre-combustion
   CO₂ is captured when producing hydrogen through any of the processes discussed above.

3. Oxyfuel-combustion
   When combustion process is performed with pure oxygen as an oxidizer exhaust gas contains only water vapor and carbon dioxide. Therefore CO₂ can be separated by condensation of water vapor. The captured CO₂ can be stored in geological formations like oil and gas dry deposits as well as aquifers.

2.2.3. Production from methanol

Alternative method is methanol cracking that occurs at significantly lower temperatures than steam reforming process.

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \]

Operating temperatures 250-350 °C, pressure of 10-25 bar over Zn-Cu catalyst.

To produce 1m³ of hydrogen approximately 0,65 kg of methanol is required [33]. Such hydrogen is more expensive than the one produced from natural gas, but way cheaper than electrolysis hydrogen. On a picture below there is a typical scheme of the process.

![Simplified process flow sheet for methanol cracking](image-url)
2.3. Hydrogen production from renewables

2.3.1. Biomass to hydrogen

Conception of hydrogen production is basically similar to coal gasification process. The process may be viewed as “combustion-like” conversion, but with less oxygen available than needed for burning. The ratio of oxygen available and the amount of oxygen that will allow complete combustion is called “equivalence ratio”. For value below 0,1 the process is called “pyrolysis”, and only modest part of biomass is converted into gaseous form while the rest is char and oily residues. Proper gasification occurs with equivalence ratio between 0,2 and 0,4. This is the region with maximum energy transfer to the gas [32].

Table 4 - Biomass conversion processes with different products [32]

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Energy consumed (kJ g⁻¹)</th>
<th>Products / process</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₀O₅ → 6C + 5H₂ + 2.5 O₂</td>
<td>5.94°</td>
<td>elements, dissociation</td>
</tr>
<tr>
<td>C₆H₁₂O₆ → 6C + 5H₂O(g)</td>
<td>-2.86</td>
<td>charcoal, charring</td>
</tr>
<tr>
<td>C₆H₁₂O₆ + 0.8 C₆H₅O → 1.8 H₂O(g) + 1.2 CO₂</td>
<td>-2.07°</td>
<td>oily residues, pyrolysis</td>
</tr>
<tr>
<td>C₆H₁₂O₆ + ½O₂ → 6CO + 5H₂</td>
<td>0.16</td>
<td>ethylene, fast pyrolysis</td>
</tr>
<tr>
<td>C₆H₁₀O₅ + ½O₂ → 6CO + 5H₂</td>
<td>1.85</td>
<td>synthesis gas, gasification</td>
</tr>
<tr>
<td>C₆H₁₀O₅ + 6H₂ → 6°CH₄° + 5 H₂O(g)</td>
<td>-4.86°</td>
<td>hydrocarbons, –generation</td>
</tr>
<tr>
<td>C₆H₁₀O₅ + 6O₂ → 6CO₂ + 5 H₂O(g)</td>
<td>-17.48</td>
<td>heat, combustion</td>
</tr>
</tbody>
</table>

There are three main types of gasifiers: updraft, downdraft and fluidized bed. Updraft reactor causes high rate of tar, oil and corrosive formation in pyrolysis zone. Downdraft reactor solves this problem by cracking all heavy products in hot charcoal bed. Fluidized bed is more useful for large scale operations due to shorter passage of time. But tars and ashes coming out together with gas fraction and have to be separated with scrubbers and cyclones.

![Gasifier types: a) updraft, b) downdraft and c) fluidized bed](image16)

The gas produced by biomass gasification has medium quality with LHV about 10-18 MJ/m³. In order to serve a source of useful hydrogen it should be upgraded till 30 MJ/m³ [32].
Biomass feedstock is unrefined product with inconsistent quality and poor quality control. Production methods vary according to crop type, location and climate. Large scale systems tend to be suitable for lower quality and cheaper fuels, while small scale systems need homogeneous good quality fuel [23]. For this process several problems has to be solved: capture of thermally split hydrogen, avoid of side reactions and usage of toxic materials. But the main challenge is corrosion processes.

Photovoltaic systems coupled with electrolyzers are commercially available. The system offer some flexibility as the output can be either electricity from PV cell or hydrogen from electrolyser. Another variation is photoelectrolysis where light is used to split water directly into hydrogen and oxygen. Such technology offers great potential for cost reduction of electrolytic hydrogen and may compete with conventional processes. Various laboratory scale PEC devices have been developed last years and demonstrated solar-to-hydrogen conversion efficiency up to 16% [23].

2.3.2. Photobiological production

The first out-of-laboratory demonstration of renewable method for hydrogen production from wastewater using microbial electrolysis cell (MEC) system is underway at the “Napa Wine Company” in Oakville, California. The refrigerator-sized hydrogen generator takes winery wastewater, and using bacteria and a small amount of electrical energy, converts the organic material into hydrogen. Typical winery in California can generate up to 10-12 M gallons of wastewater per year [27]. MEC is an electrolysis cell in which exo-electrogenic bacteria oxidise biodegradable substrates and produce electrons and protons at the anode.

Experiments have determined that the bacteria can produce an anode working potential of 0,3 V and that only additional 0,11 V are needed to produce hydrogen in theory. In practice more like an additional 0,25 V are needed due to over-potential at the cathode.

MEC-based production concept requires two key steps. First, one group of bacteria turns unused sugar and unwanted vinegar from improper fermentation into electricity. Only a small amount of electricity is produced and it is not enough to reach 1,0 V to split water in a typical electrolysis reaction. Therefore,
some additional electricity from the power grid is also used. Second, another group of bacteria uses electricity to split water molecules into oxygen and hydrogen.

About 1000 liters of wastewater per day are being processed at the “Napa Wine Company”. One of the biggest problems that the project has had to overcome so far is the bacteria variability of run-off water, making production rates difficult to predict because the bacteria have to build to a certain level of concentration to be effective. Another issue is that much of the hydrogen is being consumed by “methanogenic” microbes before leaving the solution, leading to much greater production of methane than hydrogen [27].

![Figure 17 – Principal scheme of NAPA Pilot plant [27]](image)

### 2.3.3. Solar energy for hydrogen

**Photolysis**

In developed countries it is popular to produce clean energy from solar and wind power. A solar cell is one of the main energy converter which has good potential for electricity production. Hydrogen – perfect storage media which can be used in combination with solar cells at night or cloudy weather [23].

Another modern method is to produce hydrogen using solar PV panels. Such systems produce hydrogen and electricity at the same time. Solar beams converts into electricity and this energy is used for water electrolysis. If solar beams are used directly for water destruction then it is photolysis. Such technology has good potential in reduction of energy consumption. So far maximum efficiency of photoelectrolysis is 16% [10]. The main challenge is to develop effective photo electrode materials [30].

**Photobiological method**

Photobyological production of hydrogen is based on 2 steps: photosynthesis and hydrogen production catalyzed by algae or cyanobacteria. Long term basic and applied research should be developed in this area to reproduce photosynthesis in large bioreactors. Or, as an option, artificial photosynthesis me be performed [23]:
$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2$

$4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2$

American company “Xerox” together with “CAN” in the end of last century developed an energy system working on solar cells. Solar energy converted into electricity is used in electrolysis with hydrogen flow rate 1.7-2.4 $\text{m}^3$/h. Produced hydrogen is compressed till 34.5 MPa and goes to the drier. After the process hydrogen is pumped into tankers for storage and delivered to refueling stations. 74 $\text{m}^3$ of hydrogen can replace 19 liters of gasoline and it is enough to drive 225 km.

This project after several years of performance was modernized into fuel cell production. In early 2010 “Honda Motor Company” in Torrance, California opened a new compact hydrogen solar-hydrogen refueling station. This project is developed to demonstrate what could be envisioned at the household level, where solar PV panels are used to produce electricity need for water electrolysis. The system uses 48-panel, 6-kW solar PV system [27].

Using new type of high-differential pressure electrolyser eliminates the need for the compressor. This is expected to improve system efficiency by 25% and reducing the size and cost of other key components. The station has small capacity allowing for only 0.5 kg of hydrogen produced over an 8 hour period. However, the company persuades it is sufficient to drive 10000 mile per year [27].

An interesting feature of the station is that it is designed to take advantage of “net metering” and potential future “smart grid” developments by exporting electrical power to the grid during the day and then using a similar amount of energy at night during off-peak times.

Figure 18–Hydrogen fuel station Honda Motor Company [27]
2.4. Other methods

2.4.1. Membrane technologies

The main idea of membrane technologies is implementation of gas permeable membranes with selective gas permeability. Such reactor combines conversion and separation of components, which makes the process less costly. For hydrogen production two types of membranes can be used – with oxygen and with hydrogen permeability. Oxygen membranes are made from CaTiO$_3$ which has regular crystal lattice defects at temperature higher 700 °C – missing oxygen atoms. On the right side of membrane air is circulated and oxygen molecules are captured by membrane defects and in case of partial pressure difference migrate to the other side. Electrical potential difference causes electrons motion to the opposite direction where they ionize oxygen atoms. On the left side the mixture of methane and water vapor is circulated and interacts with migrated oxygen atoms. Such type of membrane allows excluding expensive air separation process and NOx gases formation. Capital cost by means of such process can be reduced by 30% [10].

Synthesis gas as the product of steam reforming with oxygen membrane is directed to hydrogen membrane for hydrogen production. Hydrogen membranes consist of Pd, Cu, Ag and Ze. Such membranes are proton permeable. Thus hydrogen molecules in synthesis gas mixture migrate through membrane and collected on the other side. This process allows obtaining high quality hydrogen, avoiding water gas shift reaction and following hydrogen cleaning.

