DOI: 10.1070/RCR4723

Energy resources of the 21st century: problems and forecasts. Can renewable energy sources replace fossil fuels? †

Vladimir S. Arutyunov,[a, b] Georgiy V. Lisichkin [c]

[a] *Semenov Institute of Chemical Physics, Russian Academy of Sciences ul. Kosygina 4, 119991 Moscow, Russian Federation*
[b] *Faculty of Fundamental Physical and Chemical Engineering, Lomonosov Moscow State University Leninskie Gory 1, stroenie 51, 119991 Moscow, Russian Federation*
[c] *Department of Chemistry, Lomonosov Moscow State University Leninskie Gory 1, stroenie 3, 119991 Moscow, Russian Federation*

The state of the art and the major trends of development of world energy engineering are analyzed. It is concluded that throughout the 21st century the role of alternative sources will remain rather modest. Fossil fuel will still be the major source of energy until the end of the century. Because of depletion of accessible oil resources, the proportion of crude oil in the world energy balance will constantly decline, while the proportion of natural gas will grow. It is shown that energy production from any source, including alternative sources, cannot be environmentally benign if the scale of production is large. In the long term, humanity has no sources other than fusion energy, but transition to this source would not solve the problem of the planet's heat balance.
The bibliography includes 70 references.

Contents

I.	Introduction	777
II.	Current state of energy engineering	779
III.	Evaluation criteria for energy sources	781
IV.	Types and key features of renewable sources	790
V.	Key problems related to the use of renewable energy sources	799
VI.	Prediction of the development of renewable energy sources	801
VII.	Conclusion	802

I. Introduction

Energy is one of the few fundamental concepts of the surrounding world. This alone justifies the attention paid to the energy-related issues in all spheres of human activity. However, this review addresses only a relatively narrow range of issues related to energy sources, which is still vitally important for predicting the possible trends of modern industrial civilization.

If we would like that our unique civilization avoids degradation, we have to constantly increase the energy consumption (this does not rule out a decrease in the specific energy consumption for particular industrial processes as they are upgraded). How this trend can fit together with the limited potential of the Earth, which has been almost fully explored by people, is the key challenge to our society.[1]

In the light of this global energy problem, it is surprising that the major discussions on energy-related issues, especially in developed countries (moreover, not only in mass media, but also in scientific editions), are concerned with a much less significant problem of more extensive use of so-called alternative energy sources. As a result, many people have become convinced that the global transition to 'renew-

V.S.Arutyunov. Doctor of Chemical Sciences, Professor, Head of the Laboratory of Oxidation of Hydrocarbons of the ICP RAS, Professor at the Faculty of Fundamental Physical and Chemical Engineering, MSU. Telephone: +7(495)939 – 7287, e-mail: v_arutyunov@mail.ru
Current research interests: kinetics of gas-phase reactions, oxidative conversion of hydrocarbon gases, environmental and resource problems of energy and transport.
G.V.Lisichkin. Doctor of Chemical Sciences, Professor, Head of the Laboratory of Surface Chemistry of the Division of Petroleum Chemistry and Organic Catalysis at the Department of Chemistry, MSU. Telephone: +7(495) 939 – 4638, e-mail: lisich@petrol.chem.msu.ru
Current research interests: chemistry of surface compounds, heterogeneous catalysis, problems of alternative energy production.

Received 11 January 2017
Translation: Z.P.Svitanko

† The conclusions and numerical calculations made by the authors of this review are debatable and the Editorial is not responsible for their content.

© 2017 Russian Academy of Sciences and Turpion Ltd.

able', 'environmentally benign' and 'green' energy sources will solve not only the current, but also all the future energy and environmental problems of humanity and that this approach could provide for not only the comfortable living, which has been attained by the modern western society, but also for sustainable development. In turn, this promoted the appearance of various 'green' movements, which are mainly supported by prosperous amateurs who are sure that restriction of energy consumption and more stringent environmental standards, certainly without decreasing their convenience and life standards, would preserve the convenience and well-doing not only for them, but also for their descendants. Typically, the green movements have low success and support in third-world countries, in which the quality of life here and now is much more significant for people than rather hypothetical problems of generations that have not yet been born.

The idea that renewable sources are able to solve the global problem of providing people with energy, which is permanently transmitted by mass media, has got into people's minds to such an extent that even some scientists and politicians start to believe in this, although back a half century ago, top specialists in the world trends and global processes [2–5] convincingly demonstrated the incommensurability of the real potential of renewable energy generation with the global energy demand of the modern industrial society and, all the more, the future post-industrial society.

It is evident that the interest in the alternative energy sources is fuelled by difficulties in the supply of conventional energy carriers and considerable fluctuations of their prices in the world market. Sometimes this interest sharply rises, while at other times it somewhat declines, in parallel with the fluctuations of crude oil world prices. The interest is maintained by green movements and organizations and by some kind of technological intimidation from crude oil consuming countries, which try to persuade crude oil producing countries that they can do without their resources. A noticeable role in the specualations on this subject is played by the interest of the agricultural and science lobby of developed countries in subsidies and grants and the interest of mass media in various 'scientific' sensations generated by informal science and enthusiastic amateurs. As a result, alternative energy has steadily occupied a top position not only in popular editions but also in scientific periodicals.[6] In any case, the number of publications and dedicated journals addressing alternative energy is much greater than the number of those dealing with real energy production, which makes a ~40-fold higher contribution to the world energy. The same is true for energy-related research funding. The lack of commensurability of the amounts of funding and the real outcomes of scientific research related to conventional and alternative energy is clearly illustrated by the relevant data for the United Stated, the largest and the most advanced country in this field, presented in Figs 1 and 2. Certainly, new areas of research and development are always more attractive for specialists. However, most of the money is directed towards purely applied works, the practical potential of which is small if at all present, rather than towards fundamental research that would discover new horizons of science.

It is beyond doubt that humanity cannot forever rely on fossil hydrocarbon fuel, which has created and maintains the current existence of the industrial civilization. But how long the 'hydrocarbon civilization' will last and what will

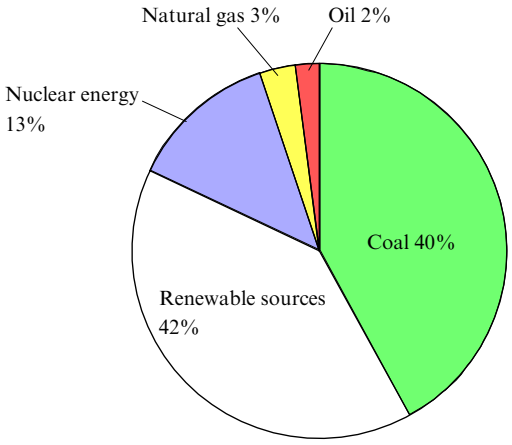


Figure 1. Distribution of funding for research related to various energy sources by the US Federal budget in 2005.[1]

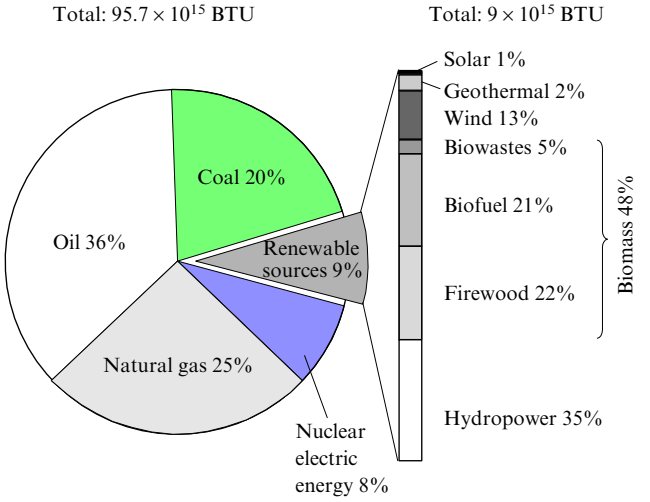


Figure 2. US energy balance as per 2011.[1]
The contributions of the sources are rounded to integers; BTU is British Thermal Unit.

come to replace it — different groups of specialists have different opinions on this subject.[7] Unfortunately, analysis of the trends of energy production, which is a purely rational sphere of human activity, has always involved and still involves emotions, everyday experience and even fantastic notions, like any other field of public interest. In some cases, these emotions and notions, which are sometimes at variance with the common sense and even with the laws of nature, have a considerable effect on the development of particular branches of energy industry as well as related areas of science and technology.

As a major consumer of new scientific achievements permanently accumulating all advanced and promising technological solutions, energy engineering is still a highly conservative branch of technology, because of its large scale. The replacement of basic technologies in energy production requires, as a rule, several decades. Therefore, unlike, for example, information technologies, in which new ideas and technological solutions can change the market in

only one or two years, in energy engineering, even the results of large technological revolutions are implemented on a large scale only several decades later. Owing to this delay, the predictions concerning energy engineering may be quite reliable, at least for the next 20 – 30 years until the service life of large power production facilities that already exist or are under construction is exhausted. This is why in this review, we were able to follow the medium-term trends in the world energy engineering and in the use of basic and prospective energy resources, considering, first of all, the real restrictions imposed by fundamental laws of nature on too optimistic predictions.

Despite the presence of a certain gap between chemistry as a natural science and energy production as a branch of engineering, we hope that this review will be of interest for readers of *Russian Chemical Reviews*, because many topics of chemistry, chemical engineering and materials science have been initiated by energy-related problems.

While working on the review, we used the largest world databases and updatable energy-related information sources such as *The Outlook for Energy: A View to 2040, International Energy Outlook, Statistical Review of World Energy, The ITER Organization Homepage* and so on, which publish materials of reputed international organizations such as the International Energy Agency (IEA), US Department of Energy (DOE), Energy Information Administration (EIA), British Petroleum Company (BP), European Photovoltaic Industry Association (EPIA) and so on. The calculations and numerical values presented in the review without references to sources are based on analysis of published data and our own estimates. This is original information that is completely our responsibility.

II. Current state of energy engineering

Before we make any predictions, we will briefly consider the current state and the scale of energy production. The state-of-the-art energy is based on five major primary sources: crude oil, coal, natural gas, hydropower and nuclear energy; recently, these sources were supplemented by renewable energy sources (RES) (Table 1, Fig. 3). By renewable sources are usually meant quite a few natural and biosphere sources of energy that do not require irreversible use of mineral energy feedstock. The production of most of the consumed energy is provided by fossil resources, the proportion of which in the world energy balance being more than 85% (see Table 1).

Table 1. Proportions of the main sources in the world production of energy in 2014 (http://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html) (see [a]).

Energy source	Percentage in the world energy balance (%)
Oil	32.6
Coal	30.0
Natural gas	23.7
Hydropower	6.8
Nuclear power	4.4
Other [b]	2.5

[a] The data discussed in the review and included in the Tables and Figures may be moved to the website archive by website owners. [b] Including RES.

As can be seen in Fig. 3, no dramatic changes are expected in the world energy in the next decades. The production of energy from all existing sources will increase and the consumption of crude oil, coal and natural gas will be higher than the current level, although their relative contributions to the world energy will be redistributed. The redistribution will mainly consist in the gradual decrease in the proportion of oil through increasing proportion of the natural gas.

Currently, the major energy problem is decreasing accessibility and, hence, decreasing proportion in the world energy balance of liquid hydrocarbons, which are the most important and most convenient fossil energy source. The products derived from this source, first of all, engine fuels and polymeric materials, constitute the basis of modern civilization. However, crude oil resources in the Earth's crust are limited and the time of oil deficiency is probably not so far off. Actually, the Oil Age has already gone and it is even possible to definitely indicate the starting point of its decline. In 1985, the amount of crude oil produced all over the world exceeded for the first time the amount of newly discovered oil resources, that is, the available oil resources clearly started to decrease.[8] Unfortu-

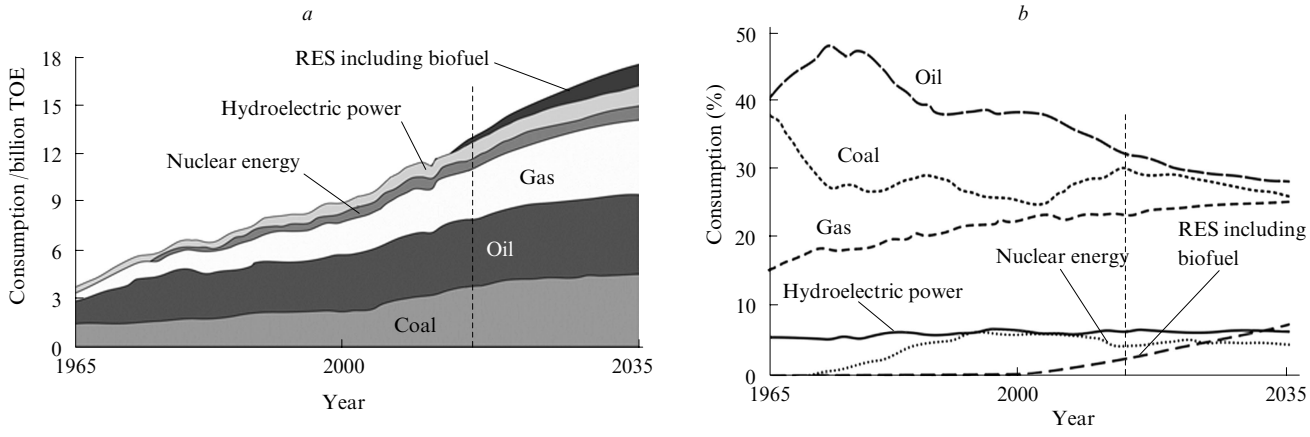


Figure 3. Current and predicted consumption of various sorts of primary energy sources in the world energy balance (TOE are tons of oil equivalent) (see URL: http://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html).

nately, it was only twenty years later, during the energy crisis of 2008, that politicians recognized the consequences of this event, highly important for world economy.

While evaluating the scale of modern energy engineering, it is more appropriate not to give the absolute values, which are hardly a clue for non-specialists, but to make comparisons with natural energy fluxes and expected changes in the world energy consumption. For instance, the energy generated by humanity has currently reached ~0.02% of the solar energy flux that reaches the Earth's surface.[4] The population of the world is supplied with energy to highly different extents. The major bulk of energy is consumed in developed countries. The United States, the population of which is only 4% of the Earth's population, use alone 20% of the world raw material and energy resources. Meanwhile, according to the IEA data, today 1.2 billion people still have no access to electric power and 2.7 billion people use mainly biomass (firewood) for heating and cooking (see http://www.iea.org/topics/energypoverty/). These values would barely change in the next 30 years.

Depending on the economic level of a country, the annual energy consumption (calculated in relation to crude oil) can differ by a factor of several tens (Table 2). It can be seen that the consumption is ~100-fold lower in the poorest countries than in the richest ones.[9] According to forecasts, by the end of this century, the Earth's population would double to reach 12–13 billion[10] and after that it may stabilize. Since the energy consumption (and hence the living standards) of the vast majority of people lags behind the modern consumption standard in the developed countries, even after stabilization of the population, economic and political stabilization in the world is impossible without at least partial decrease in the energy consumption gap between the rich and poor countries.

Due to the necessity of accelerated progress for underdeveloped countries, in the first half of the current century, the world energy consumption is predicted to grow by 1.7% per year and by the end of the century, the global energy consumption is likely to approach 0.1% of the solar energy flux that falls on the Earth. For providing the modern living standards to the whole population, the world energy production should increase almost 100-fold, *i.e.*, it should exceed 1% of the solar energy flux hitting the Earth. However, if this happens, the heat balance of the Earth will be disrupted, and to restore the balance, according to the Stefan–Boltzmann law, the average surface temperature (~300 K) with allowance for the Earth albedo should also increase by ~1%, that is, by 2–3 °C, which will inevitably cause a global climatic disaster. Moreover, the increase in the temperature will occur regardless of the way of energy generation or greenhouse gas concentration in the atmosphere, the control of which is the major concern of Kyoto Protocol enthusiasts. This exactly is the global problem of the future energy engineering and the cradle of the expected energy crisis. However, these issues are beyond the scope of the medium-term prediction we consider here.

Table 2. Annual energy consumption by various countries.[9]

Country	Consumption (expressed as barrels of oil per capita)
United States	65
Western Europe countries	50
Japan	33
Mexico	10[a]
Bangladesh	0.8
Nigeria	0.7

[a] Worldwide average.

Currently, the world energy engineering continues to develop very rapidly. According to EIA data, during the first two decades of the 21st century, the world energy consumption is expected to increase by 59%. This increase would take place despite the expected considerable increase in the efficiency of energy utilization per unit of gross domestic product (GDP). Half of the increase expected by 2020 would refer to developing countries and fossil fuel would still be the major source of energy.

In this connection, it is necessary to note that increasing the efficiency of energy resource utilization and decreasing the specific energy consumption per unit of product are now the most advantageous ways of medium-term solution of energy problems and decreasing the climatic impact of energy production. For example, in the US with permanently growing GDP, the energy consumption has been virtually stabilized in recent years. This was achieved mainly owing to the fact that the specific energy consumption per unit of GDP has been almost halved in the last 40 years (Fig. 4).

Currently, the trend for a considerable decrease in the growth rate of energy consumption per unit of GDP increase is now characteristic of all advanced countries; this makes it possible to mitigate the dependence of world economy on the supply of fossil energy resources and decrease the climatic impact of energy production. However, this only delays the inevitable depletion of fossil resources and gives additional time for the search for global solution of energy problems.

