MSc Program
Renewable Energy Systems

Hydrogen Sulphide in the Black Sea – an Alternative New Energy Source for the Local Countries. Based on the Renewable Energy for Transport Research Made for the Bulgarian Seacoast Municipality of Burgas

A Master's Thesis submitted for the degree of
"Master of Science"

Supervised by
Em.O.Univ.Prof. DSc
Venko Beschkov

Ing. Anton Tsenov BSc

Student-ID 09356708

11. October 2017, Vienna

TU WIEN

CONTINUING
EDUCATION
CENTER

Affidavit

I, Anton Tsenov, hereby declare

1. that I am the sole author of the present Master Thesis, "Hydrogen Sulphide in the Black Sea – an Alternative New Energy Source for the Local Countries. Based on the Renewable Energy for Transport Research Made for the Bulgarian Seacoast Municipality of Burgas",
   171 pages, bound, and that I have not used any source or tool other than those referenced or any other illicit aid or tool, and
2. that I have not prior to this date submitted this Master Thesis as an examination paper in any form in Austria or abroad.

Vienna, ________________ ______________________________

Date Signature

Preamble

Idea → Innovation → Revolution

I devote this work to my Russian grandfather Univ. Prof. DSc. Vasilij Grigorievich Kirkin (1904 - 1979). In his lifetime known as "The man who moved the houses", he had been combining in his inventions the forces of nature with the technology. Already in 1937, according to the first building´s moving technology developed and patented by him, a large residential block was moved in a 53 meters distance from its original location. The building of the Moscow District Administration Council was the next, followed by a 100 years old historical house of a hospital. More than 30 buildings, still standing on their "new" locations, were relocated in Moscow in accordance with Prof. Kirkin's method.

Acknowledgements

I would like to thank my supervisor Prof. Venko Beschkov for supporting, advising and guiding me and for the opportunity given to me to work with him on his inventions and innovations. All, in the second part of this work described experiments have been carried out by a team of Bulgarian researchers led by prof. Venko Beschkov from the Institute of Chemical Engineering belonging to the Bulgarian Academy of Sciences in Sofia. With this master thesis, I would like to popularize their research and development activities at such a significant area as new energy sources and environment protection. At the same time, I would like to thank to all the team members: Assoc. Profs. Elena Razkazova-Velkova, Ljutzkan Ljutzkanov and Martin Martinov, Nadezhda Dermendzhieva, Polina Panajotova, Stefan Stefanov and prof. Venko Beschkov, for the honour of having presented and used their experimental results in this work.

I am grateful to my father Vitko and my mother Olga for their unconditional standby and for the inspiration to work on this topic as well as to my brother Nikolaj for his financial support enabling my participation at the master program “Renewable Energy Systems”

I would also like to thank my wife Diana and our two children, Jana and Nikolaj, for their great support, understanding and patience without which not only the creation of this master thesis, but my entire studies would not have been possible.

Abstract

The author has divided his master thesis into two parts. In the first part is carried out an analytical and comparative research of three possible renewable energy sources (RES) for transport in the city of Burgas, a municipality on the Bulgarian Black Sea coast. Biomass, photovoltaic and wind power plants are analyzed and compared from the economic, energetic and ecological perspectives. Some innovations of the Vienna University of Technology are shortly mentioned in this connection. Based on the obtained results, in the second part of the work is presented the big potential of an innovative technology for utilization of hydrogen sulphide (H2S) from the Black Sea waters as a new energy source for electricity generation and production of hydrogen. The positive side effect of this innovation is cleaning of the seawater from the poisonous substance. A team of researchers from the Bulgarian Academy of Sciences led by Prof. Venko Beschkov, with the financial support from the BS–ERA.NET program, organized by the European Commission, successfully realized his idea of directly converting of the energy stored in the H2S into electricity. The innovation, born after many years of scientific research and experimental development work, called Sulphide Driven Fuel Cell (SDFC), uses seawater containing H2S as a fuel in an efficient and ecological way. The innovations, the progress of research and its realization made by the Bulgarian scientists as well as the future works and perspectives in this area are presented and analyzed in the second part of this thesis.

Table of contents

1 INTRODUCTION

The global development of the economy, industry and transport in the last century was mainly associated with the use of energy from fossil fuels such as coal, oil and natural gas. The technologies used for the production and use of final energy products (technologies that exist even today) have been leading to global pollution, respectively increasing of the greenhouse effect and a following global warming. The constant race to achieve maximum profits in the utilization of natural fossil resources, combined with the massive deforestation has led to major natural disasters - prolonged droughts in some regions and massive rains and floods in others.

In the last 20-30 years is being discussed more and more often about impending environmental disasters if the approaches of extracting and using of fossil energy sources get not fundamentally rethought and changed. It has begun with the realization of energy-saving so-called green environmental technologies and a gradual replacement of fossil fuels with renewable energy sources such as wind power, solar radiation, biomass, geothermal etc. The use of fuel from RES like biodiesel (BD), bioethanol and “green” electricity has been reducing the negative environmental impact already. Unfortunately, the technologies available now a days don´t allow the completely substitution of the fossil fuels yet. In addition, the rebound effect neutralizes the effect of more efficient engines and less fuel consumption by more driven kilometers and vehicles on the road.

The first part of this work analyses three different technologies for transport energy production - biodiesel, photovoltaic and wind power plants, from technical, energetic, ecological and economic points of view. It attempts to define the most suitable technology respectively a combination of technologies for the selected municipality of Burgas, a city on the Bulgarian´s Black Sea cost.

In the second part, following the negative Net Present Values (NPV) of all three reviewed technologies, a transition has been made to a new renewable energy source with a huge economic and environmental potential, namely Hydrogen Sulphide (H2S), existent in enormous amounts in the deep waters of the Black Sea. The prehistory of utilizing of H2S and the innovation of directly producing of energy from the marine water containing H2S in Sulphide Driven Fuel Cells (SDFC), the progress of research and its realization made by the Bulgarian scientists as well the future works and perspectives in this area are presented and analyzed in the second part of this thesis.