2.4.2. Plasmochemical technologies

Plasmochemical process is based on implementation of electrical charge in gas flow. Such reactors are called plasma torch. Temperature inside torch can reach 10000 °C, which make it possible to perform chemical reaction with very high partial oxidation ratio. Required for the process heat comes from combustion and expensive plasma energy is used only for acceleration of the process. Depending on type of fuel energy consumption varies between 0,1 and 0,35 kWh/m$^3$. If electricity prices are relatively low such technology can compete with catalytic processes. Efficiency of plasma torch is higher than 90% because released energy is isolated from plasma flow [10].

2.4.3. Microcatalytic reactors

Modern technologies in hydrogen energy production represent microchannel catalytic systems designed by nanotechnologies. Such reactors have very high efficiency due its compact construction. Combination with fuel cells allows creating portative electro-generating devices with extremely high performance [10].

Nowadays microcatalytic systems are used in methanol steam reforming process. However, production of such reactors remains within laboratory scale because there are still a lot of unsolved problems with construction materials. The main problem is related to fixation of active catalyst on metal support. Today traditional Cu-Zn catalysts are replaced with high temperature Zr/TiO$_2$ catalyst which has better efficiency and stability [10].

2.4.4. Hydrogen production from non-organic compounds

It is a well-known fact that hydrogen can be produces by hydrolysis of NaBH$_4$ or LiBH$_4$. Automobile hydrogen accumulators sometimes use bore hydrides of some metals. Another method – reaction of some metals (Fe, Al, Mg) with steam. An extraordinary way of hydrogen production is from hydrogen sulphide. Hydrogen sulphide is one of the components coming out from gas deposits apart from natural gas. Using plasmachemical technologies it can be converted into sulphur and hydrogen which can be used for hydrogenation processes in oil and gas industry [10].
Chapter 3. Hydrogen utilization methods

3.1. Fuel cells

In 1894 Ostwald formulated the idea of using fuel cells in industry with coal as a fuel. Only in 1952 Bacon invented first alkaline fuel cell with total power of 5 kW. Today fuel cell technology is developing with accelerated temps. They can be used in the transport, stand-alone power systems, space crafts, submarines, portable devices, military industry. The main advantage of fuel cells over traditional energy sources is the fact, that chemical energy stored in the device can be directly converted to electricity. There is no need to convert thermal energy into mechanical and thus efficiency of fuel cells can be much higher – up to 60% [10].

Figure 19– Fuel cell and heat engine comparison [11]

Figure 20–ICE and FC efficiencies [11]

Fuel cell is a chemical energy source where reactants are delivered to the electric cell from outside. Electrodes are made from certain metals where electricity is generated. Reduction component can be any type of fuel as well as hydrogen. As an oxydiser air oxygen or pure oxygen can be used. Combustion process is space separated and electron migration takes place through the conductor.

Figure 21 – Principle scheme of fuel cell stack [11]
All chemical processes take place in one cell where the electric potential is 1 V. Cells are combined in a stack to form a total. Stack with all required equipment is called an electrochemical generator.

The maximum theoretical efficiency of a fuel cell is the relation between electrical work which is in chemical processes equal to Gibbs energy to enthalpy of electrochemical reaction under constant pressure.

Electromotive force is a maximum electrical work or potential difference at both ends of an electrical chain when electricity is 0.

\[ \Delta G = -nE_F \]  

Where:
- \( n \): number of migrated electrons
- \( E_F \): Faraday number, KI/mole
- \( E \): EMF, V
- \( G \): Gibbs energy, kJ/mole

The maximum efficiency can be found from the following formula:

\[ \eta = \frac{\Delta G}{\Delta H} = \frac{-nE_F}{\Delta H} = 1 - T \Delta S / \Delta H \]  

If Gibbs energy is less than enthalpy of the process, then it is an exothermic process, and efficiency < 1.

If Gibbs energy is more than enthalpy of the process, then it is an endothermic process, and efficiency > 1.

The real efficiency can be found by the following equation:

\[ \eta = \frac{-nFU}{\Delta H} = \frac{-nFU}{nF_{\text{th}}U} = \frac{U}{E_{\text{th}}} \]  

\( E_{\text{th}} \) - thermo neutral potential \( \approx 1.48 \) V at \( T<100 \) °C.

Increasing of pressure leads to growing EMF and speeds up electron processes. However, compression cost is too high and does not justify energy profit. Therefore, all fuel cells nowadays operate under atmospheric pressure.

\( K_{\text{use}} \) - coefficient of fuel usage is a very important parameter that affects efficiency of the process. \( K_{\text{use}} \) is the relation between theoretical amount of fuel used to produce electricity and real amount. Hydrogen concentration in the cell has a strong influence on this parameter. If fuel used in the process is synthesis gas...
after steam reforming of natural gas then hydrogen concentration through the electrode surface is going down. This decreases electrical force and efficiency of the process. Considering coefficient of fuel usage efficiency looks like this:

$$\eta = \frac{U_{\text{sec}}}{E_{\text{fu}}}$$ (3.1.4.)

Concentration of hydrogen in the fuel should be more than 70-80%

In addition, feed stock with CO₂ concentration higher than 20% is not suitable for alkaline fuel cells. CO content more than 10 ppm and H₂S >1 ppm can cause serious problems for alkaline and solid polymer fuel cells.

All fuel cells can be divided by:

-type of fuel: with hydrogen, natural gas or with direct oxidation
-working temperature: 100-150°C, 200-400°C, 500-1000°C
-oxidizer type: with oxygen or air
-electrolyte type: alkaline, solid polymer, phosphoric acid, carbonate, solid oxide.

All electrolytes are used in electrolysis process as well mentioned in previous pages.

![Figure 23– Fuel cell types on combined scheme [11]](image)

### 3.1.1. Aqueous alkaline fuel cells (AFC)

These fuel cells is working under 100 °C.

Scheme of the process: Pt/Ni | H₂ | OH⁻ | O₂ | Pt/Ni

Cathode reaction:

$$\text{H}_2 + 2 \text{OH}^- \rightarrow 2 \text{H}_2\text{O} + 2e^-$$
As an electrolyte 35-45% KOH or NaOH solution can be used. KOH is more suitable due to higher conductivity. Conductivity maximum shifts to the direction of higher concentration with growing temperature. There are matrix and free electrolytes used in fuel cells. Matrix electrolyte has higher efficiency but shorter lifetime. Second type has electrolyte change which allows using air cleaned from CO₂ as an oxidizer. Ni, Pt, Ag, Pd or Au are typical materials for electrodes. One can also use spinel or perovskite which cannot be used for oxygen fuel cells [10].

The main advantage of alkaline electrolyte is unfreezing electrolyte with possibility of cold start which is very important characteristic for transport. But usage of carcinogenic asbestos and alkaline, problems with air cleaning from CO₂ made this type of fuel cells unattractive and undesirable.
3.1.2. Polymer electrolyte membrane fuel cells (PEMFC)

First solid polymer fuel cells were developed by “General Electric” in 1960s. Today such elements are recognized as the most perspective especially in transport. At the same time solid polymer fuel cells can be used as reserved power systems.

![Scheme of the process](image)

**Figure 25—Polymer electrolyte fuel cell [11]**

Scheme of the process:

Pt | H₂ | H⁺ | O₂ | Pt

Anode reaction:

H₂→2H⁺ +2e⁻

\[ E₁^0 = 0 \text{V} \]

\[ E₁ = \frac{RT}{nF} \ln \frac{a(H^+)}{p(H_2)} \]

Cathode reaction:

O₂ +4e⁻ +4H⁺ → 2H₂O

\[ E₂^0 = 1,229 \text{ V} \]

\[ E₂ = E₂^0 + \frac{RT}{nF} \ln \frac{p(O_2) a^4(H^+)}{a^2(H_2O)} \]

Total reaction:

H₂+1/2 O₂ →H₂O

EMF=1,229 V

Under working temperature of 80-90 °C gases transfer through thin layer of membrane which represents Pt on carbon support. Gas diffusion layers made with carbon material are fixed from both sides of catalytic surface. Reagent input and product output occurs through bipolar carbonic or metallic surface. Absence of liquid electrolyte requires well interconnection between electronic and ionic conductors [10].
The main problem of PEM is need of constant membrane moistening to keep high electric conductivity. Low operational temperatures cause increased concentration of carbon monoxide after fuel combustion. CO poisons Pt catalyst and thus decreases cell productivity. Nowadays there are fuel cells with power up to 500 kW. Cost of 1 cell battery contributes half of all equipment cost [10].

### 3.1.3. Phosphoric-acid fuel cells (PAFC)

Working temperature of PAFC varies between 170-210 °C.

95-98% phosphoric acid solution is used as an electrolyte in this device. Acid is stored in porous thermostable SiC matrix. Phosphoric acid was chosen due to relatively low corrosion processes and high chemical stability comparing with other acids. Glass-graphite material activated with catalyst is used in electrodes. As a catalyst Pt on carbon support is used with total content 0,35 mg/sm².
Scheme of the process:
$$\text{Pt/C} \mid \text{H}_2 \mid \text{H}^+ \mid \text{O}_2 \mid \text{Pt/C}$$

Anode and cathode reactions:
$$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$$

$$E = 0 \text{V}$$

$$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}$$

$$E = 1.142 \text{ V}$$

PAFC works under higher temperature which makes them more suitable for heat supply systems, decreases overvoltage on electrodes, catalyst sensibility to poisons and simplifies process of water remove. Electrical efficiency can be 37-42% and 80-85% in case with heat regeneration.

However, acidic environment causes corrosion processes of electrodes. In addition, working temperatures are not high enough for full fuel conversion and NOx and CO formation is not excluded. Nevertheless, such fuel cells are the best option for stand-alone energy systems. Estimated cost of energy produced by such fuel cell is 2000 $/kW and lifetime is about 40000 hours [10].