The paradoxicality of the existing energy situation is that it is easier to predict its distant future than the near-term prospects. Most of specialists believe that, despite the huge scientific and technological problems, thermonuclear fusion would become the major energy source by the end of the 21st century (perhaps, somewhat later). There are no

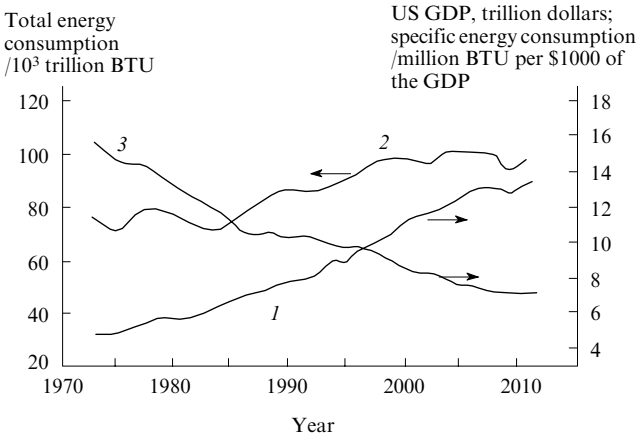


Figure 4. Efficiency indicators for the use of energy resources in the US (from Ref. 11).
(*1*) GDP, (*2*) total energy consumption, (*3*) specific energy consumption.

other alternative energy sources of an equal size at the disposal of people even in the long view. This primary source has, in principle, been technologically mastered, but still in the uncontrollable mode at a thermonuclear bomb level. The key laws of this process are understood and, although the problem has proved to be much more complicated than initially believed, one can hardly doubt that it will be solved with time.

If controlled thermonuclear fusion is available, humanity will have a virtually inexhaustible energy source for thousands of years (however, the problem of disrupting Earth's heat balance will persist). The problem of controlled thermonuclear fusion is much more sophisticated than any scientific and technological problem faced by humanity in the 20th century. Starting-up an international experimental fusion reactor is planned only for 2025 in France, and deuterium-tritium plasma experiments in this reactor will be started ten more years later (see http://www.iter.org/). Optimists are hoping that a demonstration fusion power plant would be constructed by the mid-21st century. This means that nuclear fusion energy would be available for mass-market customers not earlier than by the end of the 21st century. Therefore, a very serious challenge is to find energy resources that would be able to fill an almost hundred-year gap up to the practical implementation of nuclear fusion energy. The price of failure in solving this global energy problem is very high — inevitable decrease in the living standards of people and possibly decrease in the world population.

Well, are alternative sources able to replace the depleted fossil energy and provide the necessary amount of energy for the world economy?

III. Evaluation criteria for energy sources

Before comparing the prospects of using various energy sources and their ability to satisfy the demands of world economy, it is necessary to define the most important comparison criteria.

III.1. Consumer properties

The most important criteria determining the world demand for particular energy resources are their consumer properties. The effect of consumer qualities on the prospects of using an energy source is vividly illustrated by the change in the role of coal in the world energy. Whereas in the early 20th century, the proportion of coal in the world energy balance was more than 50%, currently it has reduced more than twofold despite the presence of huge coal resources almost in all regions. This is caused by particularly the low consumer quality of coal, first of all, the inconvenience of using a solid fuel in the transport, household and industry. A certain role is played by low environmental characteristics of coal, the complexity and high cost of transportation and low cost-effectiveness of its conversion to more convenient kinds of fuel.

Liquid hydrocarbons (crude oil) are beyond competition, among known types of energy feedstock, as regards the consumer quality. The unique nature of oil as an energy and petrochemistry resource consists in that, owing to the liquid physical state and high specific energy content, oil provides higher cost-effectiveness for the production, transportation and utilization than any other fossil energy source. Moreover, oil is rather easily processed and the range of oil products is very extensive. In this respect, neither gas, nor coal, or any other energy source can compare with oil. Therefore, it is not surprising that as soon as oil production and refining processes were implemented in industry, oil occupied the dominant position in the world energy engineering, and in the 1970 – 1980s, the proportion of oil in the world energy balance reached $\sim$50%. Oil has fairly acceptable environmental characteristics and if it was not for the expected deficiency of this energy resource, the energy supply problem would hardly be so acute.

Natural gas holds an intermediate position between oil and coal in the consumer properties. This is caused by complexity of gas transportation and use in transport and by high cost of conversion to more convenient liquid energy sources and chemicals. The obvious consumer advantages of natural gas include highest environmental characteristics among fossil fuels and the convenience of use in household, industry and basic heat and electric power generation.

Except for biofuels, almost all other renewable energy sources, in particular, hydro, wind, solar as well as nuclear power sources generate only electricity; therefore, they cannot equally compete with oil in their consumer characteristics. The difficulties associated with electricity transmission over large distances; conversion to other kinds of energy; use in transport and in many branches of industry; enormous capital investments needed for this; and inevitable losses substantially decrease the attractiveness of these sources for many consumers.

III.2. Resource base

In view of the enormous and rapidly increasing energy demand, the potential amount of reserves or annually supplied amount of energy is a key issue for evaluation of the potential significance of an energy resource. It is no use to analyze the global potential of the sources that, in principle, cannot make a contribution higher than 1% to the global energy production, although these sources can still play an important role in local energy supply and their technological development is, beyond doubt, necessary.

III.2.a. Oil

Today crude oil is a highly important natural resource determining the state of not only the global energy production but also, to a considerable extent, the geopolitical situation in the world. The oil price is an important indicator reflecting the current state of the world economy.

The limited resource base is the key drawback, which does not allow oil to be considered as the most important energy source in the world beyond two or three next decades. Although debates between supporters of organic and inorganic theories of oil origin are still continued, most of oil resources being developed are apparently of the biogenic origin. Thus, it turns out that the modern global energy production is based on a sort of 'canned energy', which was prepared by the biosphere throughout $\sim$300 million years of evolution starting from the Carboniferous period. The oil reserves are huge, but the oil consumption rate is million times higher than the rate of its natural formation in the Earth's crust. In one year, people spend the resources for the formation of which the Nature had spent approximately million years. Therefore, the resorces will inevitably be exhausted with time. The peak of oil resource discoveries was passed back in the 1970s (Fig. 5). Currently, the major amount of oil is produced from deposits discov-

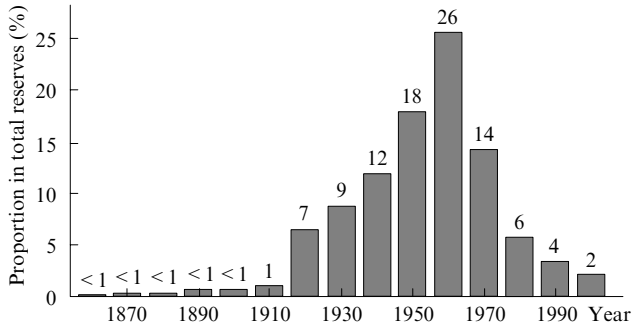


Figure 5. Proportions of giant oil deposits discovered at different times in the reserves known to date.[12]

ered decades ago (Fig. 6) and we can no longer rely on the appearance of a large number of new large deposits.

The maintenance of the world oil production level, which virtually does not increase any longer because of depletion of the resources, requires more and more expenses, *i.e.*, every next produced oil barrel is more expensive for the world economy than the previous one. From 1973 to 2003, the amount of oil produced in the world increased by ~60%, while the cost of production in fixed prices increased almost 17-fold.[13] In 2013, the global cost of oil production reached $700 billion. This is the objective cause for the permanent and inevitable rise of oil and oil product prices in the world market. The age of readily accessible and inexpensive oil has already ended.

The issue of the total amount of remaining oil resources, widely discussed in recent years, is rather technological than geological. Certainly, undiscovered deposits of liquid hydrocarbons still exist in the Earth's crust, but their volume is hardly large. A much more interesting issue is the development of the known resources located in deep water areas or represented by various types of heavy or difficult-to-recover oils. Apart from an increase in resources *via* geological exploration, the amount of potentially recoverable oil is affected by a number of important factors such as the market oil price and the advances in the production technologies. Even with the use of advanced technologies, less than half of formation oil can be recovered. Therefore, increasing investments to production technology and application of most advanced technological achievements can considerably enhance the overall recovery factor of deposits and thus contribute to the oil resources accessible for the world economy.[8, 14]

As regards the particular time of depletion of oil resources, the forecasts of specialists are substantially different (Fig. 7). The most realistic estimates predict that the peak of production (including unconventional and difficult-to-recover oils) will be attained within one or two next decades with the subsequent smooth decline, which would slow down with the advent of new technologies that would enhance the oil recovery. The obvious approach of the world oil production level to its peak is also indicated by a very low production growth rate, only ~0.5% per year, despite the critical need in oil and constant increase in the investments.

Many oil producing countries have already passed the peak of production and in most of the other, the time it will take to reach the peak is estimated as only several years. According to IEA data, only in the twenty top oil producing countries, the predicted time of full depletion of resources (the ratio of the total amount of resources to the annual production) exceeds 20 years. Certainly, there are huge unconventional oil resources mainly consisting of difficult-to-recover and heavy hydrocarbons and deep water and Arctic resources. However, the cost of recovery and the required energy expenditures are so high that the production is far from being always economically justified. A predicted estimate of the technically recoverable shale oil and other unconventional oil types has demonstrated that these reserves are large, but obviously cannot meet the enormous demands that would arise in the near future. Therefore, while remaining the most convenient and attractive energy source, oil is still forced to gradually retreat.

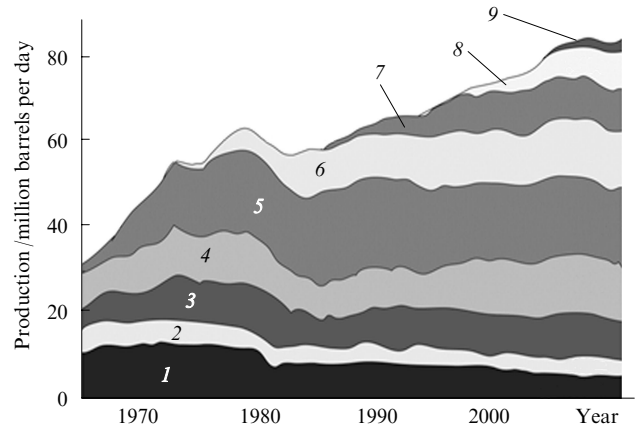


Figure 6. World oil production from the deposits discovered before 1930 (*1*) and in the 1930s (*2*), 1940s (*3*), 1950s (*4*), 1960s (*5*), 1970s (*6*), 1980s (*7*), 1990s (*8*), early 21st century (*9*) (http://www.slideshare.net/skurbatov/2012-the-outlook-for-energy-a-view-to-2040).

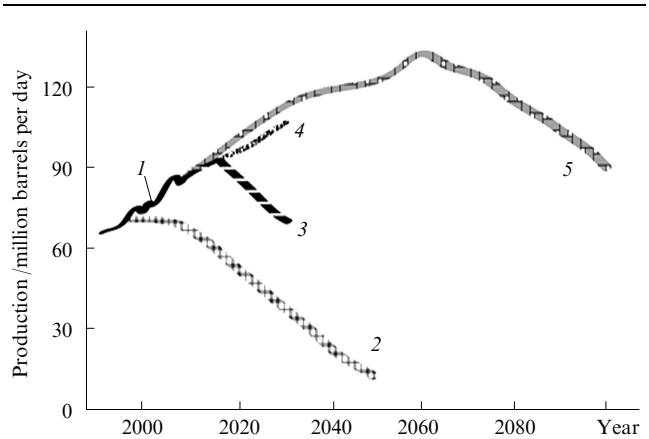


Figure 7. Actual world oil production (*1*) and world oil production predicted in different years (*2*–*5*).[15]
Prediction: (*2*) C.J.Campbell, J.H.Laherrere, 1998 (US); (*3*) S.Al-Husseini, 2015 (Saudi Arabia); (*4*) US Department of Energy, 2009; (*5*) P.R.Odell, 2004 (the Netherlands).

III.2.b. Coal

The coal reserves are huge and, according to some forecasts, they can cover the world demand of energy for the next several decades. As regards the resource base, coal has an obvious advantage over oil, which, however, is substantially canceled out by its low consumer and environmental characteristics. An attempt to create an environmentally clean coal-based energy engineering made ~20 years ago in the United States, which consumed a lot of money (see Fig. 1), proved to be economically unfeasible. Currently, the proportion of coal in the world energy balance constantly decreases; throughout the current century it will probably remain at a level of 20% (or slightly higher). The main reasons that account for a decreasing proportion of coal in the world economy are associated with the inconvenience of using solid fuel, difficulty of automation of processing processes, dangerous mining, and relatively low calorific value, which makes coal transportation over large distances uneconomical, and environmental problems associated with its application. The problem of cost-effective conversion of coal to liquid fuel has not yet been solved, despite the almost hundred-year history of such attempts. Virtually all drawbacks of coal as an energy resource are also inherent in other solid fossil fuels, *e.g.*, combustible shales and peat, which are used in energy production only on a local basis.

III.2.c. Natural gas

Currently, natural gas is considered to be the most abundant and vigorously developing energy resource. Whereas the world oil consumption has virtually reached a peak, the consumption of natural gas continues to rapidly grow (Fig. 8).

The major geologically proven reserves of conventional natural gas are concentrated in two regions — C.I.S. countries and the Middle East. By conventional natural gas resources are meant deposits with at least 0.1 billion m^3 of the gas and the initial well flow rate of >30 thousand m^3 per day. The total number of deposits with free natural gas all over the world is more than 17 000, and in more than 30 000 oil deposits, gas is present as a secondary component (petroleum gas or associated gas). Out of 4500 large natural gas deposits, only several tens (~2% of the total number) can be classified as large, and they give the major contribution to the commercial natural gas supplied for energy production and for chemical processing.[17] With the existing natural gas transportation and processing technologies, the greater part of the known deposits can serve only to meet local demands.

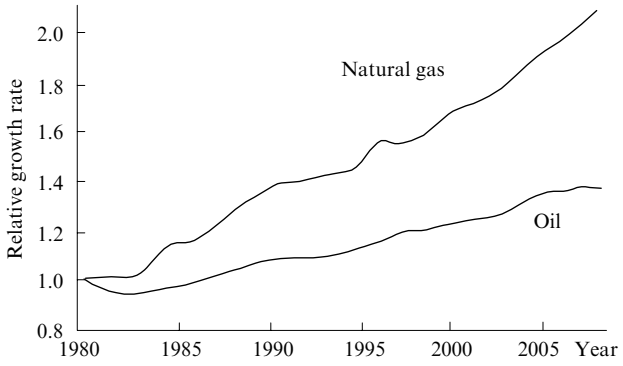


Figure 8. Relative growth rate of world oil and gas consumption (the world consumption of 1980 is taken as unity).[16]

The world gas potential (the initial potential resources of conventional natural gas) is estimated to be between 350 – 420 trillion m^3 (conservative estimate) and 500 – 550 or even up to 1000 trillion m^3 (Ref. 18). According to statistical data, more than 90% of oil and gas pools found in the world are accumulated at depths of up to 3 km. The degree of exploration of this bed is very high; therefore, in the future, mainly small pools may be discovered in it. Unfortunately, this was barely taken into account in the design of modern technologies for the production, transportation and utilization of hydrocarbon resources, meant most of all for large deposits.

The highest growth rate of conventional natural gas resources, like that for oil resources, was attained in the 1970s. In the beginning of the 21st century, 15 years later than in the case of oil, the world production rate of conventional natural gas became equal to the rate of discovery of new large deposits. Thus, the production of conventional gas also approaches its peak. However, in recent years, considerable attention has been attracted by the huge resources of unconventional natural gas. First of all, this is due to the advent of new technologies for the extraction of such resources. Thus, the huge unconventional natural gas resources can be considered to be accessible for the development of energy engineering.

The known mechanisms of formation of methane and other hydrocarbon gases in the Earth's crust[19 – 23] provide for their abundance in nature not only as large pools of conventional natural gas in porous and fractured sedimentary rocks or in the dissolved form in oil. An enormous amount of methane is scattered in sedimentary and igneous rocks or in the lake, sea and ocean silts. Methane is present in crystalline schists, marbles, gneisses, granites and other rocks, with up to 0.1 m^3 of methane being present per 1 m^3 of the rock. Small concentrations of methane are present in fresh and sea water. Methane occurs as a part of soil air and Earth's atmosphere. A lot of methane is dissolved in formation water located at a depth of 1.5 – 5 km. Natural gas sources such as coalbed methane, water-dissolved gases of subsurface hydrosphere, natural gas hydrates and some other are classified as unconventional resources.

Hard-coal deposits can serve as important sources of virtually pure methane. Large methane volumes are released in coal beds during coal metamorphism, which is accompanied by low-temperature thermochemical decay of organic matter. The amount of methane released per tonne of the coal material increases from 161 m^3 during the brown coal formation to 192 m^3 during hard coal formation.[24] Methane is accumulated as a result of adsorption in coalbed vertical faults and fractures. During production, one tonne of coal gives 6 – 8 m^3 of the gas. Since the world resources of coal are ~10^4 billion tonnes, the gas amount in the coal deposits is comparable with its amount in conventional gas deposits. According to different estimates, coal beds of the coal basins all over the world contain 85 to 262 trillion m^3 of methane. Therefore, even a moderate gas production from coal beds can make a weighty contribution to the natural gas supply for humanity.

Even now, unconventional coalbed methane occupies a noticeable place in the gas production of some countries. In the United States, the active production of coalbed methane

started in the 1950s; currently its annual output is more than 55 billion m^3, which amounts to >7% of the total natural gas production. Coalbed methane is also produced in Canada, Australia, China, India, Indonesia and in other countries. Preliminary degassing of coal beds is a necessary condition for safety of mine workers and a source of associated methane. The mines in Russia discharge >7.5 billion m^3 of methane to the atmosphere every year; however, it is virtually not utilized on an industrial scale.

One more unconventional energy source is biogas (containing mainly methane), which is formed upon bacterial fermentation of organic matter. However, shale gas and gas hydrates are now considered as the key unconventional sources of gaseous hydrocarbons. The development of an industrial process for shale gas production in the early 21st century in the US became a milestone in the world energy engineering. Before this, the shale gas was not even considered as a really recoverable resource. The transformation of the huge reserves of shale gas to accessible energy raw material can be considered as a technological revolution most prominent in the last 50 years. This increased the world energy resources by a large factor and eliminated, at least for several decades, the highly acute global energy deficit.