In the first part of the work, a small biodiesel plant with production capacity of 15.000

tones/year and photovoltaic and wind plants with equivalent capacity are compared with a large biodiesel plant with production capacity of 200.000 tones/year and respectively large photovoltaic and wind plants with similar energy output. The goal is to assess the energetic and ecological performance as well as the economics of the various renewable energy technologies for providing transport energy from the small and large-scale systems.

In order to make the energy outputs of the above-mentioned technologies comparable, they have to be brought to a common denominator such as the service output, which in the case of transport will be the energy consumption per driven kilometres. Being seen from this perspective, it means that with the energy produced by each technology should be covered the same amount of kilometres.

From technical point of view, the three technologies will be reviewed and the most appropriate will be chosen according to the specific requirements.

For the energetic evaluation, following questions have to be answered:

- How many litres of BD/100 km and in kWh/100 km are necessary to run a diesel car?
- How many kWh electricity per 100 km are necessary to run an electric vehicle?
- How much electricity must the PV and the wind power plant produce per year to supply the same number of vehicles as the BD plant? What is the corresponding capacity of the PV and the wind power plant?

For the municipality of Burgas were made following assumptions:

- Solar insolation: 1.450 kWh/m² [23]
- Full load hours wind about 2.000 h/y
- Efficiency of diesel car: 25%
- Efficiency of electric vehicle 85% (incl. battery losses)

In ecological aspect, the technology with the lowest environmental impact has to be selected. The questions to be answered here are:

- What are the greenhouse gas savings by each technology?
- Small or large-scale plants are more appropriate?
- Which technology or combination is most suitable for the selected region?

In the economic analysis, following questions will be examined:

- Which technologies are the most economic for the chosen municipality?
- Small or large-scale production is most cost effectively?

In the last section of the first part of this thesis by breaking down the research outcomes will be given concluding answers to following questions:

- Which is the most economic technology?
- Which technology achieves the best ecological results?
- Which technology is most appropriate for the region regarding the climate conditions?
- Which technology or mix of them could be the best solution for the municipality of Burgas?
- What benefits will be achieved with the implementation of the chosen technology?

This research is especially interesting to be made for the municipality of Burgas. It is the third biggest city Bulgarian´s with a population of over 200.000 inhabitants. Burgas is located on the Black Sea cost and due to its green infrastructure, technologies and quality of live it has been explained for the sixth time in sequence for the most livable city in Bulgaria. In 2014 the company “BurgasBus” [60], owned by the municipality of Burgas, obtained 67 new “Solaris” buses with diesel and gas engines and 22 new “Scoda” trolleybuses. The local government has been continuing the implementation of green technologies and further environmental improvements.

2 ASSESSMENT, ANALYSIS AND DISCUSSION OF THE SELECTED BIOMASS ENERGY CARRIERS FOR TRANSPORT

2.1 Method of approach

Three different technologies intended for transport fuel production, such as producing of biodiesel and electricity generation by photovoltaic and wind power plants will be overviewed in the first part of this work.

To be able to compare all these technologies they have to provide the same service output with the amount of energy produced by each technology.

In order to define how many kilometers could be driven with the produced energy and respectively how many cars, the fuel consumption per 100 km has to be calculated.

Depending on the various technologies, different type of transport fuels will be produced – on one hand biodiesel as a transport fuel from the biodiesel plant and on the other electricity from the photovoltaic and the wind power plants.

In the combustion engines biodiesel is used as a fuel and the consumption is measured in liter per 100 km. The electrical vehicle uses electricity as fuel and the consumption is given in kWh per 100 km. To be able to make a comparison between these different technologies the fuel consumption will be measured in the same unit namely kWh per 100 km.

For the comparison have been chosen a small-scale biodiesel plant with production capacity of 15.000 t/y and a large-scale biodiesel plant with capacity of 200.000 t/y, photovoltaic and wind power plants with the same potential will be taken into account. To compare them the unit tones per year will be converted into the unit kWh per year.

The density of biodiesel is between 860-900 kg/m^3 [1] and the energy content is 37 MJ/kg by weight or 33 MJ/l by volume [2]. The following calculations are based on the value of 900 kg/m^3 or 0,9 kg/l for the density of biodiesel and on the value of 37 MJ/kg for its energy content. Converting the MJ into kWh leads to an energy content of the biodiesel of 10,28 kWh/kg.

Accordingly to the given data the efficiency of a diesel car is 25% and this one of an electrical car is 3,4 times more namely 85% (incl. battery losses). This means that the biodiesel plant should have 3,4 times more energy output in order to have similar driven distances with both engine technologies. Accordingly the small scale biodiesel plant with its 15.000 t/y will produce fuel with energy content of 154,2 GWh. Following this result the photovoltaic (PV) or wind power plant have to deliver 45,35 GWh only. Respectively in the case of large scale plants following values for energy production were calculated – 2.056 GWh (biodiesel plant) to 604,7 GWh (PV or Wind).

For better visualization of the comparison a vehicle with both engine configuration diesel and electrical should be selected. For example, the French automobile producer Renault offers the model Kangoo in both modifications. According the technical characteristics [3] the combined energy consumption for the electrical model Renault Kangoo ZE is 15,5 KWh/100 km. The fuel consumption of the diesel version Kangoo Energy dCi 75 is 4,3 l/100 km. After converting the fuel consumption of the diesel engine in kWh by multiplying the energy content of biodiesel (10,28 kWh/kg) with the specific weight or density of biodiesel (0,9 kg/l), the energy consumption of 39,78 kWh/100 km was calculated for this engine version. Here also should be taken into account that by using of biodiesel as a fuel the engine consumption gets higher by approximately 15% in comparison with using of conventional diesel fuel [4]. On this way, the final energy consumption of this engine driven with biodiesel would be almost 46 kWh/100 km. These results show that the efficiency of the electrical engine of Renault Kangoo is triple higher than the efficiency of the diesel version.