### 3.1.4. Molten carbonate fuel cells (MCFC)

Working temperature 600-800°C

Electrolyte is a mixture of melted carbonates of alkaline metals: Li$_2$CO$_3$ + K$_2$CO$_3$ + Na$_2$CO$_3$ on a porous matrix based on LiAlO$_2$ modified with Al and Zr oxides. At the beginning electrode materials were Pt and Pd but now porous Ni is used. During oxidizing process Ni oxide is formed and then dissolved in carbonate environment. To prevent this process Sr and Ba solutions are introduced in the grid. There is also an option to use NiO modified with LiCoO$_2$, LiFeO$_2$, LiMnO$_3$ as an electrolyte. High operating temperatures allow using as the fuel not just hydrogen, but also synthesis gas and even methane [10].

![Molten carbonate fuel cell](image)

*Figure 28–Molten carbonate fuel cell [11]*
Scheme of the process:

\[ \text{Ni} | \text{H}_2 | \text{CO}_3^2^- | \text{O}_2, \text{CO}_2 | \text{Ni} \]

When synthesis gas or hydrogen is used as a fuel anode reaction looks like this:

\[ \text{H}_2 + \text{CO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2e^- \]

Anode reaction in case of carbon monoxide:

\[ \text{CO} + \text{CO}_3^2^- \rightarrow 2\text{CO}_2 + 2e^- \]

Some side reactions:

\[ 2\text{CO} \rightarrow \text{C} + 2\text{CO}_2 \]

\[ 2\text{CO} + \text{H}_2 \rightarrow 2\text{CH}_4 + 2\text{CO}_2 \]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

Formation of carbon on electrode is strongly undesired process because it poisons catalyst. To prevent it high partial pressures should be implemented.

Cathode reaction:

\[ \text{O}_2 + 2\text{CO}_2 + 4e^- \rightarrow 2\text{CO}_3^- \]

\[ E_a = E_a^{0} + \frac{RT}{4F} \ln \left( \frac{p(\text{O}_2)\cdot p^2(\text{CO}_2)}{a^2(\text{CO}_3)} \right) \]

\[ E_k = E_k^{0} + \frac{RT}{2F} \ln \left( \frac{p(\text{H}_2\text{O})\cdot p}{p(\text{H}_2)\cdot a} \cdot \frac{(\text{CO}_2)a}{(\text{CO}_3)} \right) \]

\[ \text{EMF} = E_k - E_a = E^{0} + \frac{RT}{4F} \ln \left( \frac{p(\text{O}_2)\cdot p^2(\text{H}_2)}{p^2(\text{H}_2\text{O})} \right) - \frac{RT}{2F} \ln \left( \frac{p(\text{CO}_2)\cdot p}{p(\text{CO}_2)a} \cdot \frac{(\text{CO}_2)a}{(\text{CO}_3)} \right) \]

\[ E^0 = 1,01 \text{ V at } 700^\circ \text{C and } p(\text{CO}_2)a = p(\text{CO}_2)a^{0} \]

For CO case \( E^0 = 1,03 \text{ V} \) but it does not increase its preference because CO oxidation cause overvoltage due to parallel reaction. Electrical efficiency of melted carbon fuel cell can reach 55% and total 85%. But if methane is used as a fuel efficiency goes down till 50% [10].

EMF of fuel cell depends on partial pressure of hydrogen. The main advantage of high temperature fuel cell is possibility to combine with other energy converter machines. Extra heat can be used in steam turbine and this will increase total efficiency of the process till 70%. Instability of electrode material, corrosion of materials and catalyst poisoning are the main drawbacks of such fuel cells. Market leader of melted carbonate fuel cell production is Fuel Cell Energy. They have 47% of efficiency fueled by natural gas [10].

### 3.1.5. Solid oxide fuel cells (SOFC)

The idea behind such fuel cells is oxide compositions that have ion, proton or mixed ion-electron conductivity. Solid electrolytes based on metal oxides represent ceramic materials conductivity of which caused by ion movement through crystal lattice defects. It can be ZrO\(_2\) stabilized with Y\(_2\)O\(_3\), Yb\(_2\)O\(_3\), or CaO. Working temperature: 800-1000°C.
Scheme of the process:

$$\text{Pt} \, | \, \text{H}_2 \, | \, \text{O}_2^\cdot (\text{ZrO}_2) \, | \, \text{O}_2 \, | \, \text{Pt}$$

$$E = E^0 + \frac{RT}{zF} \ln \left( \frac{p(\text{O}_2) \cdot p^z(\text{H}_2)}{p^z(\text{H}_2\text{O})} \right)$$

$$E^0 = 0.85 \, \text{V}$$

Reduction of oxygen occurs on cathode. Oxygen ions migrate through the electrolyte defects and water is formed on anode. As a fuel, hydrogen or synthesis gas can be used. Constructive specialty of such fuel cells is that electrolyte plays the role of carrying basement. Porous electrode material containing electron and ion conductors covers electrolyte from both sides. For anode Ni-ZrO$_2$ or Co-ZrO$_2$ can be used and for cathode is La$_x$Sr$_y$MnO$_3$ [10].

High operating temperatures cause problems with construction materials but at the same time allow combining technology with some thermocycles. In addition any type of traditional fuel can be used which make such type of fuel cell the most attractive for decentralised energy systems [10].

### 3.1.6. Portable fuel cells

Portable fuel cells are used for such devices as computers, laptops, cell phones etc. Such devices do not require energy source, they need just fuel supply. Methanol as the fuel in portable fuel cells is more popular than hydrogen. The main advantage of methanol is liquid storage. It is used as 0.5-4% water solution.

Scheme of the process:

$$\text{Pt-Ru} \, | \, \text{CH}_3\text{OH}, \text{H}_2\text{O} \, | \, \text{H}^+ \, | \, \text{O}_2 \, | \, \text{Pt}$$

Anode reaction:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}$$

$$E^0 = 20 \, \text{mV}$$
Cathode reaction:

\[ \frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \]

\[ E^o = -1230 \text{ mV} \]

Energy density = 6.3 kWh/kg of methanol. Efficiency around 30-40%.

Disadvantages of methanol fuel cells are toxic fuel, leakage of methanol into cathode area where it is oxidized. There are some research works which implement other fuels: ethanol, dimetilether, NaBH4. But all of them are less suitable than methanol so far.

Portable fuel cells are the most attractive commercial products due to lower price – 1000-1500 USD/kW and lifetime about 10000 h [10].

### 3.1.7. Fuel cell application

Since 1980 about 1 thousand stationary fuel cell systems were installed around the world [2].

Since 2010 fuel cells became a commercial product which can produce electricity with total power up to 1000 kW. The most promising type is PEMFC production output of which just in USA and Canada was 40 MW/year in 2009. PEMFC market is almost unlimited the only problem which has to be solved is hydrogen transport and storage. About 25% of the market can be occupied by SOFC. Stationary energy units can be useful in Russia too providing stable environmentally friendly electricity. However, fuel cell production, nowadays, is realized only abroad. Estimated price for 1kW power produced with FC is 2000-3000 USD [10].

The main fields of possible implementation: cathode protection stations, telemechanic systems of natural gas pipeline network, electrification of shift camps. The main requirements for such systems are: long operation lifetime (about 40000h), minimum 3500h of non-stop operation, technical usage coefficient >0.97 and half-year operation without technical service.

Another important market for fuel cell technology is portable devices. About 2 B people around the world use smartphones, laptops, tablets every day. Every year 500 M electronic devices are sold around the world [10]. Present recharging technology does not meet the requirements anymore. New challenge for microelectronic industry is development of micro fuel cells which can replace accumulators and batteries. Commercialization of such technologies meets different obstacles. High price of hydrogen energy, usage of expensive Pt metals, absence of hydrogen infrastructure and relatively short lifetime period are the main problems which have to be solved before FC portable devices will be used in our every-day-life.

In March, 2008 one ounce of Pt costed 2400 USD. World’s explored reserves of Pt are 65000 tones and by 2030 hydrogen economy will consume about 125 tones of it [10].

### 3.2. Internal combustion engines on hydrogen

Another way to use hydrogen to get some energy is to combust it in ICE. Many automobile companies develop special car models driving on hydrogen fuel. The main advantages of such technology are ecological properties of hydrogen and perfect motor properties.

Fuel-oxygen ratio for hydrogen is 0.42 while for gasoline this value achieves just 0.02. It makes hydrogen quite energy intensive fuel even though it has very good heating value. Considering stehiometric content of working mixture energy capacity of hydrogen is 15% less than of gasoline. However, hydrogen allows regulating working mixture content in a wider diapason. Due to high diffusivity which is 8 times better than for gasoline, hydrogen forms good mixture with air oxygen in a combustion chamber. Boiling point...
at -253 °C excludes possibility of liquid phase in a mixture. Combustion rate can reach 100 m/s which is 3-4 time faster than for gasoline. Theoretical efficiency of the process does not depend on type of fuel but increases significantly with poorness of fuel-air mixture [10].

Hydrogen in automobiles can be used in two ways. First way does not require any engine reconstruction. One should add some small amount of hydrogen to regular gasoline. Thus ICE will work almost at a same regime but quality of emissions will rise a lot. Such method can be used as transient between traditional and modern ICE unless hydrogen infrastructure is well developed.

More effective way is to use pure hydrogen, but in this case it is important to consider heating value and detonation properties of hydrogen while modernizing ICE.

Hybrid automobile is a mixture of ICE and electric engine. Such type of car allows reduce fuel consumption and reduce emissions in case of hydrogen fuel.