The major difference of shale gas deposits from conventional ones is that the former are located at 1.5–2 km depths in low-permeability sedimentary rocks, in which the gas genesis actually takes place. Because of the deep occurrence and low permeability of shale rocks, development of these resources required solution of several technological problems. Apart from the development of cost-effective deep well drilling techniques, it was necessary to devise methods for increasing gas influx to a well and maintenance of a high well flow rate for rather a long time period necessary for economic return on investment for deep drilling. The methods include efficient deep horizontal drilling and hydraulic fracturing technologies; a combination of these approaches considerably increases the effective area of gas recovery and the velocity of gas diffusion towards the well. For hydraulic fracturing, a mixture of water, sand and a set of chemicals is injected into the formation under high pressure. As the rock is fractured under the action of pressure in the horizontal part of the well, which is 1.5–2 km long, a large number of cracks is formed and the total gas recovery area increases. The sand grains consolidate the cracks, which thus cannot collapse under the formation pressure, while the chemicals, which are mainly surfactants, enhance the recovery.

After the hydraulic fracturing and injected water recovery, the well can be efficiently operated for several years, although the flow rate decreases almost twofold as soon as in the first year. Generally, cost-effective operation of a shale gas well continues only for a few years, which is several-fold shorter than that in the case of conventional gas, which is usually produced from traps in reservoir rocks that are highly permeable for the gas and are covered by impermeable rocks; in this case, production may last for several decades. However, whereas the discovery of large conventional gas traps, which have been filled with the gas migrating from low-permeability source rocks during millions of years, is a geological good luck, the shale gas is produced over large areas by successive drilling of wells at particular distances;[25] that is, shale gas can be consistently produced from enormous areas located above the gas-bearing shale rocks.

Nevertheless, the shale gas production technology, the development of which has taken ~20 years and billions of dollars of US companies, is still very sophisticated and expensive. The cost of preparing one well for operation gradually decreases and is currently estimated as approximately $5 million; this allows the US producers to bring the gas to the internal market at a uniquely low price — about $120 for 1000 m^3. This is approximately two or three times lower than the gas price in Europe and Japan.

The most hope for the future of fossil sources comes from the huge deposits of gas hydrates in the Earth's crust. Gas hydrates are non-stochiometric crystalline solids with the general formula $C_nH_{2n+2} \cdot m\,H_2O$, which can also exist at temperatures above zero under elevated pressure. Structurally, gas hydrates are inclusion compounds (clathrates), which are formed upon insertion of gas molecules into the cavities of crystalline structures composed of water molecules. Hydrocarbons with a molecular size greater than that of isobutane do not form hydrates, as they do not fit into the cavity formed by water molecules. Upon the formation of the methane hydrate, one volume of water traps 207 volumes of methane and decomposition of 1 m^3 of methane hydrate gives off 164.6 m^3 of the gas under standard conditions.[26]

Methane hydrates look like ice or dense snow. They widely occur in nature and form large deposits. At the ocean bottom at even 700 m depth, pressure is sufficient for the formation of gas hydrates even at a temperature of 10 °C. The gas resources incorporated in gas hydrates on the continents amount to ~ 10^{14} m^3. The offshore gas resources existing as the hydrates within the continental shelf and continental slope are ~1.5×10^{16} m^3 (Ref. 26), although there are also higher estimates. The energy liberated upon decomposition of gas hydrates is so high that it can initiate tectono-magmatic processes in the Earth's lithosphere.

The regularities of occurrence of gas hydrate accumulations and isotope and geochemical compositions of gas hydrate gases and waters attest to deep origin of hydrocarbon gases incorporated in the hydrates. Hydrogen and carbon are the major chemical elements that rise from the Earth's interior towards the surface in the course of permanent degassing of Earth. Hydrogen diffuses from the Earth's rock mass in the atomic or molecular form, while carbon migrates in the chemically bound form, as the CO and CO_2 oxides. At a temperature of <600 °C, these gases react to give water and methane

$$CO + 3\,H_2 \longrightarrow H_2O + CH_4$$

Water enters the crystal lattice of hydrosilicates, while methane is accumulated as gas inclusions, in particular, gas hydrates.

According to some estimates, the gas hydrate layer of pleistocene-age deposits contains at least 11.3×10^{18} m^3 or 8.5×10^{15} g of methane carbon; other sources do not give so high values for hydrate content, the resources being estimated as 2×10^{16} m^3. Nevertheless, according to estimates, more than half of organic carbon in the Earth's crust occurs, apparently, as gas hydrates. This resource exceeds twice all explored and unexplored oil, coal and gas reserves taken together.[27] It is especially important that huge methane accumulations occur in the sediments formed in the last

five million years, *i.e.*, methane that is present in these accumulations has been evolved during the time period equal approximately to one thousandths of the Earth existence time.

There are data on more than 100 known gas hydrate deposits, while the potential gas reserves in the hydrate state exceed, according to estimates, 16×10^{12} TOE. About 98% of gas hydrates are concentrated in the global ocean at 200 – 700 m depths and in ~400 – 800 m-thick bottom sediments and only 2% are in the polar continental areas. However, this resource also deserves attention, because this corresponds to 300 trillion m^3 of the gas, which is 1.5 times greater than explored gas reserves in the world. At the current level of consumption, the gas reserves present as gas hydrates identified in the US can cover the demands of the country for 104 years. More and more countries including the United States, Canada, India, China and Japan establish national programmes for investigation of gas hydrates and search for their deposits. As a result, huge gas hydrate accumulations and gas hydrate provinces were discovered; however, the design of technologies that would make methane recovery from gas hydrates not merely possible but cost-effective is still a challenge.

Thus, there are huge resources of natural gas in the Earth's crust, which are moreover constantly replenished as a result of continuing Earth degassing. The main problem of the use of this enormous potential is to develop technologies suitable for the recovery of this gas with acceptable financial and energy costs and engineering efforts. The presence of various types of natural gas in the Earth's crust is illustrated by Fig. 9. As the 'unconventionality' of natural gas is increased, on the one hand, the amount of such gas in the Earth's crust increases, but on the other hand, the recovery technology becomes more complicated and expensive.

It can be seen that there are enormous natural gas resources at the disposal of humanity (Table 3). Some kinds of resources have been poorly explored as yet, but irrespective of particular estimates, it is obvious that their amount is great and at any rational scenario of the development of our civilization, they are sufficient for tens or even hundreds of years.

Certainly, the recovery of unconventional gas is more complicated and more expensive than the conventional

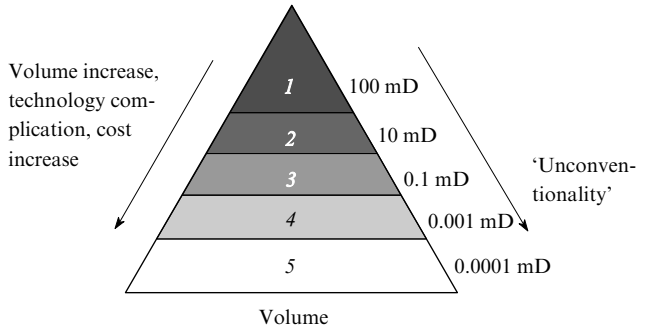


Figure 9. Various types of natural gas in the Earth's crust.
Type: (*1*) traditional gas, (*2*) tight reservoir gas, (*3*) coalbed methane, (*4*) gas hydrates, (*5*) shale gas.
The numbers stand for the permeability of reservoir rocks for the corresponding gas type /millidarcy.

Table 3. Annual production, natural gas resources and Earth degassing as of 2014.[1]

Resources	Value /trillion m^3
Annual production	3.5
Resources	
proven	209
undiscovered	280
Coalbed methane	260
Shale gas	400 – 700
Gas hydrates	20 000
Earth degassing	~1

natural gas production. However, as the most convenient gas fields are being depleted, the prime cost of the conventional gas recovery increases. As in the production of oil, it becomes necessary to develop resources that are more and more difficult and, hence, more and more expensive to recover. However, this is not a dramatic stepwise cost increase, but a smooth and, regretfully, inevitable transfer to development of increasingly expensive raw materials.

The prime cost of the shale gas production in the United States is already lower than the prime cost of the conventional gas production in Europe; this allows one to predict the profitability of gas export to Europe. While comparing this with the conventional natural gas resources in Russia, one should bear in mind that they are largely represented by arctic resources, the recovery of which can prove considerably more expensive than the shale gas recovery in the United States or in other countries and their transportation to the European and Asian markets is more expensive than the transportation of the US gas to the same regions.

The proportion of unconventional gas (tight reservoir or coalbed gas) exceeds 15% of the global gas production in the world and clearly tends to grow, perhaps, up to 40%. Currently, the total resource base is evaluated as ~100 years of the current world consumption. According to estimates, natural gas will be the largest primary source of energy by the 2030s, and this will mean the end of the almost 100-year period of oil predominance. Actually, the reserves of shale hydrocarbons are primary with respect to conventional reserves. They are distributed rather evenly over the Earth surface, and, therefore, they are generally accessible. The overall unconventional gas resources exceed even the prospective needs of humanity, at least, in the time interval in which they can be predicted. Until recently, the lack of appropriate technologies for the recovery was the only obstacle for their use. However, this obstacle no longer exists in relation to shale gas; probably, it will also be overcome in the near future for other unconventional resources. This raises the reasonable question of whether natural gas will be able to replace oil, which is certainly more convenient, in the world energy production and, what is more important, in the world economy as a whole, especially in the key areas such as transport and petrochemistry.

As regards transport applications, industrial processes for the natural gas conversion to liquid hydrocarbons, that is, synthetic oil and liquid engine fuels, have been existing for several decades. The problem of raw material supply for the modern petrochemistry is not very acute. If the production of engine fuels is excluded, the other petrochemistry consumes only ~5% of the produced oil; therefore, it is

easier to cover these needs. In addition, gas chemistry, a new branch able to produce the whole great diversity of products manufactured by the modern petrochemistry, has vigorously developed in recent years.

III.2.d. Nuclear energy

Nuclear energy is also a source that uses fossil natural resources, namely, ^{235}U isotope. The content of this isotope in natural uranium is only 0.6% – 0.7%. At the modern level of development of nuclear energy engineering and economically reasonable production cost of up to \$80 per kg of U_3O_8, the time of depletion of the ^{235}U reserves is estimated at only ~50 years. Even the transition to very expensive and sophisticated breeder reactors, which increase the degree of utilization of natural uranium 60 – 80-fold by converting also the major ^{238}U isotope to nuclear fuel, does not make it possible to rely on nuclear energy as a long-term energy source for humanity. A considerable uranium reserve not utilized as yet is sea water in which the average concentration of the uranyl carbonate complex is 3.3×10^{-6} g litre^{-1}.

Currently, the nuclear energy accounts for ~4.4% of the primary energy generated in the world, *i.e.* , its proportion is slightly lower than that of hydropower. Its proportions in the generation of electric energy are much higher: approximately one-sixth of the world and one-third of the European generation of electric energy falls to nuclear energy. In some countries (France, Slovakia, Belgium, Sweden and Switzerland), nuclear energy predominates in the electricity production. As of 2014, the total number of power reactors in the world was 439 and their total capacity was 376.8 GW; 67 more reactors were under construction. The largest number of nuclear stations (104 power units) are operated in the United States, the second largest number is in France (58 power units), and the third one is Japan (50 power units). In Russia, there are 10 power plants (33 power units). The world leader in the proportion of nuclear energy in the total amount of generated electricity (~77%) is France.

Thus, the fossil resources occurring in the Earth are quite sufficient for meeting the demands of the world energy production at least up to the end of the 21st century, but during this period a real substitute has to be prepared.

III.2.e. Hydropower engineering

The resource base of river hydropower is, unfortunately, limited. The total amount of energy that can be gained from this source can be readily estimated from the data on average altitude of Earth's surface and the average annual precipitation. According to IEA estimates, the total technically implementable potential of hydropower in the world is 14 000 TWh per year. Of these ~8000 TWh per year are considered as economically feasible. Currently, ~808 GW of hydropower is either in operation or under construction, with the estimated annual total amount of produced energy being ~7080 TWh. Thus, in view of geographic factors and inevitable loss during energy conversion, the greater part of the hydropower potential really available on Earth has already been put into action. Most of the remaining potential falls within countries of Africa, Asia and Latin America. Owing to this potential, hydropower engineering may be further developed but its proportion in the world energy balance cannot substantially increase.

III.3. Prime cost of energy production

A very important parameter affecting the decisions about construction of a particular energy production facility is the cost of the generated energy, which in turn depends on the raw material cost, the power plant equipment and the equipment service life. While calculating the prime cost, it is necessary to include the expenditures for raw material purchase, construction of all the facilities necessary for energy production and transportation to the consumer, operating costs throughout the service life of equipment, the cost of disassembly and disposal of equipment after the operation — that is, all of the expenditures throughout the full life cycle of the facility.

The cost-effectiveness of various sources of electric energy is compared using the value called levelized cost of electricity (LCOE), which is defined as the capital and operating costs of electric energy generation during the whole life cycle of the equipment divided by the total amount of energy produced during this period. Actually the LCOE value can be considered as the break-even price for the supply of this sort of energy. This value determines the cost-effectiveness and consumer appeal of various electric energy sources. The LCOE values for various electric energy sources are presented in Fig. 10.

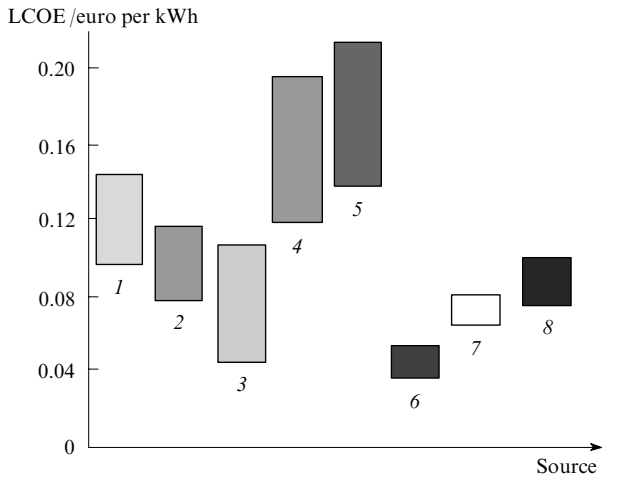


Figure 10. Levelized cost of electricity production based on various sources (https://en.wikipedia.org/wiki/Cost_of_electricity_by_source#Cost_factors).
(*1*) Solar panels, (*2*) solar cells, (*3*) wind energy, (*4*) offshore wind farms, (*5*) biogas, (*6*) coal (lignite), (*7*) hard coal, (*8*) natural gas, steam and gas cycle.

III.4. Energy return. The EROEI index ‡

The energy return of the source is one more important aspect, which is unfortunately rarely discussed by enthusiasts of alternative energy sources. Energy generation from any source always requires certain expenditures to ensure the energy generation process. It is evident that the energy spent for extraction, transportation and processing of the raw materials; generation and conversion of the energy; and

‡ The abbreviation EROEI means Energy Return On Energy Invested and is often reduced to EROI meaning Energy Return On Invested.

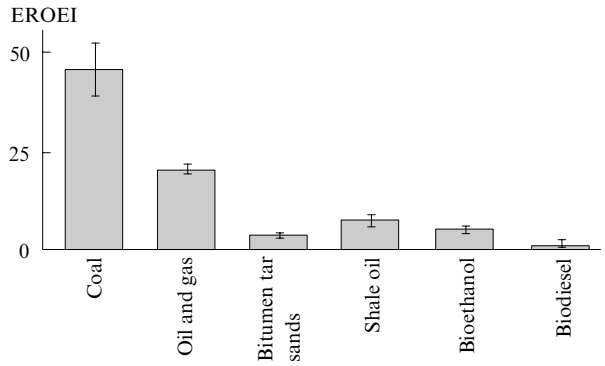


Figure 11. Average EROEI values for various types of fuel.[28]

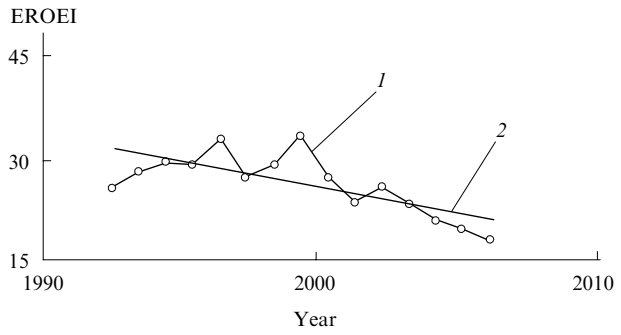


Figure 12. Trend of EROEI variation for the world oil and gas production.[28]
(*1*) World values for oil and gas, (*2*) overall trend for oil and gas.

manufacture and maintenance of the equipment should be lower than the energy delivered to the consumer. Therefore, the ratio of the useful energy to the energy spent for production can be considered as a sort of efficiency, but for the whole energy chain rather than for a single operation. This chain should include all processes, for example, for the oil industry, this is the route from oil well to car wheel. This ratio shows the energy efficiency of this energy source. The EROEI value should include all expenditures, that is, the costs of manufacture, maintenance during the service life and disposal afterwards for the equipment used for the generation, conversion and transportation of energy; restoration and recultivation of environmental objects; accident management; and compensation for environmental damage. If EROEI <1 for some energy resource, this resource is actually an energy consumer and, therefore, it cannot be considered as a primary energy source.