As result, the calculated efficiency and consumption seem to be quite realistic approach for achieving a technology comparison at the given state of technology.

The ecological appraisal will be given through the life cycle assessment (LCA) which considers the whole life cycle of the biodiesel as a product from the cultivation of the land to the final product as shown in the Figure 1 below.

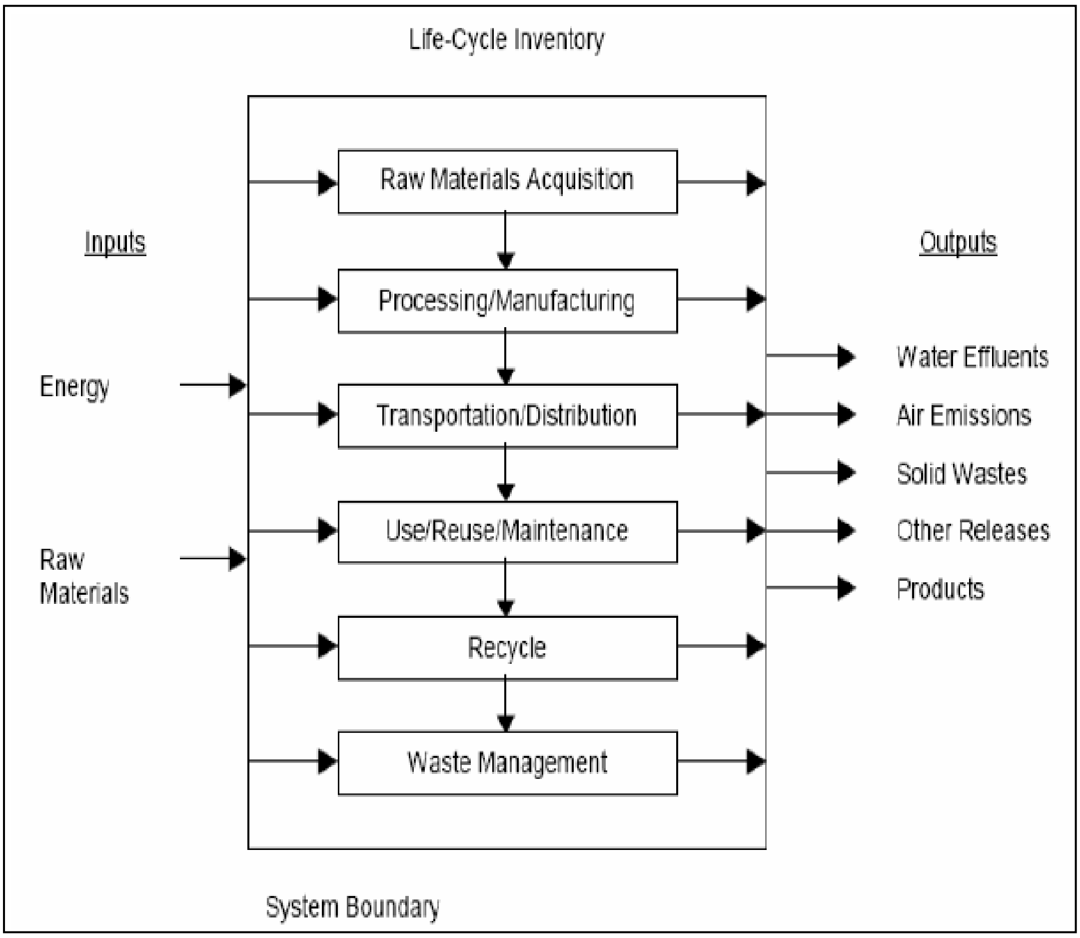


Figure 1. System boundary and main steps and flows of a LCA [8]

By means of various literature sources will be determined the greenhouse gas [GHG] savings potential of the technology within the small and large-scale biodiesel production plants. At the final part of the work, the results from the LCA of the biodiesel production technology will be compared with the other both transport fuel production technologies (PV and Wind). Their ecological impact and a final conclusion about the environmental consequences by each technology and size will be carried out.

The economical evaluation requires certain inputs on the cost and performance of the project in order to assess the economic attractiveness. For biodiesel production technology all appropriate categories of capital, operating and replacement costs, as well as the production terms, required to calculate the cost and the performance values are needed for the analysis. Under consideration of all investment and operation and maintenance (O&M) costs the Net Present Value (NPV) – the financial value of a project under certain financing conditions right before the time of investment will be calculated. The investment shall be done if the NPV is positive, which means that the future cash flows are higher than the invested capital.

Comparing the three technologies for fuel production (Biomass, PV and wind power) by having the same driven distance with the transport fuel produced by each plant, the main factors will be the investment costs and the resulting fuel costs of each technology.

The most of the costs of biodiesel are covered by the raw material prices, namely between 70 and 80% [4]. Thus, selecting of the proper feedstock has a big influence on the achieved margin and competitive position to the other technologies.

2.2 Technological overview and description of the selected / proposed applications/ installations

Biodiesel, also known as fatty acid methyl ester (FAME) is an alternative fuel for cars, which is extracted of transesterified fatty acids. Transesterification is the most common producing technology for biodiesel. Typically, these are esters of methyl, ethyl and higher alcohols derived from triglycerides, the main components of pure vegetable oil like rapeseed oil, sunflower oil, soybean oil and the like. During transesterification the oil reacts with a low molecular weight alcohol like methanol or ethanol by mixing with a certain catalyst (the most common catalyst is NaOH (caustic soda), but also KOH (potassium hydroxide) is used). By properly processing, a qualitative biodiesel can also be produced from used cooking oil (UCO) or animal fat. Although some types of diesel engines can work with pure vegetable oil, if it is transformed into biodiesel it could be used in almost all diesel engines including high-performance engines with direct injection. Biodiesel can also be used in blends with mineral diesel fuel. The blends indicator is the letter B followed by the percentage of mixture. For example, B100 means pure biodiesel and in B10 there is a 10% biodiesel added. Biodiesel as a 7% blend with fossil diesel fuel is now permitted within EN590 (2014) mineral diesel specification in Europe [6]. All diesel vehicles sold on the European market are designed to work with B5 biodiesel.