Many automobile brands started to develop hydrogen models and some of them are already present on a market. UCLA testing showed fuel consumption of 1 kg per 35 km and maximum mileage of 100 km. Exhaust does not contain CO₂, CO, CH₄ and only NOx present in amount of 0,205 g/km [10].

Japanese car “Datsun B-210” uses hydrogen which delivered into the system under -130 °C. Such temperature affects NOx emission reduction. Fuel consumption is 25 liter per 100 km and mileage 1000 km.

German research center created a model “Ford Focus C-Max” running on hydrogen. Gas compressed till 35 MPa goes to gearbox where pressure decreases till 0,35 MPa. Then, hydrogen is delivered into engine where it mixes with air and injects to cylinders. 3 tanks of 119 liter are enough to run 200 km.

In 2007 BMW presented new model Hydrogen 7. It has 2 fuel containers-74 liters of gasoline and 8 kg of hydrogen. Thus car can run 500 km on gasoline, switch to hydrogen and run additional 200-300 km [16].

![Figure 30– BMW Hydrogen 7 [16]](image)
Table 5–Main motor characteristics for different fuels in ICE

<table>
<thead>
<tr>
<th>Property</th>
<th>Hydrogen</th>
<th>Methanol</th>
<th>Methane</th>
<th>Propane</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum ignition energy, $10^{-3}$J</td>
<td>0,02</td>
<td>-</td>
<td>0,29</td>
<td>0,25</td>
<td>0,24</td>
</tr>
<tr>
<td>Flame temperature, °C</td>
<td>2045</td>
<td>-</td>
<td>1875</td>
<td>-</td>
<td>2200</td>
</tr>
<tr>
<td>Self-ignition temperature °C</td>
<td>585</td>
<td>385</td>
<td>540</td>
<td>510</td>
<td>230-500</td>
</tr>
<tr>
<td>Flame distribution rate, m/s</td>
<td>3,46</td>
<td>-</td>
<td>0,43</td>
<td>0,47</td>
<td>-</td>
</tr>
<tr>
<td>Ignition diapason on air, %</td>
<td>4-75</td>
<td>7-36</td>
<td>5-15</td>
<td>2,5-9,3</td>
<td>1,0-7,6</td>
</tr>
<tr>
<td>Detonation diapason on air, %</td>
<td>13-65</td>
<td>-</td>
<td>6,3-13,5</td>
<td>-</td>
<td>1,1-3,3</td>
</tr>
<tr>
<td>Diffusion coefficient, $\text{sm}^2/\text{s}$</td>
<td>0,61</td>
<td>0,16</td>
<td>0,2</td>
<td>0,1</td>
<td>0,05</td>
</tr>
</tbody>
</table>

ICE on hydrogen is interesting and promising area of studies, however efficiency is as low as with gasoline engines. The last step on the way to clean automobile transport is fuel cell car. Such model can achieve efficiency of 60-70%.
Chapter 4. Hydrogen transport and storage

4.1. Transport

There are three methods of hydrogen transportation: gas delivery, liquid delivery and using solid or liquid carriers for hydrogen.

To deliver liquid hydrogen special cryogenic auto and railway tankers are used. Liquefaction of hydrogen is very costly process, but in this case transport losses are minimized [10].

In USSR special vessels ТРЖВ-20, ТРЖВ-24 were developed with capacity 20 and 24 м³ for long distance transport. Nowadays, “Cryogenmash” company offer hydrogen trailers with capacity 25 and 45 м³. The most common model is LITB-45/1,0 which characteristics can be found on a table below [10].

Table 6– Hydrogen Trailer LITB-45/1,0 characteristics [5]

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume, м³</td>
<td>45</td>
</tr>
<tr>
<td>Operating pressure, МПа</td>
<td>1,0</td>
</tr>
<tr>
<td>Hydrogen weight, кг</td>
<td>2740</td>
</tr>
<tr>
<td>Evaporation losses, кг/ч (%/day)</td>
<td>1,375 (1,0)</td>
</tr>
<tr>
<td>Equipment weight, кг</td>
<td>21760</td>
</tr>
</tbody>
</table>

Trailer fueling with capacity 4500 кг causes 180 кг hydrogen losses. While making pressure difference between trailer and liquefier 1,5% of hydrogen can be lost.

Gaseous hydrogen can be delivered by pipeline or auto transport. Using trailers with pipe-containers is the easiest way to deliver gaseous hydrogen. It is profitable for small markets and high delivery cost compensates by absence of evaporation losses. One delivery provides 300-400 кг of hydrogen which is enough for 30-50 cars.

Figure 31-Compressed gas trailer, 30 cylinders with total capacity of 105 кг [27]

Hydrogen pipeline development is not a new problem in industry. There are about 16000 км of hydrogen pipelines in the world [10]. Operating pressure is about 14 МПа. Transport cost and losses are lower than for electric power lines. But such type of transport is economically feasible only for large amount of hydrogen. Pipeline transport will become the most effective when hydrogen becomes widespread energy carrier.
4.2. Storage

Once delivered for stationary uses, hydrogen is typically stored in what is known as “ground storage” in ASME-certified pressure vessels or in liquid hydrogen “Dewar” systems if the hydrogen was delivered as a cryogenic liquid. These ASME pressure vessels and liquid hydrogen storage systems must be tested and re-certified every five years. When compressed gas ground storage systems are refueled by hydrogen tube trailer delivery truck, this is called “bump stop” or “field bump” delivery. For many applications this is preferable to a smaller-scale “cylinder swap” models [27].
Figure 34– Cryogenic liquid hydrogen storage point in California [27]

Figure 35– ASME system of hydrogen storage [27]
Chapter 5. Calculation part

5.1. Choice of hydrogen production method

In the chapter 2 all possible hydrogen production methods have been described. Some of them are well developed in industry, others are still under research. Considering Russian energy policy, relatively cheap natural gas and electricity prices two methods were chosen for further investigation: natural gas steam reforming and water electrolysis.

Russia has the biggest proved reserves of natural gas – about 1688 M cubic feet [8]. Together with oil and gas after well drilling massive amount of water coming out which can be implemented for industrial purposes. Both natural gas and water are present in industry in a large amount and have relatively low prices in Russia. Therefore chosen methods seem applicable for Russian energy system. Both methods are already well developed and have certain installed power around country for different purposes.

To choose the best option the cost of 1 kg of hydrogen produced by these 2 methods was calculated.

5.1.1. Hydrogen from steam reforming of CH₄

To estimate how much will cost 1 kg of hydrogen it is necessary to know how much methane is used in the reaction and for heating purposes.

1st step of reforming – production of syngas:

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]

Then part of exhaust gas is directed to perform 2nd step - water gas shift reaction:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

Total reaction:

\[ \text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2 \]

Process parameters:

\[ T=900 \, ^\circ\text{C} \]

\[ P=1,3 \text{ bar}=0,13 \text{ MPa} \]

Temperature can be achieved by combustion of part of fuel.

![Figure 36– Schematic overview of sensible heat in the process [11]](image)

To heat feed mixture from 25 °C till 900 °C one should adjust Q₁ amount of heat which is sensible heat of the process. Heat balance of fuel heating process:
\[
Q_1 = (n_{\text{CH}_4} \Delta H_{\text{CH}_4} + n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}})_{\text{out}} - (n_{\text{CH}_4} \Delta H_{\text{CH}_4} + n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}})_{\text{in}}
\]
\[
\Delta H_{\text{CH}_4} = \Delta H_{\text{CH}_4} + \text{Cp}(T_2-T_1) = \Delta H_{\text{CH}_4}^0
\]
\[
\Delta H_{\text{H}_2\text{O}}^0 = \Delta H_{\text{H}_2\text{O}} + \text{Cp}(T_2-T_1) = \Delta H_{\text{H}_2\text{O}}^0
\]
\[
\Delta H_{\text{CH}_4} = \Delta H_{\text{CH}_4}^0 + \text{Cp}(T_2-T_1)
\]
\[
\Delta H_{\text{H}_2\text{O}} = \Delta H_{\text{H}_2\text{O}}^0 + \text{Cp}(T_2-T_1)
\]
\[
T_1 = 25 \degree C
\]
\[
T_2 = 900 \degree C
\]
\[
Q_1 = n_{\text{CH}_4} \text{Cp}(T_2-T_1) + n_{\text{CH}_4} \Delta H_{\text{CH}_4}^0 + n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}}^0 - n_{\text{CH}_4} \Delta H_{\text{CH}_4}^0 - n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}}^0
\]

For 1 mole of hydrogen:
\[
Q_1 = 0,25 \times 56,4 \times 875 + 241,8 \times 10^{-3} + 37,49 \times 875 = 12337,5 - 104515 + 142920 = 50,74 \text{ kJ/mole} = 25,37 \text{ MJ/kg}
\]
That means to heat the feed mixture of methane and water until 900°C one need to apply 50,75 kJ for 1 mole of hydrogen.

![Figure 37-Schematic overview of latent heat of the process [11]](image)

To perform the reaction, the latent heat of the process should be considered.

Heat balance of reaction:
\[
Q_2 = (n_{\text{CO}_2} \Delta H_{\text{CO}_2} + n_{\text{H}_2} \Delta H_{\text{H}_2})_{\text{out}} - (n_{\text{CH}_4} \Delta H_{\text{CH}_4} + n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}})_{\text{in}}
\]
\[
\Delta H_{\text{CO}_2} = -393,51 \times 10^{-3} + 48,2 \times 875 = -351,335 \text{ kJ/mole}
\]
\[
\Delta H_{\text{H}_2} = 0 + 29,48 \times 875 = 25,795 \text{ kJ/mole}
\]
\[
\Delta H_{\text{CH}_4} = -74,85 \times 10^{-3} + 56,4 \times 875 = -25,5 \text{ kJ/mole}
\]
\[
\Delta H_{\text{H}_2\text{O}} = -241,83 \times 10^{-3} + 37,49 \times 875 = -209,026 \text{ kJ/mole}
\]
\[
Q_2 = 50,74 + 25,795 = 48,853 \text{ kJ/mole}
\]

In total to perform steam reforming of methane with 100% efficiency we need 99,59 kJ/mole.
\[
Q = Q_1 + Q_2 = 50,74 + 48,853 = 99,59 \text{ kJ/mole} = 49,785 \text{ MJ/kg}
\]
To produce 1 kg of hydrogen 49,795 MJ is needed.