Economy always tends to utilize, first of all, energy resources with the highest EROEI values, because they give more energy for less cost. However, as the high-quality non-renewable resources are depleted, it becomes necessary to switch to lower-EROEI resources. For example, when industrial oil production started, the energy contained in one barrel was sufficient, on average, for finding, recovering and refining 100 barrels. During the past 100 years, this value gradually decreased to 20 – 30 barrels for the conventional oil production and to 3 – 5 barrels for heavy oil

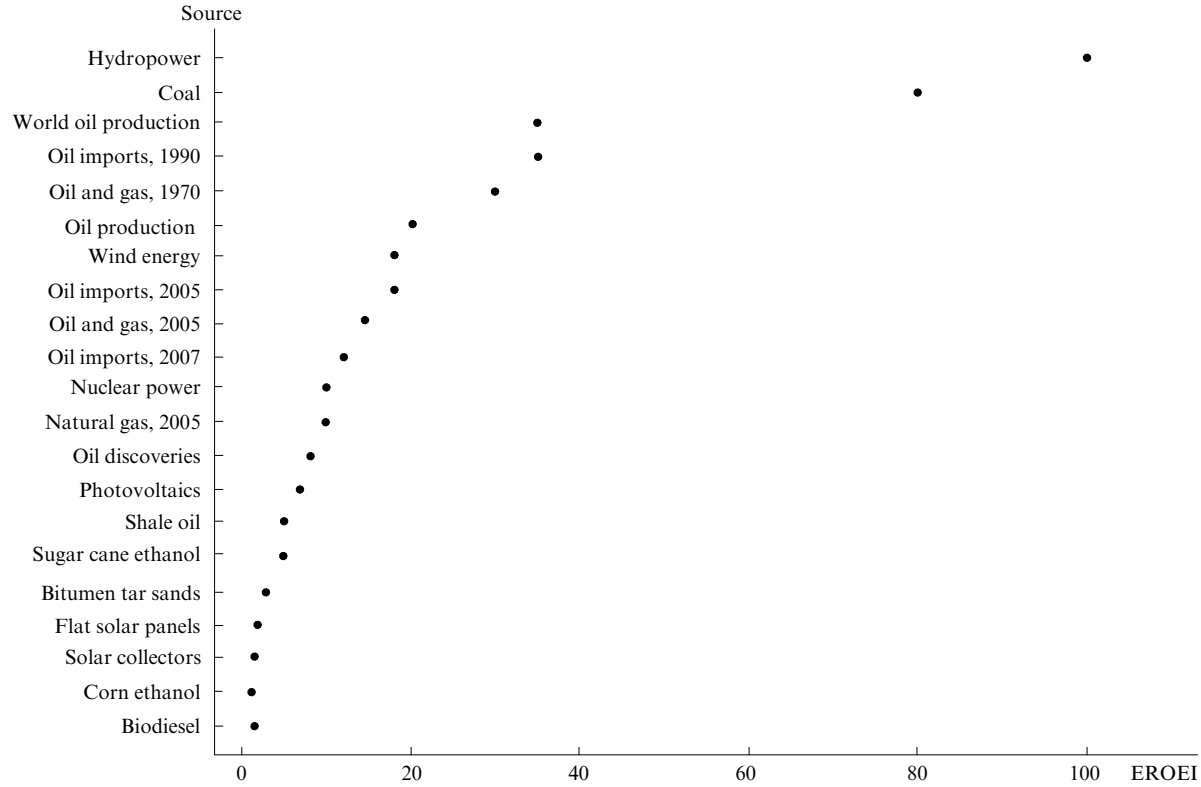


Figure 13. Variation of EROEI for energy sources in the US following the depletion of the most efficient resources (https://ru.wikipedia.org/wiki/EROEI#CITEREFMurphyHall2010).

production (Fig. 11). In other words, in the production of heavy oil, ~20% – 30% of energy it contains is spent for the proper production and primary refining of this oil.[28]

The permanent increase in the energy expenditure for the production and processing of traditional energy resources leads to rather fast decrease in the EROEI value in the world energy engineering (Fig. 12).

Certainly, while comparing various energy sources, many other parameters must be taken into account apart from the EROEI, such as reliability, accessibility, convenience of use, energy saturation and so on. For example, oil is energy saturated and easily transported, while wind energy is variable and produced locally. In any case, as EROEI of major sources decreases, it becomes more difficult to generate energy and the relative cost of energy increases. Thus, EROEI is very (if not the most) important characteristics for comparison of energy options. Analysis of the EROEI values and their variation with time for different energy sources (Fig. 13) provides an understanding of why the prime cost of energy resources and supplied energy constantly increases and why fossil fuels rather than solar energy, the EROEI of which is only slightly higher than unity, are at the base of the world energy production.

The production of energy requires considerable efforts and energy expenditures. As EROEI decreases, generation of the same amount of neat energy occupies more and more higher fraction of the economy; therefore, the permanent decline of this index as a result of depletion of the most efficient non-renewable resources is a grave economic problem. According to estimates, the threshold EROEI value at which the humanity development can continue is about 3 (the net energy gain is only 200%), which unambiguously excludes biofuel and actually also solar energy, for which the EROEI is only slightly higher than unity (see Fig. 13), from the list of promising energy sources.

III.5. Energy flux density

Enthusiasts usually compare the solar radiation that falls on Earth, the energy transmitted in the Earth's atmosphere by air mass (wind), the tidal energy or the volume of biomass produced every year by the biosphere with the current consumption of energy by world economy. This comparison may give impression that tremendous resources are available. However, by far not any energy is utilizable and by far not the whole amount of energy can be utilized. One of the most important parameters determining the practical usability of various sources is the density of the transmitted energy flux.

The amount of energy scattered in the surrounding space is indeed enormous. However, how can it be extracted? The history of physics keeps quite a few cunning designs for gaining energy from nothing, which broke against the Second Law of Thermodynamics. Alternative energy sources do not violate this Law. However, the energy they provide refers to the class of low-potential energy, that is, the specific energy density in the unit of energy carrier (energy source) is low. In order to understand what is the difference between the low-potential (abundantly scattered around us) and high-potential (used in conventional energy engineering) energy, it is sufficient to compare, for example, the energy flux of gentle wind blowing or heat flux from gentle sunlight with the concentrated energy flux in a gas turbine combustion chamber or in a nuclear reactor. It is the problem of concentrating scattered low-potential energy, which is operated by all alternative sources, that is the key obstacle for the industrial use of these sources.

III.6. Stability of energy supply

From the standpoint of consumer properties of various sources, the predictability and stability of energy supply are important factors. This is required for the operation of modern science-intensive industry. Otherwise, it is necessary to develop very expensive energy storage systems, the cost of which may happen to be considerably higher than the cost of energy sources themselves. The instability and unpredictability of energy supply is a basic drawback inherent in all alternative sources including hydropower. The dependence on natural, weather and climatic factors precludes the prediction of the amount of energy to be produced and, hence, consumers are forced to reserve facilities based on conventional energy sources, design storage systems, or often both.

III.7. Environmental characteristics of energy sources

Apart from the prime cost of the produced energy, a highly important factor affecting the development of various primary sources is the environmental safety. This factor largely determines the trends of energy engineering and contributions of various sources to the world energy balance. The environmental consequences of traditional energy production based on fossil sources are among the major points of criticism. Whereas the local adverse influence of the modern heat power industry on the environment can be largely overcome owing to gradual transition from coal to natural gas and to more advanced fuel combustion and flue gas purification processes, the global effect of hydrocarbon-based energy on the climate is still the subject of heated debate. The control of greenhouse gas emission and related man-induced impact on the climatic processes was set as a national priority in many countries.

Obviously, the Earth's climate has been changing in recent years; however, despite the huge amounts of investigations and investments in this area, there is still no convincing evidence indicating that it is the man-induced impact (in particular, hydrocarbon-based energy) that is responsible for these changes.[29,30] Moreover, there is quite a substantiated opinion of prominent Russian specialists in climatic processes [31,32] that exactly the growing atmospheric emissions of carbon dioxide caused by energy production in the world made it possible to prevent the global environmental disaster associated with the trend for decreasing atmospheric concentration of CO_2, which is natural for the current geological period, and the consequent threat of global cooling of the Earth's surface down to the complete glaciation. From this standpoint, one can only regret that the carbon period of the history of civilization is too short. In any case, estimates have shown that even the complete utilization of all the hydrocarbon resources of Earth would not raise the temperature of the Earth's surface above the temperature characteristic of warm geological periods that already happened in the history and were distinguished by especially favourable conditions for the development of biosphere.

As regards nuclear energy, currently the possibility and even the necessity of replacing it by alternative sources is debated in some countries (being actively supported by green movements). Meanwhile, nuclear energy is a reliable, technologically mature and cheap source covering a consid-

erable part of the basic consumption of electricity; it is almost free from hazardous emissions, including greenhouse gases, and is perfectly suited for large electric power plants operating in the basic mode within large power networks. Therefore, the vast majority of experts do not doubt the necessity of further development of nuclear power engineering and preserving its considerable proportion in the world energy production.

In its environmental and economic characteristics, the modern nuclear power production is superior over virtually all other energy sources. The prime cost of electric energy production at nuclear power plants (NPPs) is ~ 1 cent per kWh, which is 3 – 4 times cheaper than that for coal-fired thermal power plants. Even the modern combined-cycle gas electric power plants produce three times more expensive energy. A decrease in the cost per unit of installed capacity in NPPs to \$1.1 per kW would decrease the cost of the standard 1000 MW unit to \$1.1 billion. The radioactive contamination level from the usual coal-fired thermal electric power plant is 1000 times higher than that from an NPP of a similar capacity.[33, 34] However, the obvious necessity to develop this branch and its economic advantages do not eliminate the negative attitude towards nuclear energy in some countries. For example, in Sweden where nuclear energy accounts for more than 40% of electric energy production, there are persistent calls for prohibition of nuclear power.

Nevertheless, there is no documentary evidence for a health damage caused by the regular operation of nuclear plants. A typical 1000 MW nuclear power unit produces ~30 tonnes of high-level radioactive waste and 800 tonnes of low- and medium-level waste every year; the volume of the wastes can be markedly reduced by concentrating. For comparison, a 1000-MW coal-fired electric power plant produces annually 320 000 tonnes of ash containing 400 tonnes of heavy metals and radioactive materials to say nothing about the wastes formed during coal mining and transportation. Considering the whole production chain from raw material extraction to electricity generation, nuclear energy production yields 100 times less CO_2 and causes virtually no damage to the environment. Thus, even now, it is possible to reduce the global CO_2 emission by 8% (~0.6 Gtonnes of carbon per year). Certainly, there are some environmental problems associated with the uranium ore mining: the waste rock retains up to 85% of the uranium background radiation, the area is contaminated with hazardous heavy metal salts and is covered with dust with a high content of radioactive elements. The environmental damage caused by uranium mining can be markedly reduced by using *in situ* leaching.

Despite the ambiguous attitude towards nuclear energy of the public of some countries, who demand absolute guarantee of safety, the development of nuclear energy engineering continues and will, beyond doubt, further continue. According to some forecasts, during the period from 2000 to 2050, the energy production by this branch is expected to increase 14-fold. Transition to third-generation reactors and later to fourth-generation reactors, which are now being developed, would increase their robustness and service life and decrease the specific fuel consumption. The most far-reaching plans in nuclear power production are developed by China, Russia and India.

While evaluating a large-scale energy generation, it is necessary to consider the environmental impact of not only material contaminants (greenhouse gases, smoke, aerosols, ash dumps, spent aqueous solutions, radioactive wastes), but also electromagnetic and acoustic fields and thermal contamination. Furthermore, the construction of energy production facilities requires allocation of large land areas, the size of which highly varies depending on the type of energy source. It is evident that analysis of the environmental impact of energy production should include the impact on biotic systems.

For evaluation of consequences of using any energy source, it is insufficient to consider the environmental characteristics of the proper energy production process. It is also necessary to examine the environmental impact of constructed facilities, machines, devices for the manufacture of energy carrier and energy transfer, and industrial production of the materials and equipment involved.[35 – 37] The industrial use of any sort of energy requires the relevant industry branches for raw material extraction and processing and equipment manufacture and later the disposal of outdated or old equipment. This production activity inevitably gives rise to some wastes. Complete elimination of pollution and wastes of any industrial process in any branch of industry requires infinitely large expenditures (Fig. 14).

For specialists, the statement that a completely waste-free production process is unrealistic is trivial; nevertheless, publications often appear that call for manufacturing the products with no waste at all, like Nature does. Actually, in Nature, absolute equilibrium does not exist either and wastes able to cause disasters of planetary scale are also gradually accumulated. The most well-known global disaster was associated with accumulation of oxygen in the Earth's atmosphere as a result of vital activity of the primary oxygen-free biosphere. This led to the death of most representatives of the biosphere ~ 2 billion years ago. However, since there are multitudes of species in biotic systems and, hence, numerous feedbacks formed between them during millions of years, the Nature can maintain a nearly equilibrium state for a long time.

Although in the last decades the scale of technology-related human activity has become comparable with the scales of geological processes, the modern civilization is unable even to approach the diversity and abundance of links between the structures existing in Nature. For implementing the non-waste industry principle, it is necessary to

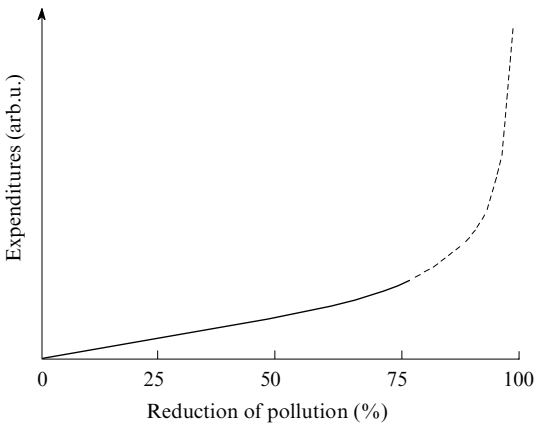


Figure 14. Relative level of expenditures *vs.* achieved reduction of pollution.[37]

connect all the production processes on Earth into a single whole, like in Nature, and to loop all material flows into one giant material-and-energy system. Actually, this would require the replacement of the biosphere by an artificial 'technosphere'. However, all estimates show that due to incommensurability of the number of technically possible links between the 'technosphere' elements with the number of links between the biosphere elements, upon any serious failure, the artificial system will deviate from the equilibrium and collapse.[3,4]

Thus, the manufacture of any energy production equipment is an unavoidable additional source of environmental pollution and the use of even a very clean energy resource is followed by a tail of environmentally problematic processes. Any energy source contaminates the environment to one or another extent and the popular views about environmental safety of renewable sources and their ability to prevent the observed climatic processes do not reflect the reality.

IV. Types and key features of renewable sources

The understanding of the necessity of gradual replacement of fossil hydrocarbon sources and the concern about global climatic changes associated with the conventional hydrocarbon-based energy stimulate the current interest in alternative renewable energy sources. The possibility of more extensive use of these sources in energy production has been actively discussed for more than half a century. The most important are hydropower, solar energy, wind energy, tidal energy, geothermal energy, energy of biomass (agricultural products, household wastes, firewood) and some less significant sorts. The use of renewable energy sources is often identified with a 'new era'; however, in reality, most of these energy generation methods are old and rather well worked out.

If hydropower is eliminated from the above list, since it should obviously be considered separately as one of the earliest and most developed industrial energy sources, recent years have witnessed a vigorous progress in the utilization of renewable sources. The growth rate of energy production from renewable energy sources (RES) was much higher than that from conventional sources, which is not surprising in view of low amount of energy produced from renewable sources so far and low capacity of particular facilities. In the initial stage of utilization of new techniques, the output can be increased rather easily and rapidly. Currently, renewable sources have steadily occupied their position as low-capacity energy sources, local sources and as components of large distributed energy networks.

Nevertheless, according to even the most optimistic assessments, the contribution of these sources (without hydropower) to the global production of primary energy does not exceed 3% (see Fig. 3 *b*). The statements that alternative and renewable energy sources would replace the depleted fossil resources in the near future and would solve the environmental problems of energy engineering, which have appeared in mass media in recent years, are, unfortunately, based on the insufficient understanding of real climatic and geosphere processes. There are also quite a number of publications that are meant to lobby for the interests of certain industrial, agricultural and scientific groups and various environmental movements. In view of the decisive role of energy production in world economy, the enormous expenditures needed to design new technologies and the immense costs of energy infrastructure, it is very important to conceive the real potentials, technological niches and practical prospects of various energy sources.

IV.1. Hydropower

Hydropower is one of the earliest types of energy (suffice it to recall water mills and water drives in the early industrial workhouses), which accounts for ~6% (see Fig. 3 *b*) of the energy produced all over the word. The modern hydropower engineering accounts for the production of 73.5% of energy from renewable sources and ~20% of all electric energy in the world, which is equivalent to the use of almost 900 million tonnes of oil per year. Iceland is the absolute leader in the hydropower production per capita. The contribution of hydropower is also high in Norway, where the proportion of hydroelectric power plants (HPPs) in the electric energy production reaches 98%, and in Canada and Sweden. In Paraguay, 100% of electricity produced in the country comes from hydropower plants.

Since the 2000s, the most active construction of hydropower plants has been seen in China; water is one of the most important energy sources in China, which accommodates up to a half of small hydroelectric power plants of the world and the largest Three Gorges Dam in the river Yangtze with installed capacity of 22.5 GW and a hydroelectric cascade with the highest capacity under construction. Even larger is the Grand Inga hydroelectric dam with a potential of 39 GW, which is planned for construction by an international consortium in the Congo river, Democratic Republic of Congo (formerly Zaire). In Russia, hydropower, like nuclear power, generates ~16% of all electric energy. Currently, world hydropower engineering is rapidly developed, with the capacity being increased by ~2% ever year.

Large HPPs refer to the most cost-friendly electric energy sources. This is due to the fact that most hydropower plants were constructed many year ago and their costs have been completely amortized. For new large plants, the generation costs are in the range of \$0.03–0.04 per kWh. Approximately 5% of the world hydropower potential is implemented in low-capacity plants. The technical potential of small hydropower engineering in the world is estimated as 150–200 GW. The generation cost at small plants (< 10 MW) is estimated at \$0.02–0.10 per 1 kWh, with the lowest cost being inherent in the regions with high-quality water resources. After the pay-off period for the high initial expenditure, the energy generation in a HPP can be even less expensive, because equipment replacement is not usually required for 50 or more years.

The concern about environmental and social problems are the key obstacles hampering utilization of the remaining hydropower potential in the world. The increase in water demand for various purposes can restrict the development of hydropower plants and reduce the volume of water available for the existing plants. When dams are constructed, artificial lakes are inevitably formed, large land areas are flooded (especially in the case of lowland rivers), and thus the environment irreversibly changes. Fields and woods are covered with water and people are evicted from long-inhabited places. For example, the artificial lake of the Krasnoyarskaya HPP (6 GW capacity; one of the ten largest HPPs in the world; maximum water reservoir volume of 73.3 km^3) has flooded 120 000 hectares of agricultural lands

and 13 750 built structures were moved during the construction.[38]

The artificial lakes needed for steady operation of HPPs cause climate changes in adjacent areas over distances of up to hundreds of kilometres and are natural collectors of contaminants. In these lakes, blue-green algae grow and eutrophication processes are accelerated, which deteriorates water quality. The construction of these water reservoirs disturbs ecosystems and natural spawning grounds of fish. The rise of water level upstream of the HPP dam gives rise to swamps, increases soil salinity and changes the adjacent vegetation and microclimate. A vivid illustration of the adverse environmental consequences of HPP construction is the river of Volga, which has turned into a chain of slightly flowing shallow lakes. The energy potential of the river has been virtually exhausted and the Russian sturgeon, which spawned thousand kilometres upstream of the river mouth 100 years ago, almost disappeared.