Important factors in the biodiesel industry are the cost of raw material, the production cost of biodiesel, the price of fossil fuels and the taxation of energy products. Unfortunately, the last mentioned factor still remains a big obstacle for the developing of the biodiesel industry in Bulgaria – there are no subsidies like in other EU countries.

Furthermore, the biodiesel producers there have to pay the same taxes as the fossil fuel ones. However, the main price building factor of biodiesel as a final product are the raw material costs. In the case of vegetable oils, they are between 70 and 80%. Figure 2 shows the high percentage cost of feedstock on total in the EU and USA.

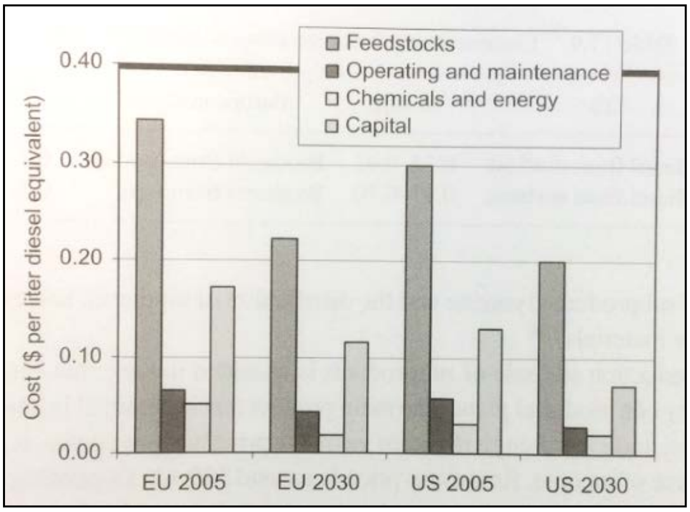
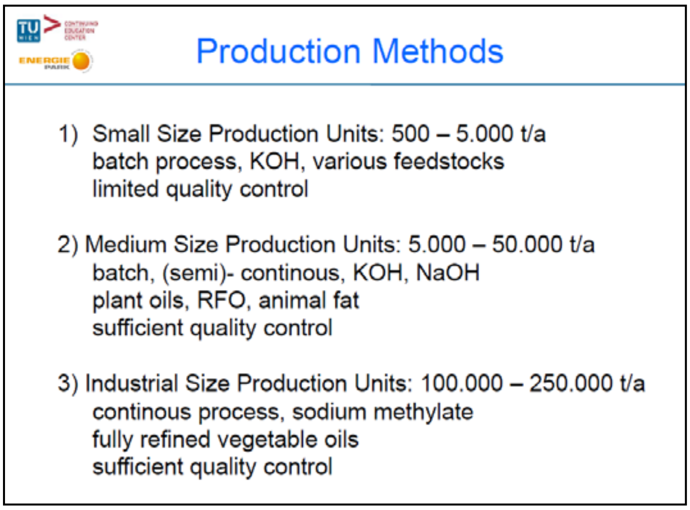


Figure 2. Production costs of biodiesel in the EU and USA [7]

Besides the proper feedstock, also the production technologies chosen for the small and large-scale biodiesel plants pay important role in the economic and ecological performance. According to the lectures of professor Mittelbach there are three production technologies available (Figure 3).



Production Methods

1) Small Size Production Units: 500 – 5.000 t/a
batch process, KOH, various feedstocks
limited quality control

2) Medium Size Production Units: 5.000 – 50.000 t/a
batch, (semi)- continous, KOH, NaOH
plant oils, RFO, animal fat
sufficient quality control

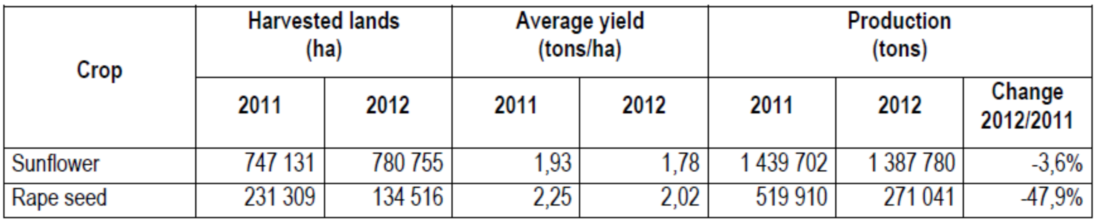
3) Industrial Size Production Units: 100.000 – 250.000 t/a
continous process, sodium methylate
fully refined vegetable oils
sufficient quality control

Figure 3. Production technologies for biodiesel [5]

For the small-scale biodiesel plant with production capacity of 15.000 t/a the batch process will be chosen as it is the simplest production method which is used in lower capacity plants with feeding of different quality. The advantages of the batch process are the low investment costs and higher flexibility. For the large-scale biodiesel plant with production capacity of 200.000 t/a the continuous reactors will be chosen. This process provides greater consistency, security and quality and better sub process options such as separation and glycerin purification [4].