Combustion heat of methane = 50 MJ/kg
Combustion heat of hydrogen = 121 MJ/kg

Which means to produce 1 kg of hydrogen we need to burn around 1 kg of methane just to achieve temperature of chemical process.

Typical boiler has efficiency about 80% thus for heating it will be necessary to supply 1.25 kg instead of stehiometric 1 kg [10].

1 kg of hydrogen = 500 moles

To produce 500 moles of hydrogen we need 125 mole of methane and 250 moles of water, in other words 2.25 kg of methane and 4.5 kg of water.

Thus we can estimate economic cost of the process considering 100% efficiency.

1 kg of methane occupies 1.4 m$^3$ and 1 m$^3$ if its natural gas.

Average cost of methane in Russia 4.065 rub/m$^3$ [13].

1.4*4.065*(2.25+1.25) = 20 rub – price of 1 kg of hydrogen produced by steam reforming of methane.

As an option part of hydrogen produced can be used to heat the reactor instead of methane. 400 g stehiometrically or 500 g considering boiler efficiency will be necessary to supply required 50 MJ of heat.

Thus price of 1 kg of hydrogen can be calculated:

1.4*4.065*2.25*2 = 25.6 rub/kg

Using hydrogen instead of methane would be reasonable from ecological point of view. It will decrease CO$_2$ emissions.

$$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$$

$$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$$

1 kg of methane = 62.5 mole

m(CO$_2$) = 62.5*44 = 2.75 kg

After 1 kg of methane combustion 2.75 kg of CO$_2$ is produced.

5.1.2. Hydrogen from electrolysis of water

To estimate how much will cost 1 kg of hydrogen produced by electrolysis one should know electricity consumption of the process.

$$\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$$

Average electricity consumption by electrolyser is 4.5 kWh/m$^3$ [10].

Electricity price for industrial purposes is 3.2 rub/kWh [7].

1 kg of hydrogen occupies 1/0.0899 = 11.12 m$^3$

Energy consumption 4.5*11.12 = 50.04 kWh = 180 MJ

1 kg of hydrogen produced by electrolysis of water would cost 3.2*50.04 = 160 rub or 2.85$ USA.

CO$_2$ emissions:
When producing hydrogen from water electrolysis the only energy required is electricity, which has no emission. Nevertheless, to produce electricity on power plant one should use certain energy source or energy carrier. In Russia electricity is mainly produced from hydropower and thermal power station. The typical fuels are coal, heavy duty oils and natural gas. As for steam reforming process it is requires natural gas for production of hydrogen. Below can be seen average values of CO₂ emissions from two production methods [33]:

<table>
<thead>
<tr>
<th>Process</th>
<th>CO₂ emissions (kg/m³ H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis</td>
<td>2.6</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 7-CO₂ emissions from SMR and water electrolysis processes

Conclusion:

1 kg of hydrogen produced by SMR process would cost 20 rub and by water electrolysis – 160 rub. Considering natural gas and electricity prices in Russia it should be noted that SMR process is more profitable than water electrolysis.

5.2. Fuel cell calculation

Now, fuel cell technology for electricity production should be chosen. Depending on application different types of fuel cells can be used. The most attractive type of application in Russia is stand-alone energy systems providing electricity and heat on the territory isolated from centralized systems. Such energy systems are developed by Swiss company “Hexis” [21]. The main idea of such systems is to provide both electricity and heat which can be regenerated from product mixture. This principle allows increasing efficiency of the system. In our research natural gas will be considered as the feed for hydrogen production. Steam reforming of natural gas results synthesis gas production which goes to the next step – water gas shift reaction to convert CO into CO₂. Both steps occur at 900 °C. Then mixture of water, CO₂ and hydrogen at 900°C goes to fuel cell. The most suitable type of fuel cell for such temperature is solid oxide fuel cell. In addition SOFC allows using any type of hydrocarbons as the feedstock. Operating pressure 1,3 bar and total power of FC stack is 1kW.

5.2.1. Calculation of SOFC efficiency

Let’s calculate efficiency of such system and estimate economic expenses.
Steam reforming of natural gas:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2
\]

K: \( \text{O}_2 + 4\text{e} \rightarrow 2\text{O}^{2-} \)

A: \( 2\text{H}_2 + 2\text{O}^{2-} \rightarrow 2\text{H}_2\text{O} (\ell) + 4\text{e} \)

Let's calculate EMF for the reaction using Nernst equation:

\[
E = E^0 + \frac{RT}{zF} \ln \frac{p(A) \cdot p(B)}{p(C) \cdot p(D)} \tag{5.2.1.}
\]

Where:

\- \( p(A), p(B) \) – partial pressure of products considering stehiometric coefficients
\- \( p(C), p(D) \) – partial pressure of reactants considering stehiometric coefficients
\- \( F = 96485.3 \text{ KI/mole} \) – Faraday number
\- \( Z \) - number of electrons in the reaction
\- \( T \) - temperature of reaction, K
\- \( R \) - universal gas constant, 8,314 kJ/kg*mole

\[
E = E^0 + \frac{RT}{zF} \ln \frac{p(\text{O}_2) \cdot p^2(\text{H}_2)}{p^2(\text{H}_2\text{O})}
\]

\[
E^0 = -\frac{\Delta G}{zF}
\]

\[
F = 96485.3 \text{ KI/mole}
\]

\[
Z = 4\text{e}
\]

\( \Delta G = -170 \text{ kJ/mole} \) for 1 mole \( \text{H}_2 \)

\[
E^0 = \frac{-170 \times 2}{4 \times 96485.3} = 0.881 \text{ V}
\]

Steam reforming process products can be divided in absorber filled with \( \text{K}_2\text{CO}_3 \) solution at 104 °C [9].

It is important to state that for SOFC product separation is unnecessary step, because the temperature inside SOFC is high enough to convert all byproducts.

\[
\text{X}(\text{H}_2) = 89\%
\]

\[
\text{X}(\text{H}_2\text{O}) = 11\%
\]

\[
\text{X}(\text{O}_2) = 21\%
\]

Dalton’s law:

\[
\text{P}_i = \text{X}_i \cdot \text{P}_{\text{tot}} \tag{5.2.2.}
\]

Where:
Xi- concentration of components, %
Ptot- total pressure of the system, bar
Pi- partial pressure of component, bar
\[ P_{H_2} = 0.89 \times 1.3 = 1.157 \text{ bar} \]
\[ P_{H_2O} = 0.11 \times 1.3 = 0.143 \text{ bar} \]
\[ P_{O_2} = 0.21 \times 1.3 = 0.273 \text{ bar} \]
900 °C=1173 K
\[ E = 0.881 + \frac{8.314 \times 1173}{4 \times 96485.3} \ln \frac{0.273 \times (1.157)^2}{0.273^2} = 0.95 \text{ V} \]

Now we can determine what are electric density and electric force at maximum possible power.
\[ N = I \times U \]

There is polarization curve for FC model AES of Hexis with diameter 1.56 sm and length 50 sm:

![Polarization curve of fuel cell](image)

Figure 39 – Polarization curve of fuel cell [11]

For every point on graph we can find corresponding power and then build new graph.
\[ N_s = 79; 148; 190; 224; 240; 248; 250; 258; 252; 247 \]

Maximum power is 258 mW/sm². For that value I=550 mA/sm² and U=0.47V.
Figure 40 – Power–current density curve of fuel cell [11]  

Electrical efficiency of fuel cell:

\[ \eta_e = -\frac{nEF}{\Delta H^0} \]

\[ \eta_e = -2 \times 0.47 \times 96485.3 / -242000 = 0.375 \]

Using value of theoretical potential \( E=0.95 \) V calculated before we can calculate theoretical efficiency:

\[ \eta_e = 0.757 \]

Fuel cell active surface:

\[ N = N_A \cdot A_{cell} \]

\[ A_{cell} = \frac{1000}{0.258} = 3876 \text{ cm}^2 = 0.39 \text{ m}^2 \]

Hydrogen flow rate can be found for 2 cases:

1. 100% conversion of hydrogen
2. 70% conversion of hydrogen

Faraday’s law:

\[ I = \frac{nF(z/\nu)}{t} \]  \hspace{1cm} (5.2.3.)

Where:

I – current, A

F- Faraday number

\( n/t \) – molar flow rate, mol/sec

\( z/\nu \) – number of electrons for 1 mole of compound

\[ I = 3876 \times 0.55 = 2131.8 \text{ A} \]
For the reaction

\[ \frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \]

\( z = 2 \) – number of electrons in the reaction

\( v_{\text{H}_2} = 1 \) mole

\( v_{\text{O}_2} = 0.5 \) mole

\( z/v = 2 \) for hydrogen, \( 4 \) for oxygen where

1. \( n/\ell = I/(z/\nu)F = 2131.8/2 \times 96485.3 = 0.011 \) mole/sec

To calculate volumetric flow rate one should use Gas state equation:

\[ PV = nRT \]

(5.2.5.)