IV.2. Tidal power plants

Tidal power plants (TPPs) can be considered as a specific type of hydropower plants. The operation of TPPs is regarded as economically feasible for the regions with tidal variation of the water level not less than 4 m. Unfortunately, such regions are few. The design capacity of a tidal power plant depends on the type of tide in the region of construction and the tidal basin volume and area. The major drawback of tidal power plants is that they are constructed only on the sea and ocean shores; furthermore, the TPP capacity is moderate, and tides occur only two times a day.

The experimental Kislogubskaya TPP in the Kola peninsula constructed in 1968, which is the only one in Russia, has been again put in operation after a ten-year idle period. The capacity of this plant is only 400 kW (the tidal rise can reach 5 m). The construction of new TPPs is planned on the White Sea and Sea of Okhotsk shores. At the Mezenskaya TPP (White Sea), it is planned to design the first in Russia 10 MW pilot unit; the TPP fully put in operation can reach a 20 GW capacity. The possibility of constructing a TPP in the Penzhina bay of the Sea of Okhotsk is considered; the tidal rise in this bay can reach 13 m, which is the highest value for the Pacific Coast. This allows for the design of an electric station of up to 90 GW capacity; if this project is implemented, this will be the world largest tidal plant. However, there are few such unique locations in the Earth.

Like HPPs, tidal plants are associated with considerable environmental problems. The construction of a dam increases the tidal amplitude. Even a minor increase in the tidal amplitude leads to considerable changes in the groundwater distribution in the coastal area, increases the flooded area, disrupts the water mass circulation, changes the ice conditions downstream of the dam and so on. Tidal plants also affect the climate, because they change the power potential, velocity and migration area of sea water.

The construction of a tidal dam can also have serious biological consequences: it may disturb the normal salt and fresh water exchange and, hence, change the living conditions of sea flora and fauna. In the basin downstream of the dam, the plant operation will affect the littoral zone — the space between the high water mark covered with water during the tide and the lower mark exposed during the ebb tide. The dam can have an adverse effect not only on the local communities of fish, animals and birds, but also on migrating species. For example, according to estimates of biologists, the construction of the dam in the Penzhina bay will be detrimental for the Okhotsk Sea herring population.

The dam construction in moderate climate regions may give rise to areas accumulating hydrogen sulfide, similar to those in the bays and gulfs separated by natural crests. The Scandinavian fjords with natural crests represent a classical example of hydrogen sulfide accumulating areas.

It is noteworthy that operation of a large (several tens of gigawatt) tidal plant may retard Earth's rotation. This retardation will be very small; however, its environmental consequences are unpredictable.

IV.3. Solar energy

Solar energy is considered as a very promising (perhaps, the most promising) alternative energy source. This is the only primary source of renewable energy getting to the Earth that provides energy for all secondary sources, except for geothermal energy, which does not have a considerable global potential. This resource is enormous: the solar flux that hits the upper boundary of the Earth's atmosphere every year is huge, about 5.6×10^{24} J. This value is $\sim 5\,000$ times higher than the annual energy requirements of the humanity. However, $\sim 35\%$ of this energy is reflected back by the Earth's surface. The rest of energy is spent for heating the Earth's atmosphere, evaporation – condensation cycle in the atmosphere, wave formation in seas and oceans, air and ocean currents, wind and photosynthesis. During all these processes, high-potential solar energy of the ultraviolet and visible ranges is converted to low-potential energy of heated Earth's surface (the average Earth's surface temperature is ~ 20 °C), which is emitted as infrared radiation back to the outer space.

Considerable progress achieved in recent years in the solar energy engineering gives a lot of hope to its followers. Indeed, together with the wind energy, solar energy engineering is a rapidly developing branch of industry (Fig. 15) with annual world capital investment of > \$15 billion. The technological development of this branch reached a level at which it is possible to gain 200 – 600 kWh a year from 1 m^2 of installed solar energy collectors. In 2014, in Europe alone (mainly in the southern part) solar energy collectors generated almost 100 million MWh, and solar-radiation based energy generation all over the world reached 186 mil-

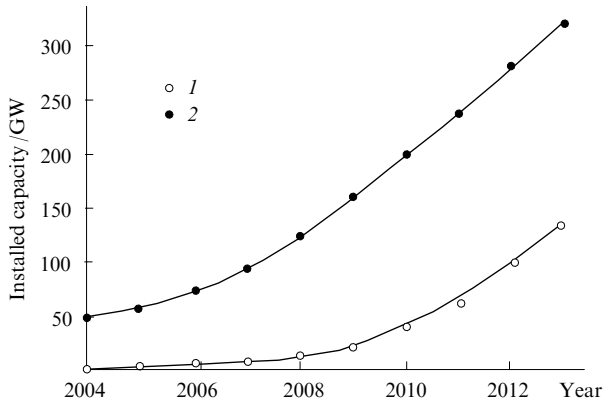


Figure 15. Variation of the installed capacity of solar (*1*) and wind (*2*) power units in the world from 2004 to 2013.[40]

lion MWh. According to data of the EPIA, which is the largest industry association, the total capacity of photoelectric installations reached 179 GW in 2014.[39]

There are two main routes of using solar radiation for energy production:

— photovoltaics (photoelectric converters, photovoltaic cells) based on conversion of solar radiation directly to electricity by means of photoelectric effect;

— thermal solar power generation, which uses solar radiation for heating of a working medium, *e.g.*, water, which then acts as a source of heat or serves for steam generation for steam turbine drives.

In recent years, impressive advances were made in solar energy engineering. Whereas in the late-1960s, the cost of photoelectric panels was ~\$100 000 per kW of the peak (maximum possible) capacity, now they cost < \$2000 per kW. However, as such a panel is connected to a power grid, approximately the same sum must be spent for additional equipment — fittings, converters and connecting circuits. The cost of the produced electricity depends on the solar light intensity. For example, the cost of photoelectric energy in the Mediterranean region is \$0.35 to \$0.45 per kWh. In the most favourable regions with the use of advanced technologies and solar concentrators, the cost of electric energy is in the range of \$0.10–0.15 per kWh. A relevant long-term task is to decrease the cost of electric energy for systems with solar concentrators down to < \$0.05 per kWh.

In the 1980s, the first thin-film photocell was designed on the basis of inexpensive amorphous silicon; this triggered more intensive research related to solar energy. Thin-film silicon cells became leaders in the world market: they accounted for 80% of the sales volume of solar cells. Owing to cheapening of solar panels, the cost of electric energy generation based on photoelectric cells decreased more than 30-fold in 50 years. New ways for decreasing the financial expenditures in this field appear every year. In the period from 2006 to 2008, the consumption of silicon was reduced from 10 to 8.7 g per W of installed capacity due to the use of novel energy-efficient technologies.

Switching to heterojunctions (heterostructures) such as gallium and aluminium arsenides and the use of solar concentrators with a concentration ratio of 50–100 can increase the efficiency from the current 20% to 35%. In 1989, a two-layer cell was designed based on two semiconductors, gallium arsenide and antimonide. The first transparent layer (gallium arsenide) absorbs visible light and converts it to electricity, while the infrared part of the radiation passes through this layer to be absorbed and converted to electricity in the second one (gallium antimonide). As a result, the efficiency was 37%, which is quite comparable with the efficiencies of modern thermal and nuclear power plants.

The recent technological innovations have markedly extended the prospects of solar energy and enabled the construction of rather large energy facilities corresponding to industrial medium-capacity electric power plants. Currently, two types of thermal solar electric power plants are usually constructed — tower plants (Fig. 16) and distributed (or modular) plants.

The thermal solar towers use a receiver with a field of mirrors (heliostats), which ensure energy concentration by several thousand times. The sun rays are reflected from a multitude of mirrors and are concentrated in the receiver located on the central tower. The installation has a complex system for following the Sun by some heliostats based on the computer-controlled rotation of mirrors. The major drawback of the solar power towers is high cost and large area they occupy. A 100 MW solar electric plant requires an area of 200 hectares, whereas a 1000 MW nuclear power plant occupies only 50 hectares.

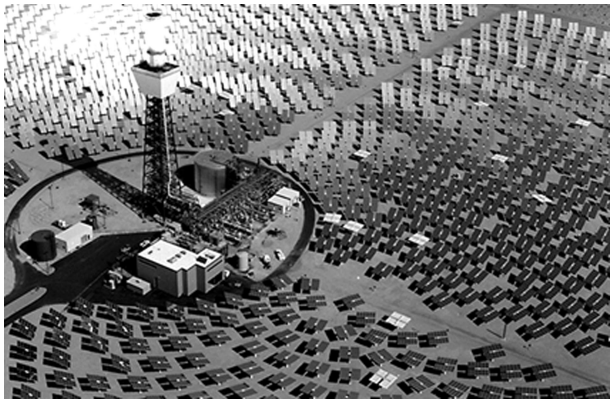


Figure 16. Solar tower electric power plant (https://yandex.ru/images/search?text=солнечные%20электростанции%20картинки).

The distributed solar power plants are composed of a large number of separate modules. Each module consists of a supporting stand with a mounted parabolic concentrator of solar radiation and a receiver located at the concentrator focus and used for heating the working fluid. The heated working fluid is fed to a thermal engine connected to an electric generator. At a moderate capacity, modular type solar electric power plants are more economic than the towers. In the modular solar power plants, linear solar energy concentrators with the highest concentration ratio of ~100 are used most often.

The advantages of thermal solar power plants include the possibility of integration into conventional thermal electric power plants. They can be included, as solar furnaces, into conventional thermal cycles together with the combustion chambers for fossil fuel. However, with the cost of energy from modern solar power plants being \$0.10–0.15 per kWh even under the most favourable conditions, solar energy is still too expensive to compete without subsidies in the domestic markets. Therefore, the research and engineering works carried out today are aimed, first of all, at decreasing the energy cost down to \$0.05–0.08 per kWh and, in the long view, to a level of < \$0.05 per kWh.

Solar energy can also be converted to direct electrical current by means of solar-cell arrays — devices consisting of thin films of silicon or another semiconductor material. Advantages of photovoltaic converters (PVC) are the absence of movable parts and high reliability and stability. Furthermore, the service life of PVC is rather long. They have low weight, are simple in maintenance and can use both direct and scattered solar radiation. The modular design is suitable for installations of almost any capacity, which is very convenient for consumers. The drawbacks of PVC are high cost and low efficiency.

Solar-cell arrays serve for energy supply in the outer space, while in the Earth they are used mainly for up to 1 kW power supply for remote consumers or for radiopositioning and low-duty electronic facilities.

In the United States, which have a top position in solar energy production, several large projects are in progress, based on both photovoltaic conversion of radiation and thermal effect. The largest project, the Ivanpah electric power station in the Mojave Desert, was officially put in operation in 2014 after a long period of construction, testing and development. It includes a system of 300 000 controlled flat mirrors located in a $\sim$16 km^2 area, which concentrate solar radiation to three identical 140 m high towers. In the receivers located in the upper part of the towers, the heat of solar radiation converts water to steam, which is directed to the turbine blades producing electric energy as in usual thermal power plants. According to estimates, this energy should be sufficient for covering the needs of 140 000 households of California. Each tower has a control centre, while the common centre controls operation of the whole system. Each mirror can change the angle and the tilt direction in response to a command from the centre. Every two weeks the mirrors are washed. The whole system comprises 22 million parts. The maximum capacity of the plant is 392 MW and the cost is \$2.2 billion, which is several times more than the cost of thermal plants of the same capacity.

Solar energy engineering is associated with serious environmental problems. Thermal solar electric power plants markedly increase the temperature of the surrounding air. For example, more than 300 000 mirrors of the above-mentioned Ivanpah plant heat the air very much (the receiver temperature reaches 540 °C), which kills the birds flying nearby. During operation of large photovoltaic plants, the surrounding air temperature can be considerably lowered, and this may cause water vapour condensation to form mist and, hence, decrease the transparency of the atmosphere and decrease the efficiency of photoconverters. As noted above, the construction of large solar plants requires land areas measuring tens of square kilometres; therefore, such facilities have to be designed only in deserts. One more considerable problem of solar energy engineering is unfavourable environmental impact of industrial production of the mirrors and especially materials for photovoltaic cells. The manufacture of silicon and arsenides is associated with hazardous chemical processes, and the problem of disposal of these materials has to be solved in the near future.

In view of the foregoing, it cannot be ruled out that Ivanpah would become the last electric power plant of this type. However, the major problems of solar energy production are huge specific capital investments and the complexity of equipment, which much exceed the same characteristics for other sources, and also variability and unpredictability of the amount of produced energy.

IV.4. Wind electric energy

Wind power engineering, which appeared back at the end of the 19th century, has been the most vigorously developing type of renewable energy industry during the last six years, with the annual growth rate being almost 30% (see Fig. 15). By the beginning of 2015, the total installed capacity of all wind generators was 369 GW and the proportion of electricity they generated was 3% of all the produced electric energy. More than 30% of the installed capacity is in China, $\sim$18% is in the US and $>$10% is in Germany. The wind plants, which are mainly represented by offshore installations in the coastal area, cover $\sim$40% of electric energy

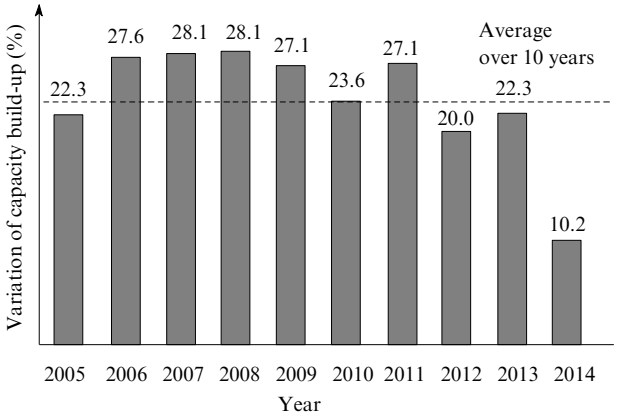


Figure 17. Variation of capacity build-up in world wind energy production (http://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html).

requirements in Denmark, 8.6% in Germany and 1.3% in China. According to the plans for further development of wind energy production, by 2020 the capacity of wind power units in the EU countries alone would reach 180 GW. However, this high rate of growth inherent in the initial stage of exploration of this energy source can hardly be maintained in the future. The regions most appropriate for wind energy units from the geographic and consumer standpoints have already been utilized, which leads to an expected decrease in the rate of development of this type of energy production (Fig. 17).

In the near future, a noticeable technological progress is expected, in particular, development of $>$5 MW turbines (80% of the world wind energy production uses 1.5 – 2.5 MW turbines). The wind generator capacity depends on the area swept by the blades and the elevation above the ground. For example, for a 3 MW turbine, the total height of the wind generator is 115 m: the tower height is 70 m and the rotor diameter is 90 m. A wind generator starts to produce electricity at a wind speed of 3 m s^{-1} and switches off at a wind speed of $>$25 m s^{-1}. The produced energy is proportional to the wind speed cubed; the maximum power is attained at a wind speed of $\sim$15 m s^{-1}.

The most appropriate places for deployment of wind generators are the offshore areas near the coast. However, the cost of their construction is 1.5 – 2 times higher than that for onshore construction. The offshore wind power plants are usually constructed in the sea at a 10 – 12 km distance from the shore. The towers are mounted on the foundations of piles driven to a depth of up to 30 m. The energy of wind, unlike the fossil fuel energy, is almost inexhaustible, accessible and more environmentally benign; however, the construction of wind power plants is associated with some technical and economic difficulties, which hamper the propagation of wind energy production. In particular, the variability of wind flows brings about the problem of uncertain electricity generation. What is most important is that wind energy is one of the most expensive sorts of energy: the average incremental cost of 1 kW of installed (peak) power produced by a large modern wind plant is $\sim$\$1000 ; for an offshore plant this characteristics can be 35% – 100% higher. The cost does not include the potential expenditures for integration with power networks

and manufacture of energy storage facilities. The prime cost of the electric energy produced by the best onshore electric power plants has now decreased to \$0.03–0.04 per kWh. As the average wind speed decreases, the prime cost of electricity sharply increases. The considerable variations of the prime cost of electric energy generated by wind in different countries and regions (from \$0.03 to \$0.20 per kWh) are caused by different power plant designs, scatter of capital investments and average wind speed. The wind energy is not yet competitive in most markets and only preferential tariffs for this sort of energy mitigate the situation.

It is noteworthy that the popular view about the environmental cleanliness of wind energy production is a delusion.[41,42] Indeed, a single wind farm is harmless. However, on going to large-scale generation of electricity, the construction of wind power plants requires considerable land areas; for manufacturing of tens of thousands of wind turbines, it is necessary to establish a new branch of industry (meanwhile, any industrial production is associated with environmental issues). It is necessary to sharply increase the manufacturing of aluminium and/or glass reinforced plastics, and these are fairly hazardous production processes. In the short term, it will be necessary to solve the disposal problem for outdated or old equipment.

Yet another important problem related to the use of wind generators is the strong vibration of supporting parts, which is transferred to the ground. A considerable proportion of acoustic energy (a 250 kW wind turbine creates a 50–80 dB noise) is in the infrasonic range, and this energy has an adverse effect on humans and many animals. As shown by experience of operation of a large number of wind power units in the US, this noise is unbearable by birds and animals, which leave the power plant area, that is, the site of a wind power plant and adjacent areas become unsuitable for living.