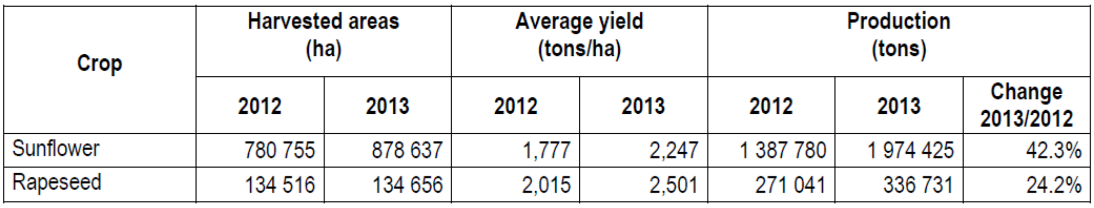
In order to make the right decision for the proper feedstock the last available Bulgarian agrarian reports (2013 and 2014) for sown and harvested sunflower and rapeseed (Table 1, Table 2) were taken into consideration. The main oil crops growing in Bulgaria are rape and sunflower. In the region of Burgas, the total area sown with rape is about 13.000 to 14.000 ha. The whole Bulgarian south east region, part of which is Burgas, has over 32.500 ha sown with rape (the third biggest rape area in Bulgaria) with average yield of about 2,5 t/ha. Sunflower cultivation is not typical for this region of Bulgaria [10]). The rape yield in 2012 decreased with almost 42% and remained on this level in 2013. On the other hand, the average yield of rape in t/ha is ca. 15% higher than for sunflower.

Table 1. Production of oil seed crops in 2011 and 2012 [9]



Crop	Harvested lands (ha)		Average yield (tons/ha)		Production (tons)		
	2011	2012	2011	2012	2011	2012	Change 2012/2011
Sunflower	747 131	780 755	1,93	1,78	1 439 702	1 387 780	-3,6%
Rape seed	231 309	134 516	2,25	2,02	519 910	271 041	-47,9%

Table 2. Production of oil seed crops in 2012 and 2013 [10]



Crop	Harvested areas (ha)		Average yield (tons/ha)		Production (tons)		
	2012	2013	2012	2013	2012	2013	Change 2013/2012
Sunflower	780 755	878 637	1,777	2,247	1 387 780	1 974 425	42.3%
Rapeseed	134 516	134 656	2,015	2,501	271 041	336 731	24.2%

The prices for both crop cultures (Table 4, Table 5) are moving in the same area of about 650-700 BGN[1].

---

[1] BGN (Lev) - Bulgarian currency, 1 € = 1,95 BGN, (author)

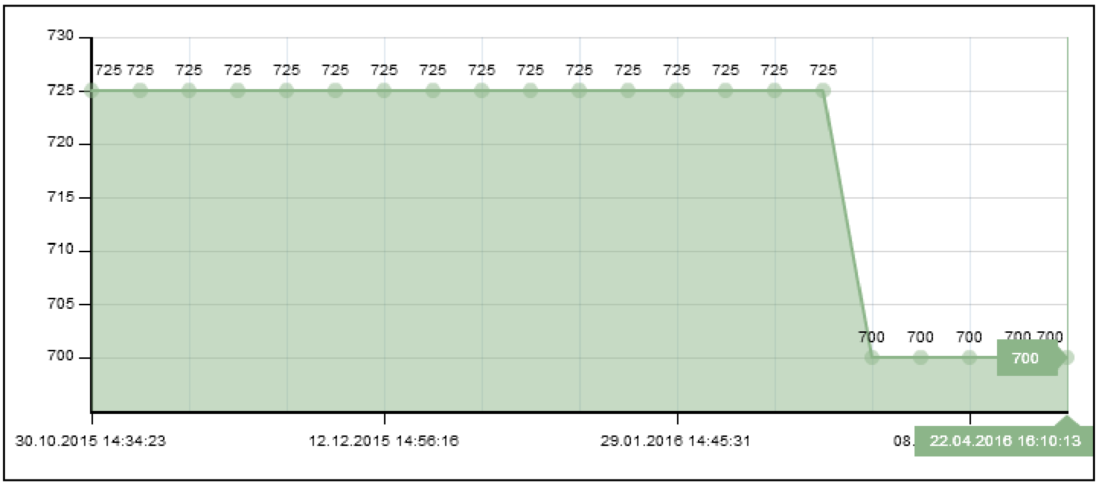


Figure 4. Bulgarian stock price of rapeseed for the last 6 months [11]

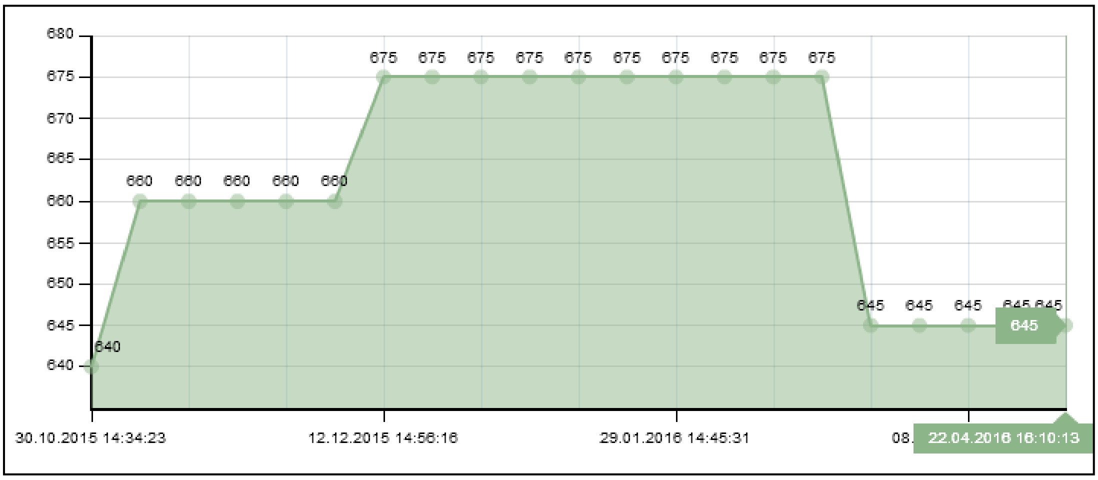


Figure 5. Bulgarian stock price of sunflower seed for the last 6 months [11]

From importance is also the fact that the municipality of Burgas and all the Black Sea resorts nearby are well visited by national and international tourists during the summer months. The quantity of used cooking oil (UCO) increases in times and by well-organized collections could be used as additional feedstock at least at the small-scale plants. Here the usage of UCO could be assumed at 50-60% in summer and up to 30% for the rest of the year. This would significantly reduce the price of produced biodiesel. The other part of feedstock is vegetable oil from local producers (for rapeseed) and national producers (for rapeseed and sunflower). The required feedstock for the large-scale plant will also be provided from local and national rapeseed and sunflower suppliers. If there is any further demand, it could be covered by the international market e.g. by the low priced Ukrainian market. Therefore taking into consideration above mentioned facts and data and in order to be more flexible and able to react adequately on any price fluctuations, the multi feedstock production scheme will be chosen for the small-scale plant and the single feedstock for the large-scale biodiesel production plant.