Where:

\( n \) - molar flow rate, mol/s

\( R \) - universal gas constant, 8,314 kJ/kg*mole

\( P = 1 \) atm

\( T = 900 \) °C

\[ V = 0.011 \text{ mole/s} \times 0.082 \text{ atm} \times 1 \text{ mole} \times K \times 1173 \text{ K} / 1 \text{ atm} = 1.058 \text{ l/s} = 3.8 \text{ m}^3/\text{h} \]

2. For the case of 70% of hydrogen usage:

\[ n/\ell = 0.011 / 0.7 = 0.0157 \text{ mole/sec} = 5.42 \text{ m}^3/\text{h} \]

To sum a rise theoretical effectiveness of SOFC is 75.5% and real one 37.5%. It should be noted that such efficiency is achieved for 1kW power cell. Using polarization curve hydrogen flow rate was calculated. For 100% conversion it is 3.8 m³/h and for 70% conversion it is 5.42 m³/h.

### 5.2.2. Calculation of PEMFC efficiency

There is another suitable fuel cell technology that can be used in stand-alone power generation system. Polymer electrolyte fuel cell operates at 70 °C and requires high purity of hydrogen. Steam reforming process occurs at 900 °C and therefore product mixture has to be cooled and separated. Main products of steam reforming are hydrogen, carbon dioxide and water vapor. Carbon dioxide is separated in absorber with \( \text{K}_2\text{CO}_3 \) solution. Mixture of hydrogen and water vapor is cooled in condenser till 70 °C, pure hydrogen goes to fuel cell stack and condensed water back to reformer.

Let’s calculate amount of heat that is released by cooling from 900°C till 70°C.

Heat balance of the process:

\[ Q_i = (n_{\text{H}_2} \Delta H_{\text{H}_2} + n_{\text{CO}_2} \Delta H_{\text{CO}_2})_{\text{in}} - (n_{\text{H}_2} \Delta H_{\text{H}_2} + n_{\text{CO}_2} \Delta H_{\text{CO}_2})_{\text{out}} \]

\( T_1 = 900 \) °C

\( T_2 = 70 \) °C
\[ \Delta H_0^\circ = \Delta H_{\text{in \ A\&A \ CO}_2} \]

\[ Q_3 = n_{\text{H}_2} C_{\text{H}_2}(T_2-T_{\text{ref}}) + n_{\text{CO}_2} C_{\text{H}_2O}(T_2-T_{\text{ref}}) - n_{\text{H}_2} C_{\text{H}_2}(T_1-T_{\text{ref}}) - n_{\text{CO}_2} C_{\text{H}_2O}(T_1-T_{\text{ref}}) \]

\[ Q_3 = 28,85 \times (70-25) + 0,25 \times 41,8 \times (70-25) - 29,48 \times (900-25) - 0,25 \times 48,2 \times (900-25) = \]

\[ = 1298,25 + 470,25 - 25795 - 10543,75 = -34,57 \text{ kJ/mole} \]

Regenerated heat can be used for heating of feed mixture in the steam reforming process.

Theoretical efficiency of fuel cell can be found through Nernst equation:

\[ E = E_0 + \frac{R \cdot T}{z \cdot F} \ln \left( \frac{p(O_2) \cdot p^2(H_2) \cdot p^2(H_2O)}{p^2(H_2O)} \right) \]

The only difference from SOFC calculation is operating temperature.

\[ E = \frac{8,314 \times 343}{4 \times 96485,3} \ln \frac{0,273 \times (1,157)^{0,2}}{0,273^{0,2}} = 0,881 + 0,00738 \times 1,589 = 0,893 \]

\[ \eta_e = -nEF/\Delta H^0 \]

\[ \eta_e = -2 \times 0,893 \times 96485,3 / -242000 = 0,712 \]

*Figure 41 – Polarization curve for PEMFC*

For every point on graph we can find corresponding power and then build new graph.

\[ N_i = 0,156 ; 0,84 ; 0,402 ; 0,52 ; 0,63 ; 0,696 ; 0,7 ; 0,695 \text{ W/sm}^2 \]

Maximum power is 0,7 W/sm². For that value I=1,4 A/sm² and U=0,5 V.

Then real FC effectiveness will be:

\[ \eta_e = -nEF/\Delta H^0 \]

\[ \eta_e = -2 \times 0,5 \times 96485,3 / -242000 = 0,398 \]
FC surface of 1kW power can be found from equation below:
\[ N = N_s A_{cell} \]
\[ A_{cell} = 1000/0.7 = 1428 \text{ sm}^2 = 0.14 \text{ m}^2 \]

Let's calculate hydrogen flow rate for 2 cases:

1) 100% hydrogen conversion

Faraday's law:
\[ I = \frac{nF(z/v)}{1} \]
\[ I = jA = 1428 \times 1.4 = 1999.2 \text{ A} \]

For reaction:
\[ \frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \]
\[ z = 2 \text{ number of electrons} \]
\[ v_{\text{H}_2} = 1 \text{ mole} \]
\[ v_{\text{O}_2} = 0.5 \text{ mole} \]
\[ \frac{z}{v} = 2 \text{ for hydrogen and 4 for oxygen, where} \]
\[ n/t = \frac{1}{(z/v)}F = 1999.2/2 \times 96485.3 = 0.01036 \text{ mole/sec = 0.0746 kg/h} \]

To determine volumetric flow rate of hydrogen one should use gas state equation:
\[ PV = nRT \]
\[ P = 1 \text{ atm} \]
\[ T = 70 \degree \text{C} \]
\[ V = 0.01036 \text{ mole}/c \times 0.082 \text{ atm}$\text{liter}$/\text{mole} \times 343 \text{K/1 atm} = 0.289 \text{ liter/s = 1.04 m}^3/\text{h} \]

2. 70% hydrogen conversion

\[ n/t = 0.01036/0.7 = 0.0148 \text{ mole/sec = 1.48 m}^3/\text{h} \]

**Conclusion:**

Theoretical and real efficiency were determined for PEMFC: 71.2% and 39.8% respectively. Such effectiveness was achieved due to 1kW power load and can vary depending on scale of the equipment. Using polarization curve hydrogen flow rate was calculated. For 100% conversion it is 1.05 m$^3$/h and for 70% conversion it is 1.48 m$^3$/h.

### 5.3. Overall efficiency calculation

Before fuel cell and steam reforming parameters were calculated including efficiency, energy consumption and hydrogen flow rate. Suggested technology represents combination of FC and SRM and thus overall efficiency of such technology should be calculated. It will allow comparing SOFC and PEMFC technologies and choosing the best one for our case.
5.3.1. SMR+SOFC

Electrical efficiency of combined process:

\[
\eta_{el} = \frac{P_{el}}{(n/t)_{CH4}(\Delta H_{CH4}+Q_1+Q_2)}
\]  

(5.3.1.)

- \(Q_1\)-sensible heat, kJ/mole
- \(Q_2\)-latent heat, kJ/mole

\(\Delta H_{CH4}\) – combustion heat during reaction:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2
\]

\[
\Delta H^0 = (n_{\text{CO}_2} \Delta H_{\text{CO}_2} + n_{\text{H}_2\text{O}} \Delta H_{\text{H}_2\text{O}})_{\text{out}} - (n_{\text{CH}_4} \Delta H_{\text{CH}_4} + n_{\text{O}_2} \Delta H_{\text{O}_2})_{\text{in}}
\]

\[
\Delta H^0 = -393,53 - 2 \times 241,83 - (-74,87 + 2 \times 0) = -802 \text{ kJ/mole}
\]

Natural gas steam reforming:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2
\]

\[
(n/t)_{CH4}=1/4 \ (n/t)_{H2}=0,011 \times 0,25 = 0,00275 \text{ mole/s}
\]

Determination of volumetric flow rate of hydrogen:

\[
P V = nRT
\]

\[
P = 20 \text{ atm}
\]

\[
T = 900 \text{ °C}
\]

\[
V = 0,00275 \text{ mole/s} \times 0,082 \text{ atm} \times 1/\text{mole} \times K \times 1173 \text{ K} \times 20 \text{ atm} = 0,013 \text{ l/s} = 0,0468 \text{ m}^3/\text{h}
\]

\[
(n/t)_{H2O} = 1/2 \ (n/t)_{H2} = 0,011 \times 0,5 = 0,0055 \text{ mole/s} = 0,456 \text{ kg/h}
\]

\[
V = 0,0055 \text{ mole/s} \times 0,082 \text{ atm} \times 1/\text{mole} \times K \times 1173 \text{ K} \times 20 \text{ atm} = 0,026 \text{ l/s} = 0,095 \text{ m}^3/\text{h}
\]

If 70% conversion of hydrogen:

\[
(n/t)_{CH4}=1/4 \ (n/t)_{H2}=0,011 \times 0,25/0,7 = 0,0039 \text{ mole/s} = 0,066 \text{ m}^3/\text{h}
\]

\[
(n/t)_{H2O} = 1/2 \ (n/t)_{H2} = 0,011 \times 0,5/0,7 = 0,0078 \text{ mole/s} = 0,65 \text{ kg/h} = 0,135 \text{ m}^3/\text{h}
\]

\[
\eta_{el} = 1/(0,00275 \times (802 + 50,74 + 48,85)) = 40,33\%
\]

If 70% conversion of hydrogen:

\[
\eta_{el} = 1/(0,0039 \times (802 + 50,74 + 48,85)) = 28,44\%
\]

Effectiveness of the process can be increased if using heat of water vapor after steam reforming process. It can be used in steam turbine or as a district heating energy carrier.
5.3.2. SMR + PEMFC

In case of PEMFC some of energy is regenerated during condensation of water vapor. Thus overall effectiveness will be:

$$\eta_{el} = \frac{(P_{el})}{(n/t)_{CH4} (-\Delta H_{CH4} + Q_1 + Q_2 + Q_3)} \quad (5.3.2.)$$

$Q_1$-sensible heat, kJ/mole

Heat balance of the process

$$Q_1 = (n_{CH4} \times \Delta H_{CH4} + n_{H2O} \times \Delta H_{H2O})_{out} - (n_{CH4} \times \Delta H_{CH4} + n_{H2O} \times \Delta H_{H2O})_{in}$$

$$\Delta H_{CH4 out} = \Delta H_{CH4} + Cp(T_{in}-T_{amb}) = \Delta H_{CH4}^0$$

$$\Delta H_{H2O out} = \Delta H_{H2O} + Cp(T_{out}-T_{amb}) = \Delta H_{H2O}^0$$

$$T_{in}=25 \, ^{\circ}C$$

$$T_{out}=70 \, ^{\circ}C$$

For 1 mole of hydrogen:

$$Q_1 = 0.25 \times 56.4 \times 45 + 0.5 \times (241.8 \times 10^3 + 37.49 \times 45) - 0.5 \times (-285.84 \times 10^3) = 634.5 - 121743.5 + 142920 = 21.81 \, kJ/mole = 10.9 \, MJ/kg$$

Thus to heat up feed mixture till 70 °C it is necessary to apply 21.81 kJ for every mole of hydrogen.