In some countries, the operation of wind generators disturbs the TV signal for 1–2 km around the generator, as the blade rotation frequency is close to the frequency of the TV synchronizing signal. Wind generators are also sources of radio interferences. The installations constructed in heavy wind regions (mountain ridges, seashores) can interfere with bird and insect migrations: modulation of the wind flow by the blades creates a sort of regular structures in the air, which hamper the orientation. In Belgium, it has been found that this disturbs the stability of field ecosystems located in the wind installation area, in particular, crop yield decreases.[43] Unrecoverable consequences of the large-scale wind energy production are also possible: air streams would be dissipated and weakened, the wind chart would change, and hence the climatic equilibrium and the heat and moisture transfer would be disturbed.

IV.5. Geothermal energy

Geothermal energy engineering uses the energy contained in the Earth's interior to produce electricity. In the volcanic areas, water that circulates in subsurface horizons at relatively small depths is superheated above the boiling point, rises to the surface along the cracks and, in some cases, bursts out as geysers. The subsurface hot water can be accessed by well drilling.

More frequently encountered are dry high-temperature rocks, from which energy can be derived by water injection and subsequent extraction of superheated water. High rock beds with temperatures of < 100 °C are also located in many geologically low-activity regions; therefore geothermal energy is widely used in many countries.

The geothermal energy is classified into two types: petrothermal and hydrothermal energy.

Petrothermal energy is related to the temperature of the Earth's interior. The average rate of temperature rise with increasing depth is ~ 2.5 °C per every 100 m. At a 5 km depth, the temperature is ~ 125 °C, while at a 10 km depth it is ~ 250 °C. For extracting the energy, two wells are drilled, and water is injected into one well; then water is heated while migrating to the adjacent well from which is comes out as steam. The key problem associated with this type of energy production is low cost-effectiveness.

The hydrothermal energy production is based on utilization of the superheated underground water of natural sources located in many volcanic zones, including the Kamchatka area; Kuril, Japanese and Philippine islands; and vast areas of Cordilleras and Andes. The principal benefit of the geothermal energy is that it is virtually inexhaustible and does not absolutely depend on the environmental conditions, time of the day or the season. Water or a steam/water mixture can be utilized, depending on temperature, for hot-water or heat supply, production of electric energy or simultaneously for both purposes. The high-temperature heat of volcanic regions and dry rocks is preferably used for electricity generation, the plant design being dependent on the applied source of geothermal energy.

Large volumes of underground thermal water are present in the North and South Caucasus, in the Kamchatka area and in some other regions of Russia. By 2006 in Russia, there were 56 explored thermal water deposits with a flow rate of $> 300\,000$ m^3 per day. Twenty deposits are industrially operated; among these are Paratunskoye (Kamchatka), Cherkesskoye and Kazminskoye (Karachay-Cherkessia and Stavropol Territory), Kizlyarskoye and Makhachkalinskoye (Dagestan), Mostovskoye and Voznesenskoye (Krasnodar Territory). Currently, geothermal energy provides for 30% of electricity production in the Kamchatka (Mutnovskaya, Pauzhetskaya and Verkhne-Mutnovskaya geothermal power plants).

An environmental problem arising upon the use of underground thermal waters is associated with the necessity to inject the waste water back to the underground aquifer. Thermal waters contain considerable amounts of salts of various elements (boron, lead, zinc, cadmium, arsenic). The steam contains hydrogen sulfide, ammonia, phenols and radon, which causes radioactive contamination of the environment. The discharge of waste water to rivers leads to thermal pollution and considerable hazard for hydrobionts. At elevated temperature, the dissolved oxygen concentration decreases and is no longer sufficient for many fishes (for example, trout lives only in cold water), while mineral impurities depress aquatic organisms. Therefore, the waste water is injected back into the Earth's interior *via* specially drilled wells. However, the consequences of this operation in the case of large-scale energy production are difficult to predict.

The extraction of a steam/water mixture from wells is accompanied by atmospheric emission of steam and toxic gases; steam, which expands as it gets to the surface, generates a lot of noise. The environmental impact of geothermal power plant operation is easy to follow by

looking at the Pauzhetskaya power plant. Within two or three kilometres from the plant, one can see bare stems (without bark or leaves) of stone birch, and the roar of steam coming to the surface can always be heard far away; meanwhile, the plant capacity is only 12 MW, which is almost five times lower than the capacity of the main turbines of the nuclear-powered icebreaker Arktika.

The potential total capacity of geothermal power plants in the world is lower than the total capacity of most plants based on some other renewable energy sources. However, in view of rather high energy density, the geothermal energy production develops in some regions where fossil resources are either absent or relatively expensive. Unlike the energy derived from oil and coal, geothermal energy does not need to be processed or transported by long distances and comes much cheaper. Currently, the geothermal electricity is generated in 24 countries and the total installed capacity of geothermal electric power plants in the world reached 10.7 GW in 2010.

The geothermal energy engineering continues to steadily develop, although not so rapidly as solar or wind energy engineering. Asia-Pacific countries are leaders in this field; they produce 47.6% of the geothermal energy generated all over the world. North America accounts for 42.3%, and 10% are produced in Europe. However, despite the high and stable rate of development of geothermal energy production, which has existed for more than a hundred years, its real potential is too small to make a significant contribution to world energy.

IV.6. Biomass energy

The use of biomass energy, together with solar energy, is the main expectation of people who hope that energy demands of humanity can be met by means of renewable sources. In many developing countries, a considerable part of household energy requirements is met by combustion of biomass, mainly firewood and agricultural wastes. However, with a global deficiency of food products and permanent degradation of agricultural lands, it is unrealistic that the rapidly growing energy demand of people could be met at the expense of green energy (in essence, agriculture).[44] Certainly, this does not rule out wider utilization of biomass wastes and domestic wastes for energy production. For example, a modern urban district with a population of 100 000 people generates $\sim$40 000 tonnes of solid combustible domestic waste every year; combustion of this waste would provide half of the district residents with hot water and decrease the natural fuel consumption by 10% – 15%.

The technologies of energy production from bio-based feedstock are quite diverse. If we put aside the purely domestic application of wood fuel (firewood or wood pellets, which are made of pressed wood processing chips, *etc.*), then all the plant raw materials actually or potentially applicable for industrial energy production are commonly classified into several generations. The traditional agricultural crops with high contents of fats, starch and sugars were the first to be used. The plant fats are well converted to biodiesel serving as diesel fuel. The plant starches and sugars are processed to ethanol, which can be used in carburetor engines either by itself or as a petrol additive increasing the octane number. However, apart from the problems associated with intensive agricultural production (soil depletion, high cost of soil treatment, watering, fertilizers and pesticides), withdrawal of even a part of food crops from the foodstuff market directly affects the prices of food for people.

The non-edible waste of cultivated crops, grass and waste wood are classified as the second generation of bio-based feedstock. This feedstock can be obtained for lower cost than the first-generation one. However, the costs of harvesting, preparation and processing sharply increase. This feedstock mainly contains cellulose and lignin. They can be directly burnt (like firewood), gasified (to obtain combustible gases) or pyrolyzed to give liquid and gaseous products. The key drawbacks of the second generation bio-based feedstock are large land resources occupied for its production and relatively low output per unit area.

Algae are considered as the third-generation bio-based feedstock; they can be produced without using land resources and may provide high concentration and fast reproducibility of biomass. However, the use of natural water bodies may bring about serious environmental problems because of penetration of artificially produced organisms to the environment. Along with growing algae in open ponds, it is possible to grow them in small bioreactors located, for example, near electric power plants. The rejected heat of thermal electric power plants can cover $>70\%$ of the heat requirements for growing algae.

Currently, the biomass production by cultivation of phytoplankton in artificial water basins constructed at the sea coast is considered in some European countries as a promising trend (fourth-generation feedstock). The subsequent methane fermentation of biomass and hydroxylation of the resulting methane give methanol as a biofuel. The major reason for the use of microscopic algae is high productivity of phytoplankton, up to 100 t ha^{-1} per year. Furthermore, there is no need to use fertile soil and freshwater and no competition with agricultural production.

From the energy production standpoint, the use of this biosystem has substantial economic advantages over other ways of solar energy conversion. However, implementation of such projects is yet hampered by low oil prices.

Biofuels can be solid, liquid or gaseous. Solid biofuels include wood such as firewood (often wood processing waste) or wood (fuel) pellets; liquid biofuels include alcohols (methanol, ethanol, butanol), ethers, biodiesel and bio furnace oil, which are prepared from plant feedstock; gaseous biofuels are various gas mixtures, which consist of methane, carbon oxide, hydrogen and other gases, formed upon thermal decomposition of bio-based feedstock in the presence (gasification) or in the absence (pyrolysis) of oxygen or upon bacterial fermentation of bio-based feedstock.

Apart from agricultural products, ligno-cellulose compounds, which remain after the parts of biological raw materials suitable for food industry have been utilized, can also serve for the production of biofuels. Beside biological fermentation processes, biofuels can be produced by pyrolysis, which converts biomass to a liquid; the liquid can be transported, stored and utilized more easily and less expensively. According to some estimates, with existing technologies, pyrolysis of wastes and waste biomass can cover up to 20% of the demand of Germany for motor fuels; by 2030 with the progress of technologies, this value is expected to increase to 35%, with the production prime cost being <0.80 euros $litre^{-1}$. The liquid products of pyrolysis of such wastes as branch timber, stumps and coniferous tree bark can also be used. The yield of fuel fractions from a tonne of waste wood reaches 100 kg.

One of widely used types of biofuel is biogas, the product of fermentation of organic wastes (biomass), which is mainly a mixture of methane and carbon dioxide. Biomass decomposes under the action of methanogenic bacteria. The fermentation of chicken manure, cattle farm wastes and household garbage may afford biogas, which contains 70% – 80% of methane and can act as a full-scale substitute for natural gas.

In some countries poor in energy resources, for example in India, biogas is widely employed for domestic purposes. Sweden, Germany and other European countries implement projects of conversion of agricultural and wood processing wastes to biogas followed by production of electricity and synthetic motor fuels. Biogas can become a significant additional source of hydrocarbons, because the annual renewable biomass resource in the world is estimated at 200 billion tonnes.

China is the world leader in the use of this sort of fuel. In 2008, there were ~30 million single biogas production units in China, which supplied fuel for ~22% of rural population of the country. The volume of the gas obtained in this way was ~6.5 billion m^3 as of 2005. The significance of this type of waste processing for developing countries is, first of all, in the possibility of gas supply to rural population for heating of their homes and for cooking. In developed countries (for example, in Germany), the most part of biogas is delivered to electric power plants. In recent years, this type of biogas application has also been characteristic of China. For waste disposal, agricultural holdings construct small thermal electric power plants capable of supplying electricity for up to 10 000 flats.

Finally, some microbes, for example, *Botryococcus braunii*, accumulate hydrocarbons (mainly isoprenoids) during the living activity in amount of up to 40% of their total dry mass.

In 2007, the great interest in biofuel initiated a plan of George Bush, the then US President, who proposed that consumption of petrol in the country should be reduced by 20% in 10 years to be replaced by biofuel. This would lead to a 10% decrease in the crude oil consumption in the United States. The Energy Independence and Security Act he signed (EISA, 2007) stipulated the annual production of 36 billion gallons (~100 million tonnes) of ethanol by 2022. Of these, 16 billion gallons (~45 million tonnes) of ethanol had to be derived from a non-edible source (cellulose). During implementation of this Act, more than 200 plants have already been constructed and are producing ~45 million tonnes of bioethanol per year.

The use of bioethanol as a part of automotive petrols is indeed favourable for decreasing the air pollution caused by motor vehicles. Owing to the presence of an oxygen atom in the ethanol molecule, petrol is enriched in oxygen, which contributes to more complete fuel combustion, decrease in the exhaust gas toxicity and particulate content. Moreover, the addition of 10% ethanol, which has an octane number of 108, raises the fuel octane number by 2 – 3 points. However, ethanol is a less 'energy dense' carrier than petrol; the fuel mileage of automobiles that run on E85 (a mixture of 85% ethanol and 15% petrol) is ~75% of the standard fuel mileage. For cars with conventional engines, fuels containing up to 15% ethanol added to petrol are applicable, only specially adapted flexible-fuel cars being able to run on E85 or pure ethanol.

For many years, Brazil where bioethanol is manufactured from sugar cane, has been the world leader in bioethanol production and use as an automotive fuel. The filling stations in Brazil offer E20 or E25 as a conventional petrol (the number shows the content of the ethanol/water azeotrope containing 96% EtOH and 4% H_2O).

Apart from biomethanol and bioethanol, biobutanol is also considered as a prospective biofuel. Biobutanol production started in the early 20th century by means of the bacteria *Clostridia acetobutylicum*, but later the production switched to oil feedstock. Butanol is not corrosive and can be transported *via* the existing fuel infrastructure. It is readily miscible with conventional oil-based fuels, and the calorific value of butanol is close to that of petrol. The possible feedstocks for butanol production include sugar cane, beetroot, corn, wheat, manioc and, in the future, also cellulose.

In Europe, biodiesel based on animal, vegetable and microbial fats is the most popular biofuel. The possible feedstocks include rapeseed, soybean, palm and coconut oils or any other raw oil as well as food industry and cooking wastes. Biodiesel production processes based on algae are being developed.

In 2010, the world output of liquid biofuels reached 105 billion litres (~100 million tonnes), which amounted to 2.7% of the world fuel consumption by road vehicles. The bioethanol production output was 86 billion litres and that of biodiesel was 19 billion litres. According to the data for 2013, the production output of bioethanol decreased, although it consumed 42% of the total corn crop of the United States.[45] The proportion of the US and Brazil in the world ethanol production is ~90%. The top five manufacturers of biofuel are presented in Fig. 18.

Currently, the intensity of research into biomass utilization technologies is very high.[46 – 51] The most rapid progress occurs in the bioethanol production from agricultural wastes[47 – 50] and various types of algae.[51] More extensive utilization of lignin is still an important challenge.[52] Attention is attracted by the possibility to mitigate the human-induced impact on atmospheric processes by means of increasing use of biomass energy[53 – 56] and by extending the range of chemicals produced from bio-based feedstock.[57]

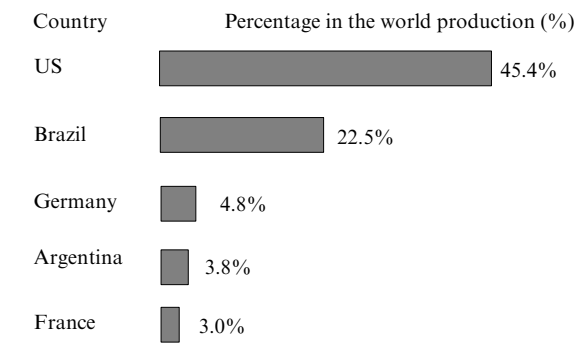


Figure 18. Shares of top five countries in the production of biofuel (IEA data, 2013).

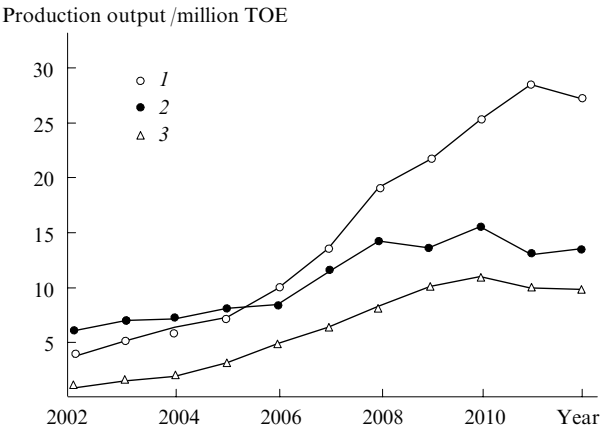


Figure 19. Biofuel production by top producers (IEA data). (*1*) US, (*2*) Brazil, (*3*) EU.

The trend of biofuel production by world leaders can be evaluated from the data shown in Fig. 19. Like for other alternative energy sources, the initial period of vigorous development is followed by the clear trend of decreasing growth rate and even by a decline, which is caused by saturation of the market and, what is more important, by depletion of the physical possibility for economically substantiated building-up of the production output. The world market of biofuel has already reached quite a substantial level, having exceeded $100 billion. According to the Russian Federal Service of State Statistics (Rosstat), the Russian export of plant-based fuels (including those made of straw, oilseed residues, wood chips and wood) exceeded 2.7 million tonnes in 2010. Russia is one of the three top exporters of fuel pellets to the European market, but only $\sim$20% of the produced biofuel is consumed directly in Russia. The potential production output of biogas in Russia is estimated as 72 billion m^3 per year, the possible electricity generation from this biofuel may reach 151 200 GWh and the possible generation of heat is 169 344 GWh. In 2012 – 2013, more than 50 small biogas electric power plants with installed capacity from 350 kW to 10 MW and the total capacity of $>$120 MW were planned to be put in operation in 27 regions of Russia.

The use of biomass on an industrial scale, like the use of any other energy source, has adverse environmental consequences. For example, the desire to increase the area for planting technical crops resulted in eradication of tropical rainforests. In Indonesia and Malaysia, expansion of oil palm plantations for increasing the production of palm oil resulted in clearing of most of forests in the 1980s – 1990s. A similar situation occurs in Brazil where Amazon tropical rainforests, which are often called Earth's lungs, are cleared to make sugar cane plantations.

For intensification of technical crop cultivation, it is necessary to widely use fertilizers and crop-protection agents, and this results in soil biodegradation. The habitats of animals and the microecosystems are destroyed. The practice of bush and peat bog burning for the preparation of agricultural lands and high consumption of fuel by motor vehicles for transporting palm oil made Southeastern Asia one of the world largest sources of greenhouse gas emissions.

One more hazard of using the biomass of technical crops has been noted in the literature: unlike grain crops, poplar, willow, eucalyptus and some other fast-growing plants synthesize pronounced amounts of isoprenoids, which are oxidized by air oxygen to give tropospheric ozone detrimental for health.

IV.7. Hydrogen energy

Among various sorts of alternative energy, so-called hydrogen energy arouses the most enthusiasm. It is the subject of thousands of publications both in mass media and in specialized scientific editions. In some countries, there are generously supported state programmes aimed at organizing large-scale industrial production of hydrogen and at forming the infrastructure for its consumption (in this connection, the term 'hydrogen energy' appeared). This large attention is caused by the commonly accepted view that hydrogen is an efficient and environmentally clean fuel, since hydrogen combustion yields only water and the calorific value of hydrogen, 140 MJ kg^{-1}, is much higher than the calorific values of hydrocarbon fuels (for methane, this value is $\sim$50 MJ kg^{-1}).