2.3 Technological and energetic appraisal of the selected / proposed applications /installations

„Production of any biofuel is a work process, in which materials (feedstock crops) are concentrated, refined and otherwise transformed at free energy costs. Energy return on energy investment (EROEI), which is a measure of energy efficiency, is calculated from the following equation:

$$EROEI = \frac{\text{Energy returned to society}}{\text{Energy required to get that energy}}$$

EROEI less than one is considered to be „unsustainable" energy production process. Energy tapping from renewable resources is a function of land, labor, water, raw materials and others, which by themselves need input energy. Different energy production technologies have different EROEI values" [12].

According to above cited Firrisa from the University of Twente (NL) different European countries are yielding different EROEI value based on their corresponding yield and the energy efficiency for rapeseed yields in Bulgaria shown in Figure 6 is between 1,3 - 1,5 (depending on the research based). With value higher than one in both cases, it can be considered as sustainable energy production process.

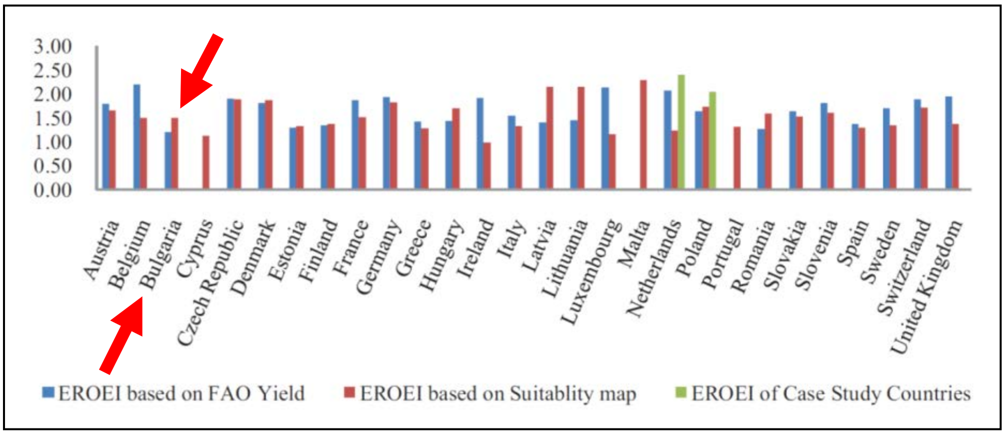


Figure 6. EROEI values from different rapeseed yields in the EU countries [12]

The operating hours for small and large BD production plants could be 24 hours per day, which means continuous operation based on a three-shift production. 10% for maintenance and unexpected breaks will be assumed.

Like fossil diesel fuel, biodiesel clouds when the weather gets colder - crystals of wax get formatted. Due to this fact, the storage temperature of the biodiesel should be not less than 5°C. Located on the Black Sea cost Burgas has a mild climate with not that cold winter period and relatively convenient summer temperatures. Besides, the municipality is well connected by high- and railway with the rest of the country and worldwide by the sea for direct transportation of produced BD. The biggest Bulgarians refinery „Neftochim Burgas“ is located in this region, just nearby, and as a biggest customer will without delay collect the produced bio fuel. By appropriate contracts with the vegetable oil supplier, an on schedule feedstock delivery could be managed. That is why a storage system will not be integrated, but even there would be build any, it would not need much of investment due to the well climate conditions and small storaged quantities.

2.4 *Ecological appraisal of the selected / proposed applications / installations*

The utilization of BD as a biofuel in transport sector leads to huge environmental benefits such as reduction of carbon dioxide (CO2) emissions (Figure 7).

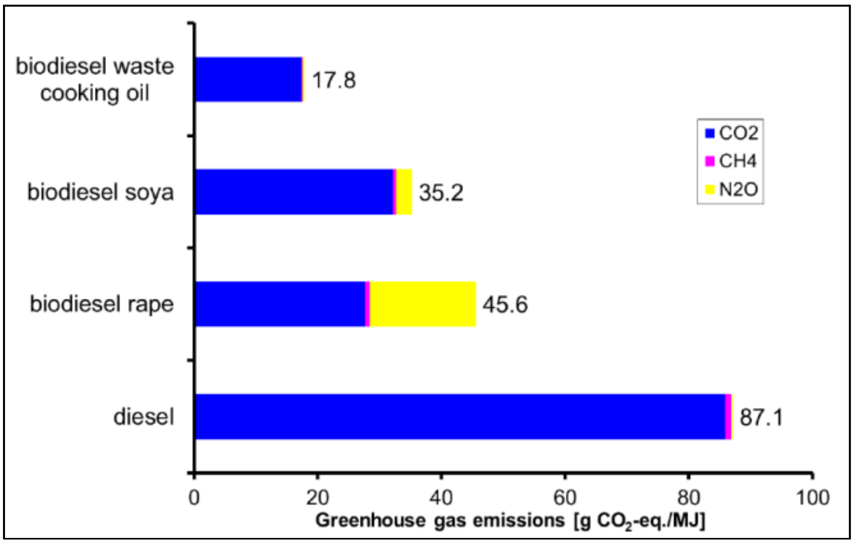


Figure 7. Share of GHG Emissions [6]

In addition, the emissions of other GHG such as carbon monoxide (CO), sulfur oxides (SOx) and methane (CH4), but also hydrocarbons are cut down. Unfortunately, as shown on the above diagram, using of biodiesel causes an increase of nitrogen oxides (NOx) emissions (due to the absorption of the nitrogen contained fertilizer by the crops (especially rape) used for producing of the vegetable oil as feedstock). However, there are already some technological solutions for reducing of these NOx emissions such as a delay of the injection point in the engine and the use of an oxidation catalyst that filters this fraction. The Selective Catalytical Reduction (SCR) technology displayed on Figure 8 uses ammonia for converting of nitrogen oxides into harmless nitrogen and water.