$Q_2$-latent heat, kJ/mole

$$Q_2 = (n_{CO2} \times \Delta H_{CO2} + n_{H2} \times \Delta H_{H2})_{out} - (n_{CH4} \times \Delta H_{CH4} + n_{H2O} \times \Delta H_{H2O})_{in}$$

$$\Delta H_{CO2 out} = \Delta H_{CO2} + Cp(T_{in}-T_{amb}) = -393.51 \times 10^3 + 48.2 \times 45 = -391.342 \, kJ/mole$$

$$\Delta H_{H2 out} = \Delta H_{H2} + Cp(T_{out}-T_{amb}) = 0 + 29.48 \times 45 = 1.326 \, kJ/mole$$

$$\Delta H_{CH4 out} = \Delta H_{CH4} + Cp(T_{in}-T_{amb}) = -39.85 \times 10^3 + 56.4 \times 45 = -72.312 \, kJ/mole$$

$$\Delta H_{H2O out} = \Delta H_{H2O} + Cp(T_{out}-T_{amb}) = -241.83 \times 10^3 + 37.49 \times 45 = -240.142 \, kJ/mole$$

$$Q_2 = -97.835 + 1.326 + 18.078 + 120.071 = 41.64 \, kJ/mole$$

Total heating value:

$$Q = Q_1 + Q_2 = 21.81 + 41.64 = 63.45 \, kJ/mole = 31.72 \, MJ/kg$$
To produce 1 kg of hydrogen it is necessary to use 0,63 kg of methane. Considering efficiency of the heater (0,8) it will be 0,79 kg of methane.

\[ \Delta H_{\text{CH}_4} \text{— combustion heat of methane, } -802 \text{ kJ/mole} \]

\[ (n/t)_{\text{CH}_4} = 1/4 \times (n/t)_{\text{H}_2} = 0,0103 \times 0,25 = 0,002575 \text{ mole/s} \]

Determination of volumetric flow rate of hydrogen:

\[ PV = nRT \]

\[ P=20 \text{ atm} \]

\[ T=900^\circ C \]

\[ V=0,002575 \text{ mole/s} \times 0,082 \text{ atm*l/mole*K} \times 1173 \text{ K} / 20 \text{ atm} = 0,0121 \text{ l/s} = 0,0445 \text{ m}^3/\text{h} \]

\[ (n/t)_{\text{H}_2O} = 1/2 \times (n/t)_{\text{H}_2} = 0,0103 \times 0,5 = 0,00515 \text{ mole/s} = 0,333 \text{ kg/h} = 0,0247 \text{ m}^3/\text{h} \]

In case of 70% conversion of hydrogen:

\[ (n/t)_{\text{CH}_4} = 1/4 \times (n/t)_{\text{H}_2} = 0,0103 \times 0,25 / 0,7 = 0,00367 \text{ mole/s} = 0,063 \text{ m}^3/\text{h} \]

\[ (n/t)_{\text{H}_2O} = 1/2 \times (n/t)_{\text{H}_2} = 0,0103 \times 0,5 / 0,7 = 0,00745 \text{ mole/s} = 0,475 \text{ kg/h} = 0,035 \text{ m}^3/\text{h} \]

\[ \eta_{el} = 1 / (0,002575 \times (802 + 21,81 + 41,64 - 34,57)) = 46,75\% \]

In case of 70% conversion of hydrogen:

\[ \eta_{el} = 1 / (0,0039 \times (802 + 21,81 + 41,64 - 34,57)) = 30,86\% \]

**Conclusion:**

Efficiency of combined technology SRM+SOFC is 40,33% and 28,44% for 100% and 70% conversion of hydrogen respectively. Same parameters for PEMFC will be 46,75% and 30,86%. Such low results can be explained by small scale of energy system. It is clear that PEMFC technology more effective process and it gets more attractive with growing power load. Within 1kW scale both technologies are interesting for research and economic feasibility will be calculated for both processes.

### 5.4. Economic calculation

In this part of the thesis such economic parameters economic feasibility of FC technology development was analyzed. For that purpose capital cost (CAPEX) and 1st operation year income were estimated and such parameters as NPV, PI, IRR, payback period of chosen technologies were calculated. Considering previous market analysis and efficiency calculation two technologies will be considered: SMR+SOFC and SMR+PEMFC. Existing commercialized technology developed by “Hexis” is taken for comparison with two chosen technologies.
5.4.1. CAPEX estimation

Stand-alone power generation systems of 1kW power can be used on the oil and gas field in the regions without centralized electrification. CAPEX concludes cost of SRM equipment, FC, fuel, installations and logistics.

\[
\text{CAPEX} = \lambda \cdot ((C_{\text{CRM}} + C_{\text{FC}} \cdot N_{\text{cells}}) + C_{\text{inst}} + C_{\text{feed}})
\]

\(C_{\text{CRM}}\) - cost of SRM equipment, mln.rub

\(C_{\text{FC}}\) - cost of FC, mln.rub

\(N_{\text{cells}}\) - number of FC stucks

\(C_{\text{feed}}\) - price of Water and natural gas, thousand rub

\(\lambda\) - coefficient considering logistics expenses

**Estimation of productivity and cost of required SMR system:**

Cost of hydrogen strongly depends on expenses for SRM system. In case of 200 000 m³/day productivity such equipment will cost 100 M USD. Such hydrogen would cost 75 USD per 1000 m³. CAPEX are higher for smaller scales and share of SRM price in hydrogen cost grows from 25% till 50%. If SRM productivity less than 1000 m³ CAPEX will represent 75% of hydrogen cost. In our case power generation system of 1kW power will consume 130 m³ of hydrogen in case of SOFC and 35 m³ in case of PEMFC.

Cost of SMR depends on many factors:

- technological scheme of the process
- feed content
- power load
- complicity of technology
- level of income of participants
- local security standards
- level of automatization of the process
- inlet feed pressure
- region of construction, access to transport
- transport cost for equipment delivery
- quality of specialists
- ecological standards
- climate

Cost of process technology varies with capacity of the plant. For plant capacities of 250-1000 m³/h H₂ with supply pressure of 16 bar investment cost can be seen on the table: [16]
Considering all mentioned factors it was estimated that average cost of SRM system is 40000 USD/1000 m³. The decision was to buy technology with productivity of 500 m³/day. Such system will provide hydrogen flow rate that is enough for 4 SOFC or 17 PEMFC.

Table 8 – SMR plant Investment cost

<table>
<thead>
<tr>
<th></th>
<th>250 m³/h H₂</th>
<th>1000 m³/h H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Low-temp. steam reforming</td>
<td>71%</td>
<td>70%</td>
</tr>
<tr>
<td>Water electrolysis</td>
<td>65%</td>
<td>154%</td>
</tr>
</tbody>
</table>

Table 9 – Calculated flow rate values for SOFC and PEMFC technologies

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>SOFC</th>
<th>PEMFC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100%</td>
<td>70%</td>
</tr>
<tr>
<td>(n/t)H₂, mole/s</td>
<td>0,011</td>
<td>0,0157</td>
</tr>
<tr>
<td>V_H₂, m³/h</td>
<td>3,8</td>
<td>5,42</td>
</tr>
<tr>
<td>V_CH₄, m³/h</td>
<td>0,0468</td>
<td>0,066</td>
</tr>
<tr>
<td>V_H₂O, m³/h</td>
<td>0,095</td>
<td>0,135</td>
</tr>
</tbody>
</table>

Figure 42 – Estimated cost of 1 kg of hydrogen [23]
Figure 43 – Compact energy system made by Hexis, combination of SRM and SOFC with total power 1 kW

Estimation of heat recovery system

In case of using PEMFC temperature of hydrogen flow should be reduced from 900 °C to 70 °C. Recovered heat can be used for heating purposes or for electricity generation by means of steam turbine. Based on JM Davy Company data heat recovery system can cost between 50 and 100% of SRM price depending on complexity of the system. Considering high inlet temperature it was decided to use 100% value, thus heat recovery system will cost 20000 USD.

Estimation of FC price

Nowadays, fuel cell production occurs only abroad and estimated cost of 1 kW is 2000-3000 USD [11]. PEMFC uses Pt metal as electrode material and SOFC uses cheaper materials. Therefore, it was considered that PEMFC price is 3000 USD and SOFC price is 2000 USD.