However, in reality, everything is not that simple. First of all, it is necessary to recall that hydrogen is a secondary energy carrier, which is virtually absent in the Earth as a fossil resource§ and must be obtained from a more abundant and cheap raw material. Currently, hydrogen is produced on an industrial scale by conversion of the same fossil hydrocarbons, that is, natural gas, coal and oil. The cost of hydrogen production from other sources, in particular, by water electrolysis is several times higher, which rules out their industrial application.[58] However, the development of hydrogen energy production based on natural gas (and other hydrocarbons) as a hydrogen source for solving global environmental problems is hardly reasonable, because the hydrogen production processes are accompanied by evolution of huge amounts of carbon dioxide. Since the contribution of industry-induced CO_2 emission to the greenhouse effect causes concern even now, large-scale switching to hydrogen fuel produced by natural gas reforming or water electrolysis, the energy efficiency of which is markedly less than 100%, would considerably increase the carbon dioxide emission.[59] Therefore, considering a global environmental effect of hydrogen energy production is of no sense. Only local benefits can be gained under specific conditions of densely populated urban areas, and only in the case of acceptable cost-effectiveness of hydrogen production technologies.

Since the electrolysis of water using traditional energy sources must be discarded, as this would require consumption of much more energy than would be obtained on hydrogen combustion, the application of the energy of nuclear power plants in the off-peak load periods is considered as an option. However, electrolysis could become a global industrial source of hydrogen only after the advent of nuclear fusion energy.

Among the methods of economically feasible production of hydrogen from water other than the use of nuclear fusion

§ Hydrogen is present among volcanic gases and fluids related to Earth degassing.

energy, only three methods seem encouraging so far. The achievements of biotechnology and microbiology imply the theoretical possibility of creating microbial strains able to generate hydrogen.[60, 61] However, these research and development works are at an early stage and it is difficult to predict the result. Furthermore, it is just one more version of bioenergy engineering, the prospects and limitations of which have been discussed above.

One more way is to use direct solar electric energy for water electrolysis. This is an interesting approach, but it is associated with considerable difficulties and is unable, in principle, to cover a reasonable part of world energy consumption (see Section IV.3).

Finally, one more approach is the development of photocatalysts that cleave water on exposure to solar light. It can be expected that this approach would be rather efficient, although large-scale industrial application of photocatalysis would require detailed feasibility study. And again, this is a type of solar energy engineering that may prove useful for a local, but by no means global energy production.

The problem of hydrogen transportation from the production site (most likely, equatorial deserts) to the consumption site (middle latitudes) is far from being solved. This cannot be done by conventional gas pipelines, as the hydrogen permeation through microscopic leaks is substantially higher than that of methane; it is known that hydrogen can penetrate even through undamaged metal structures. Probably, it would be necessary to use pipes made of composite materials, the manufacture of which would require large capital investment and a knowingly environmentally harmful manufacturing process. Furthermore, the density of gaseous hydrogen is eight times lower than the density of methane; therefore, the cost of pipeline transportation would be higher by almost an order of magnitude and the pipes should have a three times larger diameter. One should also take into account embrittlement of the metal that is to be used to manufacture compressors and check valves (even in the case of polymeric pipes).

The long-distance pipeline transportation of hydrogen as a cryogenic liquid has now absolutely no prospects from the economic standpoint. The most real liquid sources of hydrogen for transport applications, for example, for fuel cells (FCs), are methanol and dimethyl ether, which can be converted to hydrogen directly on board of the vehicle. G. Olah, laureate of the Nobel Prize in chemistry of 1994, is very enthusiastic about the use of methanol as a liquid hydrogen source.[62] He believes that we are on the eve of methanol-based rather than hydrogen-based economy age. The main difficulty on this route is to design catalysts for methanol synthesis with a nearly 100% selectivity and high operation stability.

Enormous problems are associated with the storage of hydrogen. The storage period of hydrogen even as a cryogenic liquid should not exceed 5 days because of large losses. It is more practicable to store hydrogen as compounds. The US Department of Energy formulated the following key requirements to a hydrogen storage material:

— it should contain at least 6.0 mass % of hydrogen at room temperature;

— the sorption – desorption of hydrogen should be reversible at temperatures not higher than 120 °C;

— the system should be safe and remain in the operating state for at least 5000 charge – discharge cycles.

Currently, there are no solutions that would meet these requirements even roughly.[58, 63]

The sorbents that take up hydrogen *via* physical adsorption cannot meet these requirements because of the nature of the phenomenon. Indeed, in this case, a relatively high content of the adsorbate can be attained only at cryogenic temperatures (77 K). Conversely, in the case of metal hydrides and intermetallic compounds, with high hydrogen contents, high temperatures are required for hydrogen release and binding.¶

This not only complicates the engineering implementation of the idea, but also sharply increases the danger of system application as a whole. It is necessary to find materials with a hydrogen binding energy intermediate between the energies of chemical bond in hydrides and van der Waals bond in adsorbents. Of interest in this respect are metal-doped cage coordination compounds[64, 65] and composite materials based on covalent light metal hydrides.[66, 67]

Finally, one more key problem of hydrogen energy engineering is the disposal of hydrogen. Almost all specialists agree that electric energy should be generated by means of fuel cells, the operation principles of which were discovered by W.R.Grove back in 1839. Over the last 50 years, FCs have been considerably upgraded; they are now installed in various devices such as artificial Earth satellites and submarines. The fabrication of FC demonstration models does not cause serious difficulties. However, the manufacture of economically available FCs that would withstand performance tests for at least 1000 h remains a problem. For several decades past, researchers have been unable to find a cheap and easily disposable material for bipolar plates. In the case of large-scale production, this material must be chemically stable, possess high electrical and thermal conductivities, high strength and so on. In the design of such a material, the following principal questions should be answered:

— how to attach platinum or another metal catalyst to the plate surface, so that it is not deactivated over the whole guaranteed period of operation and not washed away from the surface during operation;

— how to ensure the stability of catalyst operation in the presence of traces of poisons (CO, H_2S and so on);

— what material should be used to fabricate the proton-conducting membrane, the key requirement to which is stability under conditions of hydrogen peroxide formation in the system along with water (recall that H_2O_2 is currently produced by hydrogen oxidation with oxygen in the presence of carbon-supported platinum).

In the solid oxide fuel cells, hydrogen-containing compounds (methanol, methane) can be used as hydrogen sources, but such FCs operate at very high temperature. However, it cannot be ruled out that particularly these cells may be demanded in the future even for transport applications.

Good financing of the research into FCs all over the world (several billion dollars annually) and recruiting of

¶ This statement does not refer to some intermetallic compounds that readily absorb and release hydrogen close to room temperature (*e.g.*, well-known $LaNi_5$). Unfortunately, the hydrogen capacity of these materials is low (approximately 1.5 mass %). Furthermore, additional energy is required for the endothermic process of hydrogen release from hydrides.

highly skilled specialists for this research give hope that efficient and inexpensive FCs for motor vehicles would be devised in the next decade; in any case, these studies are closer to success than those related to the problems of hydrogen production and storage. Currently, FC-based portable power sources and stationary units for hybrid electricity, heat and cold generation systems are already commercially available (ENCE GmbH, Switzerland).

A modern subject of hydrogen energy engineering is to switch road vehicles to electricity and/or hydrogen as an internal combustion engine fuel, which may minimize atmospheric pollution in big cities.

To implement large-scale manufacture of electric vehicles equipped with FCs and electric motors, it is necessary to solve the above-described problems, first of all, to learn how to obtain and transport hydrogen and store hydrogen on board of the car and also to create explosion-proof infrastructure for fuelling the vehicles. Although this is in principle possible, considerable time will apparently elapse until it is possible to manufacture hydrogen-driven vehicles.

The application of hydrogen as a fuel for internal combustion engines, which does not require a high degree of its purification, unlike the FC application, is complicated by the absence of extensive infrastructure and difficulty of hydrogen storage on board of the car. In addition, when hydrogen is used as a fuel, very high temperature develops in the engine cylinders and, hence, the nitrogen oxide concentration in the exhaust gases increases.

As regards battery-driven vehicles, which are already manufactured by some companies, in this case, the emissions of carbon dioxide and other pollutants are merely translocated from the vehicle operation places to the sites of electric power plants. Recall that 85% of electric energy is generated as a result of combustion of organic fuel. Moreover, mass production and the subsequent disposal of car batteries are also associated with serious environmental consequences.

To summarize, it can be stated that the widespread view that hydrogen energy is a matter of the near future is too optimistic. Naturally, research and technological, economic and organizational problems may be overcome with time; however, this may require decades. Hence, the expectation to solve global environmental problems by means of hydrogen energy is unfortunately groundless.

V. Key problems related to the use of renewable energy sources

As noted above, the most important and the only primary source of renewable energy that gets to Earth is the solar radiation energy. All other renewable resources are secondary with respect to this one; they result from conversion of only a minor portion of solar energy, and, therefore, they are inferior to it in the potential. Is at least this, most prominent, source able to solve the world energy problem? Unfortunately not. And here is the reason why.

The total solar radiation energy flux that falls on Earth is $\sim 1.74 \times 10^{17}$ W; the energy flux that passes through a 1 m^2 plane arranged perpendicular to the radiation at the entry to the Earth's atmosphere is 1367 W m^{-2}. This value is called the solar constant. Due to absorption by the Earth's atmosphere, the maximum solar radiation flux at sea level at the equator is only ~ 1000 W m^{-2}. The daily average solar radiation flux through a unit horizontal plane is at least three times lower due to the alternation of day and night and the change of the angle of the sun above the horizon.[4] In the middle latitudes in winter, this value is two times lower. Thus, even at the equator, using very complex and expensive equipment and with virtually limiting efficiency of solar energy conversion attainable to date (30%), only 90 MW can be obtained from a 1 km^2 area. This corresponds to a small regional electric power plant and is 20 times lower than the capacity of a typical industrial thermal electric power plant, not to say about the variability of produced energy throughout the day and the year and, hence, the necessity to have expensive energy storage facilities.

Biofuel-based energy is actually a type of solar radiation energy, which is converted in this case to more convenient sorts of energy by virtue of photosynthesis in green plants rather than using engineering equipment; therefore, it is expedient to evaluate its potential. According to the most modest estimates, ~ 200 billion tonnes of dry green plant biomass (annual primary biosphere product) is formed on Earth every year, which is 20 times more than the total mass of fossil fuels consumed by people. By burning this biomass, it is possible to obtain up to 500×10^{21} J of energy. Meanwhile, the total amount of biomass on Earth is an order of magnitude greater: up to 2×10^{12} g in relation to dry matter.

However, the giant amount of green mass produced by the biosphere does not mean that it can be really utilized in the production activity of people. The main parameters characterizing the Earth's biosphere have been almost invariable for more than 2 billion years after the formation of oxygen atmosphere. This stability is caused by high intensity of biosphere processes in which the material and energy fluxes inside the system are several orders of magnitude more intense than the inward and outward fluxes. According to estimates,[4] people do not violate the equilibrium of the biosphere until they take up $< 1\%$ of the primary biota product. However, even now the consumption of net primary products of the biosphere produced on land as food, fodder and fuel has exceeded 10% and continues to grow. Taking account for real losses, even utilization of virtually all available products of the biosphere cannot cover the short-term energy requirements of people. An attempt to implement such a project would destroy natural ecosystems and violate the equilibrium of global biosphere processes.

Thus, the low density of the primary energy flux (solar radiation on Earth's surface) and low efficiency of conversion of this energy by green plants (on average, somewhat increasing 1%) eliminate any hope for a global role of the renewable green energy. As shown by the results of simulation of global civilization development processes at a current level of energy consumption in developed countries, not more than 500 million people can exist on Earth at the expense of renewable energy sources,[3] and this is more than 10 times lower than the already existing Earth's population.

The key obstacle restricting the possible contribution of the biofuel energy to world economy is the very low density of energy flux resulting from the agricultural production of biofuel (Table 4). In reality, even the presented values are too high, the average optimistic estimate being only 0.073 W m^{-2}, which is $\sim 10\,000$ times lower than the energy of solar rays that fall on the same area.[68] For comparison,

Table 4. Thermal energy flux densities obtained, on average, from unit area per year for various sources of biofuel.[68]

Feedstock	Formal flux /W m^{-2}	Estimate from Ref. 68 /W m^{-2}
Sugar cane	0.37 – 0.47	0.30 – 0.36
Corn-based ethanol	0.141 – 0.264	–
Palm oil	0.29 – 0.627	–
Soybeans	0.043 – 0.073	–
Biofuel on average	0.155	< 0.15

the conversion of solar energy by photovoltaic solar power plants in Spain corresponds to energy with a flux density of ~4.8 W m^{-2}, which is ~40 times higher than the presented estimate. However, the fabrication of artificial photoconversion systems with a capacity needed for industrial energy production is equally unrealistic. This is caused not only by the necessity to withdraw huge areas from economic operations and natural ecosystems (hundreds of thousand square kilometres, which is comparable with the areas of large Western European countries). Also, this would require cosmic capital investments for sophisticated engineering equipment and great amounts of structural materials, the production of which would exceed the economic potential of the world.

If one compares the biofuel-based energy and solar energy from the standpoint of the density of solar radiation flux to be converted, the efficiency of real photovoltaic converters (~25%) does not differ fundamentally from the efficiency of solar energy conversion by some agricultural crops (*e.g.*, corn), which reaches 5% – 7%. However, the agricultural production is much less expensive, although because of low density of the primary energy flux taken up by plants, agriculture is a subsidized activity in most regions of the world. The real solar energy engineering is among the most expensive energy sources and, despite the long-lasting declaratory efforts along this line, it occupies a modest place in the energy balances of even developed countries. Suffice it to note that the above-mentioned world largest solar electric power plant, Ivanpah, is twice inferior in the capacity to only one gas turbine, about a hundred of which are installed every year in the United States alone.

Thus, the low density of energy flux is the most important factor that restricts the potential of all alternative energy sources.† Therefore, it is not surprising that, despite the long-lasting efforts and many-billion expenditures, the contribution of all alternative energy sources, including the solar, wind and biofuel energy, to the energy production output of even technologically the most advanced countries does not exceed 2% – 3%. The low density of the primary (solar) energy flux and low efficiency of solar energy conversion by plants eliminates any hope for a global role of renewable green energy. It is for this reason that agricultural production refers to the least cost-effective (often unprofitable) field of human activity supported by donations from other sources.

Now consider one more highly important characteristics of alternative sources — the energy return (EROEI). In

† This was indicated back 40 years ago by Academician P.L.Kapitsa.[5] Unfortunately, even many specialists still did not hear him.

Table 5. EROEI values for various sources of ethanol and biodiesel.[68]

Feedstock	Most reliable EROEI value
Ethanol	
Sugar cane (Brazil)	5
Corn (US)	1.25
Corn (other countries)	0.18 – 1.48
Biodiesel	
Palm oil	3
Rapeseed oil	1.5
Soybeans	1.43 – 3.54
Wheat (China)	1.09

2006 in the North America and in Europe, the EROEI of the wind energy production was ~20, which promoted its fast development. However, the number of convenient sites for installing wind generators decreases, and this is one of the factors responsible for decreasing the growth rate of wind energy facilities. For biofuel, the situation is much worse. Even for the production of ethanol from sugar cane (the most efficient feedstock for biofuel production), EROEI does not exceed 5. In other cases, this characteristics is close to unity (Table 5, Figs 11 and 13), *i.e.*, the production of biofuel actually cannot be considered to be energy production — this is only redistribution of one sort of energy to another.

The data presented in Table 5 and in Figs 11 and 13 clearly demonstrate why the world energy engineering is based on fossil fuels rather than on solar energy with an EROEI only slightly higher than unity and why biofuels such as bioethanol and biodiesel, the production of which in most countries is characterized by EROEI of only 1.2 – 1.5 (Table 5), would never become a major primary energy source for the automotive transport all over the world. The threshold value of EROEI at which the humanity can still develop is ~3; therefore, the biofuel, as well as solar energy are unambiguously eliminated from the list of prospective global energy sources.

We have considered the physical restrictions of principle that prevent the creation of global alternative energy engineering and cannot be overcome by technological development. However, there are also economic characteristics that directly determine the attraction and, therefore, the rate of development of various fields. These factors are not beneficial for alternative energy sources either. We will consider this in relation to solar energy. As a reason in favour of the future global role of solar energy, the following calculation is often given: the area of large deserts on Earth is ~20 million km^2 (the area of Sahara alone is ~7 million km^2). This area is hit by ~5×10^{16} kWh of solar energy every year. With the efficiency of solar energy conversion to electricity being 10%, it is sufficient to use only 1% of the desert area for deployment of solar power plants to cover the current world energy consumption. This looks convincing at the first glance. However, we will estimate the cost of such project. There is a real example of the above-mentioned world best and largest solar power plant Ivanpah with a peak capacity of 392 MW; the cost of its construction was $2.2 billion, or $5612 per kW of

installed capacity. Since the plant generates energy only in daytime, the real average capacity would be approximately three times lower, that is, only 123 MW. In other words, specific capital investments would be \$17 870 per kW of installed capacity. This is not just expensive, but fabulously expensive! For example, 1 kW costs \$2000 – 4000 at a nuclear power plant and \$500 – 1000 at a thermal electric power plant operating on natural gas, that is, ~18 – 36 times lower; moreover, electricity is generated permanently irrespective of the weather conditions. Furthermore, the cost of facilities of energy storage and transportation over thousands of kilometres from the deserts to industrial consumption regions has not been taken into account. And there are also other drawbacks of solar energy. It is commonly accepted that deserts are the location of choice for solar power plants. However, this brings about very serious problems of solar plant operation related to inevitable dusting and abrasion damage of solar cells, especially during the sand storms; solution of these problems would bring about great expenditures, in particular, for the delivery of freshwater needed to wash the panels from dust into these deserts.