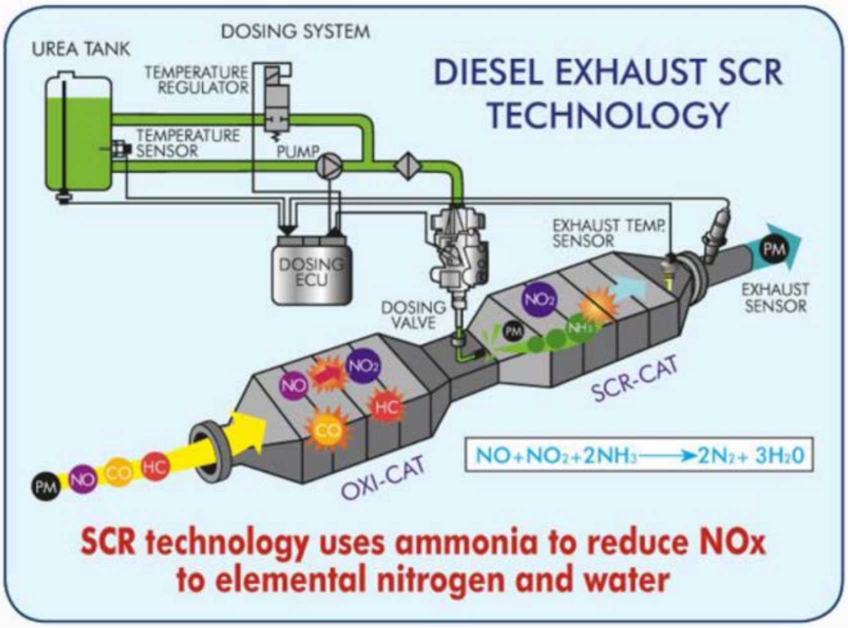


Figure 8. Selective Catalytical Reduction (SCR) [6]

By using of biodiesel as a fuel, the noise produced by the engine is reduced and the engine life extends due to the higher lubricant properties of BD compared to the conventional diesel. Besides, the ester reacts solvent as additive anti-dirt which doesn´t produce char. The engine, the fuel supply and injection system remains cleaner. This effect increases by higher proportion of ester in the fuel mixture.

Biodiesel is more biodegradable than the fossil diesel (in 21 days there are 98,3% degraded in comparison to the 50% for conventional diesel), so that eventually spills could be considered as much less harmful to the environment. With its higher flashpoint of about 150°C compared to the 50°C of fossil diesel it´s more secure in perspective of safety transportation. Finally, the bad image of the diesel vehicles as such causing more pollution than those based on gasoline gets improved to environmentally friendly cars when driven on biodiesel.

As already mentioned the use of biodiesel has environmental benefits. Their quantification is usually done by the so-called Life Cycle Assessment (LCA) where the net amount of emissions produced during the whole production, supply and combustion processes are measured and specified. The results of the LCA depend amongst others especially on the used raw materials, subproducts and processes. Accordingly to Zobaa and Bansal (2011) [4] for every ton of fossil diesel are emitted 2,8 t of CO2 and for every ton of BD 400 kg less carbon are emitted (2,4 t of CO2). It can also be assumed that the CO2 content will be recaptured in the next crop used for the vegetable oil as feedstock. On this way, taking into account the complete carbon cycle (Figure 9), the CO2 emissions are very low (but not zero due to the accompanying processes).