Estimation of transport cost and logistics

Hydrogen produced by steam reforming process has to be directed to fuel cell unit. Some FC can be placed nearby SRM equipment, some of them might be installed a bit further. \( \lambda \) – coefficient considering transport expenses between SRM and FC unit. It is considered to use 10% of total equipment cost.

In case of large distance special auto trailers for liquid hydrogen can be used. For small scale production cryogenic containers of 45 m³ volume are the most suitable.

Estimation of fuel cost for SOFC

Natural gas price in Russia for industrial purposes is 4,065 rub/m³ or 5,69 rub/kg [13]. Methane consumption for 100% and 70% hydrogen conversion are 0,0048 and 0,066 m³/h respectively. It should be mentioned, that some part of methane is used for heating purposes to achieve process parameters. \( \text{LHV}_{\text{CH}_4} = 50 \text{ MJ/kg} \). To heat 1 kg of hydrogen it is necessary to apply 25,37 MJ of heat. Thus methane consumption = 25,37/50*0,0792 =0,04 kg/h=0,056 m³/h or 0,08 m³/h in case of 70% hydrogen conversion. In total one need 0,1 m³/h if 100% conversion and 0,145 m³/h if 70% hydrogen conversion. Thus total price of methane for 1 FC is from 3560 to 5163 rub. per year (8760 operating hours).
Water consumption is 0.456 kg/h if 100% conversion and 0.65 kg/h if 70% conversion of hydrogen. Water price for industrial purposes in Moscow is 45 rub./m\textsuperscript{3} or 0.045 rub./kg [17]. Thus, total price of water is between 179 to 256 rub. per year (8760 operating hours).

**Estimation of fuel cost for PEMFC**

Methane consumption for 100% and 70% hydrogen conversion are 0.0445 and 0.063 m\textsuperscript{3}/h respectively. It should be mentioned, that some part of methane is used for heating purposes to achieve process parameters. LHV\textsubscript{CH\textsubscript{4}} = 50 MJ/kg. To heat 1 kg of hydrogen it is necessary to apply 10.9 MJ of heat. Thus methane consumption = (10.9/50)\times0.0747 = 0.016 kg/h = 0.022 m\textsuperscript{3}/h or 0.032 m\textsuperscript{3}/h in case of 70% hydrogen conversion. In total one need 0.066 m\textsuperscript{3}/h if 100% conversion and 0.095 m\textsuperscript{3}/h if 70% hydrogen conversion. Thus total price of methane for 1 FC is from 2350 to 3383 rub. per year (8760 operating hours).

Water consumption is 0.333 kg/h if 100% conversion and 0.475 kg/h if 70% conversion of hydrogen. Water price for industrial purposes in Moscow is 45 rub./m\textsuperscript{3} or 0.045 rub./kg [17]. Thus, total price of water is between 131 to 187 rub. per year (8760 operating hours).

**5.4.1. Capital cost estimation**

SOFC:

\[ C_{SMR} = 20000 \text{ USD} \]
\[ C_{FC} = 2000 \text{ USD} \]
\[ N = 4 \]
\[ C_{inst} = 1.5(C_{SRM}+C_{FC}\cdot N_{FC}) \]
\[ C_{fuel} = (C_{CH\textsubscript{4}} + C_{H\textsubscript{2}O})\times4 = (5163+256)\times4 = 21676 \text{ rub} = 417 \text{ USD} \]
\[ \text{CAPEX} = 1.1(20000+4\times2000) + 1.5\times28000 + 417 = 73217 \text{ USD} = 3807284 \text{ rub} \]

PEMFC:

For PEMFC it is important to consider heat recovery system price.

\[ \text{CAPEX} = \lambda \cdot (C_{SMR}+C_{FC}\cdot N_{cells} + C_{rec}) + C_{inst} + C_{feed} \]

\[ C_{SMR} = 20000 \text{ USD} \]
\[ C_{FC} = 2000 \text{ USD} \]
\[ N = 17 \]
\[ C_{REC} = 20000 \text{ USD} \]
\[ C_{instal} = 1.5(C_{SRM}+C_{REC}+C_{FC}\cdot N_{FC}) \]
\[ C_{fuel} = (C_{CH\textsubscript{4}} + C_{H\textsubscript{2}O})\times17 = (3383 + 187)\times17 = 60690 \text{ rub} = 1167 \text{ USD} \]
\[ \text{CAPEX} = 1.1(20000+20000+17\times2000)+111000+1167 = 193567 \text{ USD} = 10065484 \text{ rub} \]
“Hexis” technology:

Alternative option is to use Hexis technology which can be seen on a picture. Such technology has power of 1 kW and contains mini SRM, SOFC stuck, heat exchanger and desulphuriser. Such system costs 19000 Euros or 1083000 rub. [33]

\[
\text{CAPEX} = 1,1 \times 21348 + 104 = 21004 \ \text{USA} = 1092208 \ \text{rub.}
\]

**5.4.2. The 1st operation year income estimation**

Final product of technology is electricity.

1st operation year income can be found from formula below:

\[
B = N_{\text{FC}} \cdot P_{\text{FC}} \cdot 8760 \cdot k \cdot C_{\text{el}} \quad (5.4.2)
\]

70% of Russian territory has decentralized electrification systems. Such regions use diesel and gasoline electric generators and the price of such electricity is about 27 rub./kWh [1]. In this project stand-alone power generation systems based on fuel cell technology has been estimated and therefore this price will be considered for income calculation.

For SOFC technology \( B = 236528 \times 4 = 946112 \) rub from 4 kW power.

For PEMFC technology \( B = 236528 \times 17 = 4020976 \) rub from 17 kW power.

For Hexis technology \( B = 236528 \) from 1 kW power.

Using special program developed in MS Excel such economic parameters as NPV, IRR, PI has been calculated.

Results of the calculation can be seen below:

1) SMR+SOFC technology

*Table 10 - SMR+SOFC economic parameters*

<table>
<thead>
<tr>
<th>Early OPEX</th>
<th>Growth of exploitation cost</th>
<th>Discount rate</th>
<th>Growth of electricity tariff</th>
<th>Income taxes</th>
<th>CAPEX, mln. rub</th>
<th>Amortization period</th>
<th>1st year income, mln.rub</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,00%</td>
<td>4,00%</td>
<td>10,00%</td>
<td>5,00%</td>
<td>20,00%</td>
<td>3,8</td>
<td>20</td>
<td>0,95</td>
</tr>
</tbody>
</table>

Discounted revenue, mln.rub

<table>
<thead>
<tr>
<th>Discounted EBITDA, mln.rub</th>
<th>Discounted net profit, mln.rub</th>
<th>Discounted cash flow, mln.rub</th>
<th>NPV, mln.rub</th>
<th>Payback period</th>
<th>PI</th>
<th>IRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>14,37</td>
<td>10,69</td>
<td>7,04</td>
<td>8,93</td>
<td>5,13</td>
<td>7,51</td>
<td>2,35</td>
</tr>
</tbody>
</table>
2) SMR+PEMFC technology

Table 11. SMR+PEMFC economic parameters

<table>
<thead>
<tr>
<th>Early OPEX</th>
<th>Growth of exploitation cost</th>
<th>Discount rate</th>
<th>Growth of electricity tariff</th>
<th>Income taxes</th>
<th>CAPEX, mln. rub</th>
<th>Amortization period</th>
<th>1st year income, mln. rub</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,00%</td>
<td>4,00%</td>
<td>15,00%</td>
<td>4,00%</td>
<td>20,00%</td>
<td>10,065</td>
<td>20</td>
<td>4,02</td>
</tr>
</tbody>
</table>

Discounted revenue, EBITDA, mln.rub | Discounted net profit, mln.rub | Discounted cash flow, mln.rub | NPV, mln.rub | Payback period | PI | IRR |
41,7 | 31,8 | 22,45 | 26,19 | 16,3 | 4,71 | 2,6 |

3) “Hexis” technology

Table 12. Hexis economic parameters

<table>
<thead>
<tr>
<th>Early OPEX</th>
<th>Growth of exploitation cost</th>
<th>Discount rate</th>
<th>Growth of electricity tariff</th>
<th>Income taxes</th>
<th>CAPEX, mln. rub</th>
<th>Amortization period</th>
<th>1st year income, mln. rub</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,00%</td>
<td>2,00%</td>
<td>10,00%</td>
<td>5,00%</td>
<td>20,00%</td>
<td>1,26</td>
<td>20</td>
<td>0,24</td>
</tr>
</tbody>
</table>

Discounted revenue, EBITDA, mln.rub | Discounted net profit, mln.rub | Discounted cash flow, mln.rub | NPV, mln.rub | Payback period | PI | IRR |
3,57 | 3,28 | 2,12 | 2,75 | 1,49 | 8,17 | 2,18 |
Conclusion

In this Master thesis work possibility of using fuel cell technology as stand-alone power generation system in Russia has been estimated. At the beginning overview of hydrogen market in the world and Russia was given and described all hydrogen production and conversion methods. The most suitable way to produce hydrogen is by steam reforming of natural gas which is 8 times cheaper than to produce hydrogen from water electrolysis.

As fuel cell technologies SOFC and PEMFC were chosen and efficiencies were calculated. Overall effectiveness of energy system with SOFC is 40.33% for 100% hydrogen conversion and 28.44% for 70% conversion. In case of PEMFC technology overall effectiveness will be 46.33% and 30.86% respectively. In addition, hydrogen flow rates for both technologies were estimated. These values allow estimating the size of SMR equipment and its price.

After estimation of all CAPEX parameters and 1st year operating income economic feasibility of 3 different technologies has been calculated in the program developed by means of MS Excel. There such values as NPV, PI, IRR and payback time were calculated.

All obtained data allow to state that fuel cell technology for decentralized energy supply in Russia is a promising field of study and should be developed in industrial scale.
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