Now recall that the installed capacity of all energy sources on Earth has already exceeded 3.65 TW. If these sources are replaced by solar electric power plants such as Ivanpah located in deserts, their construction would cost \$66 trillion, which exceeds the world GDP in 2010. Moreover, there is a more serious physical restriction: 1% of the desert area amounts to 200 thousand km^2 (one-third of the area of France), and the whole this area would have to be covered by sophisticated engineering facilities. The economy has neither production capacities to manufacture this amount of sophisticated engineering equipment nor feedstock to manufacture the appropriate amount of construction materials. We say nothing about the expected doubling of energy consumption by the middle of this century.

The above reasons demonstrating that there are no grounds for hoping for the global role of solar energy in the world energy balance by no means deny its role as an important source of local energy supply.

Similar reasoning can be presented for wind energy, the major drawbacks of which are the lack of stability of energy production and high cost of wind generators. The offshore wind energy generation is one of the most expensive sources of electricity. The cost of electric energy production at offshore wind power plants varies from \$0.125 to \$0.20 per kWh, although the equipment manufacturers hope for reducing this value down to $<$\$120 per MWh by 2020.

One more problem is still a low unit capacity of wind generators. To reach an installed capacity of 1000 MW corresponding to a typical thermal electric power plant, 660 large wind turbines are required, which occupy an area of 970 km^2. As noted by specialists, even if the wind turbine height is brought to the height of a skyscraper, as few as 13 000 of these giants would be needed to cover the requirements of New York. The rated capacity of a wind power plant is the maximum generation value attained if a heavy wind rotates the blades all the time, but since there can also be calm weather, the actual capacity is not more than 26% of the rated one. Thus, the presented values should be multiplied by four. The construction of wind power plants pays off, on average, 10 years after commissioning, which is economically justified if the annual average wind speed is > 5 m s^{-1}.

VI. Prediction of the development of renewable energy sources

Currently the research and development related to renewable energy sources are rapidly advanced. The installed capacity of wind generators has reached ~370 GW, the total installed capacity of solar energy is ~200 GW, and that of geothermal energy is ~20 GW. The total contribution of renewable sources to the world energy is ~2.5%. Together with the hydropower, the proportion of which in the word energy generation is ~7%, this contribution is ~9.5%.

However, if hydropower, which has a limited potential for further development and which can rather be classified as a conventional energy source, is left aside, the installed capacities of renewable sources, even in developed countries, are incommensurable with the capacity of conventional energy production. Despite the enormous investment to renewable energy, its proportion in the energy balance is still very low. For example, in the energy balance of the US where the investments to renewable energy sources reached almost a half of all budget allocations for the research and development in energy engineering, the proportion of renewable sources is only several percent (see Fig. 2).

Along with the retardation of the growth rate of almost all sorts of alternative energy engineering observed in recent years [69] despite the active support by the governments of some European countries and the United States, an evident decrease in funding for this branch is observed (Fig. 20). Moreover, funding decreases most of all in developed countries, which acted as the driving force of the scientific and engineering development of renewable energy production only a few years ago. Apparently, this is indicative of a gradual saturation of the economically justified market of these technologies, which cannot be further extended even with the help of large state subsidies or preferences given to this branch.

Funding for research and development in the field of alternative energy sources in the United States started to be reduced especially sharply after 2008, when the success of shale gas and shale oil production and the prospects for

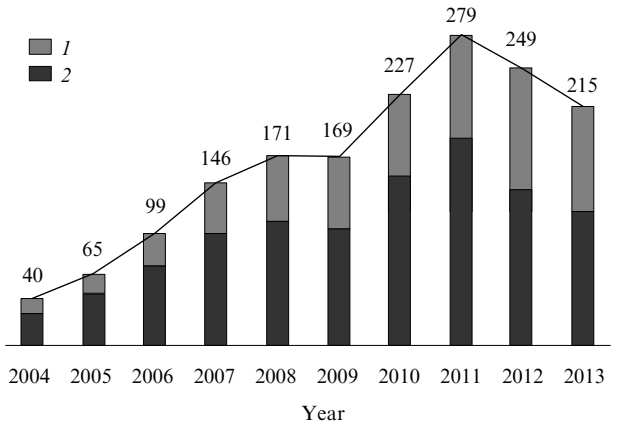


Figure 20. Total investment to renewable energy sources in developing (*1*) and developed (*2*) countries in the period from 2004 to 2013 (billion dollars).[40]

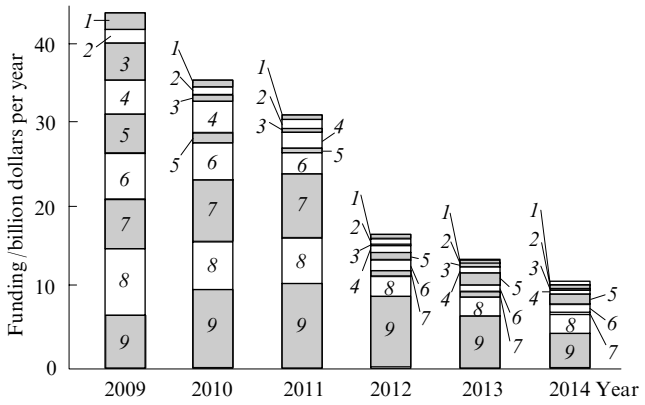


Figure 21. Changes in the funding for particular energy engineering branches in the US after the beginning of large-scale shale gas production.[70]
(*1*) Advanced technologies for fossil fuel, (*2*) nuclear power, (*3*) electric networks and transport, (*4*) high-speed railways, (*5*) electric transport and batteries, (*6*) energy efficiency, (*7*) biofuels, (*8*) multifuel engines, (*9*) renewable energy.

Table 6. Predicted dynamics of contributions of renewable sources and coal to world energy and the US and China energy /GW (DOE data, 2010).

Source	2007	2015	2020	2035
Prediction for the US				
All energy	995	1069	1082	1216
Coal	313	325	326	337
Wind	16	64	64	69
Sun	1	1	1	1
Prediction for China				
All energy	716	1021	1242	1924
Coal	496	625	750	1233
Wind	6	39	63	130
Sun	0	4	6	6
Prediction for the world				
All energy	4428	5005	5740	7009
Coal	1425	1545	1671	2366
Wind	93	277	347	486
Sun	8	45	53	64

meeting the energy requirements of the national economy by means of domestic unconventional types of fossil fuel became obvious. The limited role of renewable sources and the decisive role of the fossil sources for global energy production have long been understood by leading specialists. Therefore, the sharp reduction of federal funding for 'environmentally clean' technologies (Fig. 21) started in the US almost immediately after the beginning of large-scale industrial exploration of shale gas.[70]

It is predicted that in the near future, the proportion of renewable energy sources in the US energy balance would either remain constant or decrease. Even in the EU countries, slow economic growth and budget deficit brought to the forefront the obvious fact that renewable energy sources cannot compete with the traditional energy carriers.[69]

VII. Conclusion

According to forecasts of specialists of the most reputed energy organizations (see the Introduction), in the medium term (25 – 30 years), the production of energy on the basis of all the existing sources will increase. The consumption volumes of crude oil, coal and natural gas will be higher than now, although some redistribution of their contributions to the world energy balance will take place (see Fig. 3). This will mainly be related to a gradual decrease in the proportion of oil with gradual increase in the proportion of natural gas.

The total energy consumption, according to IEA forecasts, will increase every year by approximately 1.6%: from 10 579 million TOE in 2003 to 22 112 million TOE in 2050. This is much slower than the world energy growth rate in 1971 – 2003, which was on average 2.1% a year. Nevertheless, by the mid-21st century the energy consumption in the world will be twice that in the beginning of the century.

It is predicted that by 2035, the contributions of the three major fossil energy sources will be virtually equal, being ~25% for each of them (see Fig. 3); in other words, after ~20 years, the traditional fossil resources will still account for at least 3/4 of the energy produced on Earth. According to the IEA basic scenario, in 2050, too, the proportion of fossil sources will be at least 85%, despite the development of nuclear energy engineering and the use of renewable sources.

Unlike the forecasts made in the beginning of the current century about the future switching of the world energy production to alternative sources, currently the role of these sources is evaluated much more realistically. Even daring predictions of the development of world energy engineering assign a modest role to renewable sources, namely, a level of only a few percent by 2035. According to a DOE forecast, their contribution will be ~6% (Table 6). The BP forecast of 2015 is more optimistic and assigns a contribution of 8% to renewable sources. According to the latest estimates that take into account the trends of the US internal economic policy, it is assumed that this contribution can hardly exceed 3% in the near future.[69]

Thus, at any scenario of the development of world energy engineering, the role of alternative sources will remain modest up to the end of the current century, although certainly their technological development will continue and new applications for them will be opened. The understanding of this fact accounts for the fast change in the energy priorities in the United States and other developed countries.

Without denying in any way the importance and necessity of the development of all accessible energy sources, we have to acknowledge that even the scales of global energy problems and the proposed solutions based on alternative energy sources are incommensurable. The views that renewable sources are able to solve global problems of the humanity and provide for its sustainable development are harmful, first of all, as they draw considerable resources and efforts to unrealistic goals. What is more important, this is an irretrievable loss of time needed for solution of strategically important challenges.

References

1. V S Arutyunov *Neft' XXI. Mify i Real'nost' Al'ternativnoi Energetiki* (Petroleum of the 21th century. Alternative Energy Sources. Myths and Realities) (Moscow: Eksmo, 2016)
2. J W Forrester *World Dynamics* (New York: Wiley, 1971)
3. N N Moiseev, in *Sochineniya* (Works) (Moscow: MNEPU, 1997) Vol. 3, p. 92
4. V G Gorshkov *Fizicheskie i Biologicheskie Osnovy Ustoichivoi Zhizni* (Physical and Biological Foundations of Sustainable Life) (Moscow: VINITI, 1995)
5. P L Kapitsa *Physics-Uspekhi* **19** 169 (1976)
6. G Mao, X Liu, H Du, J Zuo, L Wang *Renew. Sust. Energy Rev.* **48** 276 (2015)
7. N Abas, A Kalair, N Khan *Futures* **69** 31 (2015)
8. P R A Wells *Oil Gas J.* **103** (7) 20 (2005)
9. N A Dobretsov, A E Kontorovich, V V Kuleshov *Herald Russ. Acad. Sci.* **71** 463 (2001)
10. S P Kapitsa *Obshchaya Teoriya Rosta Chelovechestva* (General Theory of Human Growth) (Moscow: Nauka, 1999)
11. M Radler, L Bell *Oil Gas J.* **109** (1) 37 (2011)
12. W L Kelley, D R Harrell, R S Bishop, K Wells *Oil Gas J.* **107** (22) 20 (2009)
13. R Sandrea *Oil Gas J.* **102** (26) 34 (2004)
14. V S Arutyunov, L N Strekova, A L Lapidus, F G Zhagfarov *Gazokhimiya na Sovremennom Etape Razvitiya* (State of the Art of Gas Chemistry) (Moscow: Gubkin Russian State University of Oil and Gas, 2015)
15. L Maudzheri *Sci. Amer.* **301** 56 (2009)
16. G Cohen, F Joutz, P Loungani *Energy Poicy* **39** 4860 (2011)
17. M A Agee, in *Natural Gas Conversion V (Studies in Surface Sciences and Catalysis*) Vol. 119 (Amsterdam: Elsevier, 1998) p. 931
18. V A Skorobogatov, V I Starosel'skii, V S Yakushev *Gaz. Prom-st'* (7) 17 (2000)
19. A Melvin *Natural Gas: Basic Science and Technology* (Bristol, Philadelphia: Adam Hilger, 1988)
20. L M Zor'kin, M I Subbota, E V Stadnik *Metan v Nashei Zhizni* (Methane in Our Lives) (Moscow: Nedra, 1986)
21. T Gold *Zh. Vses. Khim. O-va im. D I Mendeleeva* **31** 547 (1986)
22. B Valyaev *Gaz. Prom-st'* (7) 6 (1997)
23. K G Ione, V M Mysov, V G Stepanov, V N Parmon *Neftekhimiya* **41** 178 (2001)
24. V S Arutyunov, A L Lapidus *Vvedenie v Gazokhimiyu* (Introduction to Gas Chemistry) (Moscow: Gubkin Russian State University of Oil and Gas, 2005)
25. J Yuan, D Luo, L Feng *Appl. Energy* **148** 49 (2015)
26. Yu F Makogon *Gaz. Prom-st'* (5) 10 (2001)
27. K A Kvenvolden *Chem. Geol.* **71** 41 (1988)
28. C A S Hall, J G Lambert, S B Balogh *Energy Policy* **64** 141 (2014)
29. V S Arutyunov *Ros. Khim. Zh.* **45** (1) 55 (2001)
30. V S Arutyunov *Ros. Khim. Zh.* **49** (4) 102 (2005)
31. M I Budyko *Izmeneniya Okruzhayushchei Sredy i Smeny Posledovatel'nykh Faun* (Environmental Changes and Sequential Faunal Shifts) (Leningrad: Gidrometeoizdat, 1982)
32. M I Budyko, A B Ronov, A L Yanshin *Istoriya Atmosfery* (History of the Atmosphere) (Leningrad: Gidrometeoizdat, 1985)
33. D A Krylov, V A Ovseichuk, G P Sidorova *Energiya: Ekonomika, Tekhnika, Ekologiya* (5) 2 (2015)
34. D A Krylov, G P Sidorova *Energiya: Ekonomika, Tekhnika, Ekologiya* (12) 2 (2015)
35. G V Lisichkin, in *Okhrana Sredy Obitaniya: Mify i Real'nost'. V Vserossiiskaya Konferentsiya 'Khimiya pod Znakom Sigma'* (Habitat Protection: Myths and Reality. Vth All-Russian Conference 'Chemistry Under the Sign of Sigma', Omsk, 2016) p. 3
36. E N Sosnina, O V Masleeva, E V Kryukov *Teploenergetika* (8) 3 (2015)
37. G V Lisichkin *Ros. Khim. Zh.* **41** (1) 78 (1997)
38. Yu I Vinokurov, A T Zinov'ev, K M Epishev *Polzunovskii Vestnik* (4/2) 47 (2011)
39. A M Usachev *Naukovedenie* **7** (4) (2015). DOI: 10.15862/10EVN415
40. *Renewable Energy Trends in 2013. Chem Views Magazine* 02.09.2014. DOI:10.1002/chemv.201400087
41. J G McGowan, A L Rogers, J F Manwell *Wind Energy Explained: Theory, Design and Application* (London: Wiley, 2009)
42. B V Ermolenko, G V Ermolenko, M A Ryzhenkov *Teploenergetika* (11) 72 (2011)
43. E N Sosnina, O V Masleeva, G V Pachurin *Ekologiya i Prom-st' Rossii* (9) 8 (2013)
44. V S Arutyunov *Ros. Khim. Zh.* **51** (6) 94 (2007)
45. I Medvedkova, T Trudaeva *MOSTY. Analitika i Novosti o Torgovle i Ustoichivom Razvitii* **6** (3) (2013)
46. N Sarkar, S K Ghosh, S Bannerjee, K Aikat *Renew. Energy* **37** 19 (2012)
47. A Gupta, J P Verma *Renew. Sust. Energy Rev.* **41** 550 (2015)
48. R Parajuli, T Dalgaard, U Jorgensen, A P S Adamsen, M T Knudsen, M Birkved, M Gylling, J K Schjorring *Renew. Sust. Energy Rev.* **43** 244 (2015)
49. S K Maity *Renew. Sust. Energy Rev.* **43** 1427 (2015)
50. S K Maity *Renew. Sust. Energy Rev.* **43** 1446 (2015)
51. T Suganya, M Varman, H H Masjuki, S Renganathan *Renew. Sust. Energy Rev.* **55** 909 (2016)
52. A J Ragauskas, G T Beckham, M J Biddy, R Chandra, F Chen, M F Davis, B H Davison, R A Dixon, P Gilna, M Keller, P Langan, A K Naskar, J N Saddler, T J Tschaplinski, G A Tuskan, C E Wyman *Science* **344** 709 (2014)
53. E Tvinnereim, E Ivarsflaten *Energy Policy* **96** 364 (2016)
54. N L Panwar, S C Kaushik, S Kothari *Renew. Sust. Energy Rev.* **15** 1513 (2011)
55. C O Tuck, E Perez, I T Horvath, R A Sheldon, M Poliakoff *Science* **337** 695 (2012)
56. S K Rose, E Kriegler, R Bibas, K Calvin, A Popp, D P van Vuuren, J Weyant *Climat. Change* **123** 477 (2014)
57. M Besson, P Gallezot, C Pinel *Chem. Rev.* **114** 1827 (2014)
58. T Abbasi, S A Abbasi *Renew. Sust. Energy Rev.* **15** 3034 (2011)
59. B M Bulychev *Ros. Khim. Zh.* **50** (6) 3 (2006)
60. A A Tsygankov *Ros. Khim. Zh.* **50** (6) 26 (2006)
61. P A M Claassen, T De Vrije *Int. J. Hydrogen Energy* **31** 1416 (2006)
62. G A Olah, A Goeppert, G K S Prakash *Beyond Oil and Gas: The Methanol Economy* (Weinheim: Wiley-VCH, 2006)
63. G Q Ning, F Wei, G H Luo, Q X Wang, Y L Wu, H J Yu *Appl. Phys. A* **78** 955 (2004)
64. S N Klyamkin, E A Berdonosova, E V Kogan, K A Kovalenko, D N Dybtsev, V P Fedin *Chem. Asian J.* **6** 1854 (2011)

65. S N Klyamkin, S V Chuvikov, N V Maletskaya, E V Kogan, V P Fedin, K A Kovalenko, D N Dybtsev *Int. J. Energy Res*. **38** 1562 (2014)
66. S P Malyshenko, S V Mitrokhin, I A Romanov *J. Alloys Compd*. **645** 84 (2015)
67. S Mitrokhin, T Zotov, E Movlaev, V Verbetsky *J. Alloys Compd*. **580** 90 (2013)
68. C de Castro, O Carpintero, F Frachoso, M Mediavilla, L J de Miguel *Energy* **64** 506 (2014)
69. M Shein *Neftegazovaya Vertikal'* (1 – 2) 6 (2017)
70. P E Lewis, M J Economides, O Ajao *Oil Gas J*. **110** (10) 30 (2012)