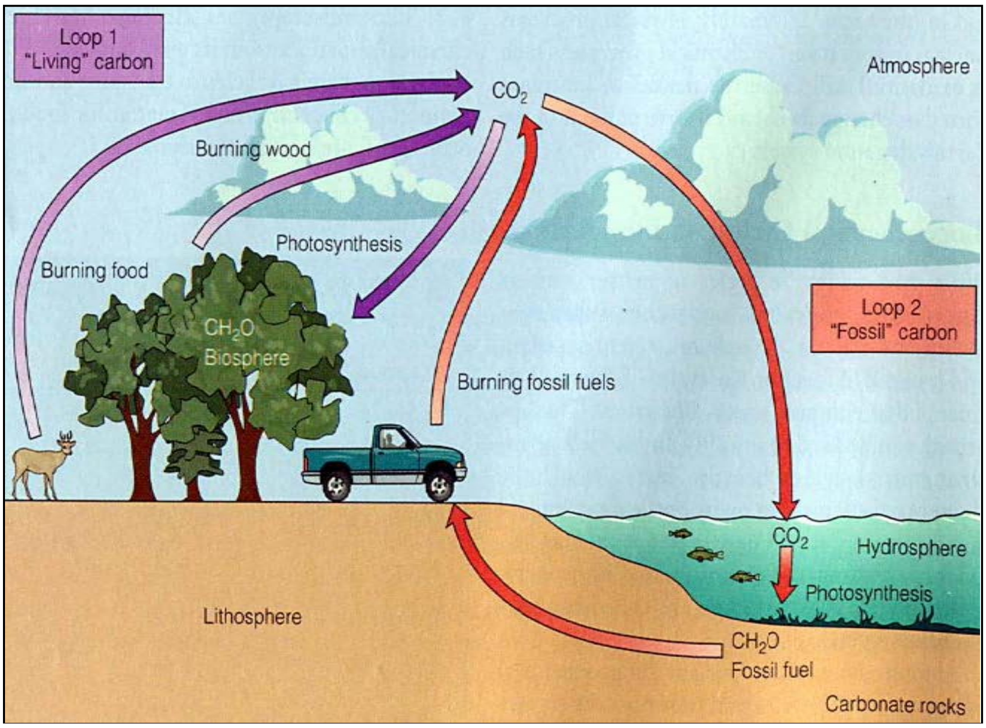
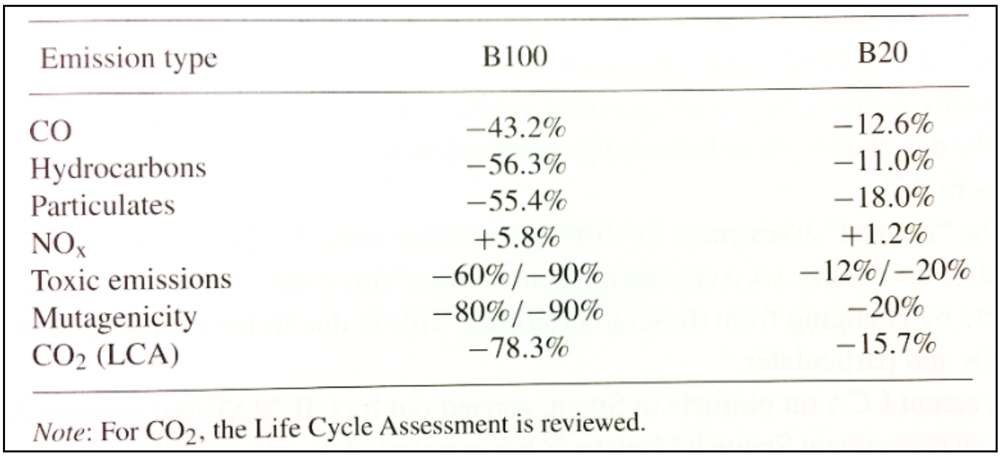


Figure 9. CO2 Cycle [6]

Other advantage of using biodiesel is that its virtually free of sulfur (<0,0024 ppm). The combustion of fossil diesel releases sulfur into the atmosphere in form of SOx, which leads to building of acid rain. The content of oxygen in the BD improves the combustion process, which reduces CO emissions by at least 20%. Also the particulate emissions from biodiesel are at least 40% lower in comparison to the conventional diesel fuel (Table 3). Reducing of hydrocarbons and CO2 emissions are also visible there [4].

Table 3. Comparison of BD versus fossil diesel emissions [4]



Emission type	B100	B20
CO	−43.2%	−12.6%
Hydrocarbons	−56.3%	−11.0%
Particulates	−55.4%	−18.0%
NO_x	+5.8%	+1.2%
Toxic emissions	−60%/−90%	−12%/−20%
Mutagenicity	−80%/−90%	−20%
CO_2 (LCA)	−78.3%	−15.7%

Note: For CO_2, the Life Cycle Assessment is reviewed.

A LCA on biofuels in Spain, carried out by CIEMAT[2] and the Spanish Environment Ministry showed that the replacement of fossil diesel by pure BD (B100) leads to reduction of 57% (in case of producing of biodiesel from raw vegetable oils) and of 88% (in case of using of UCO) in emission of GHG (CO2eq). In case of 10% biodiesel (B10) the reduction is respectively 6% and 9% [4]. Similar results are obtainable from the lectures of professors Jungmeier and Mittelbach (Figure 10).

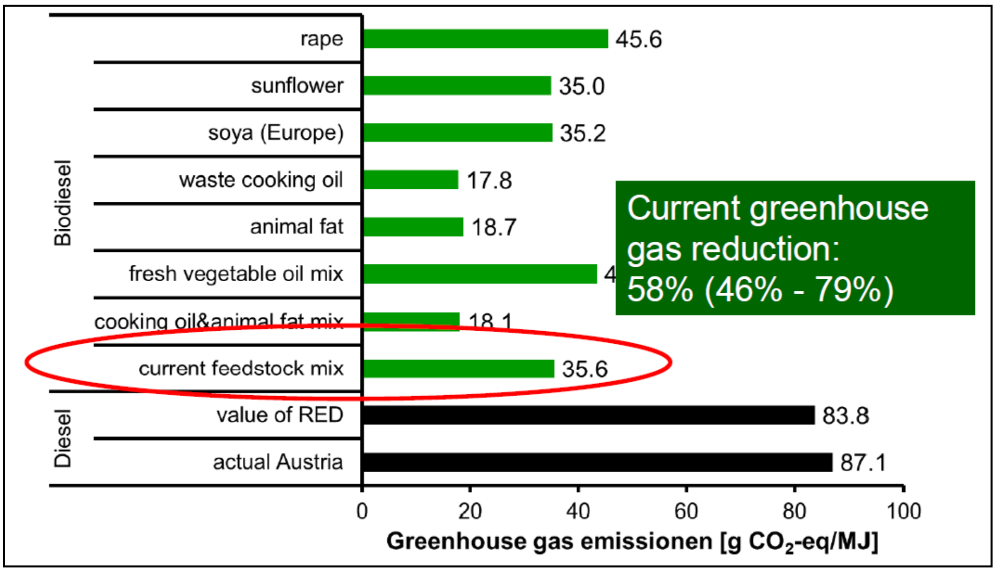


Figure 10. Reduction of GHG emissions BD versus fossil diesel [6]

---

[2] Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (Spanish)

Also interesting to be mentioned here is the fact that the biofuels have lower GHG emissions compared even to the EV Tesla (Figure 11). This is due to the non-green energy mix applied for the battery loading as well the production processes used there.

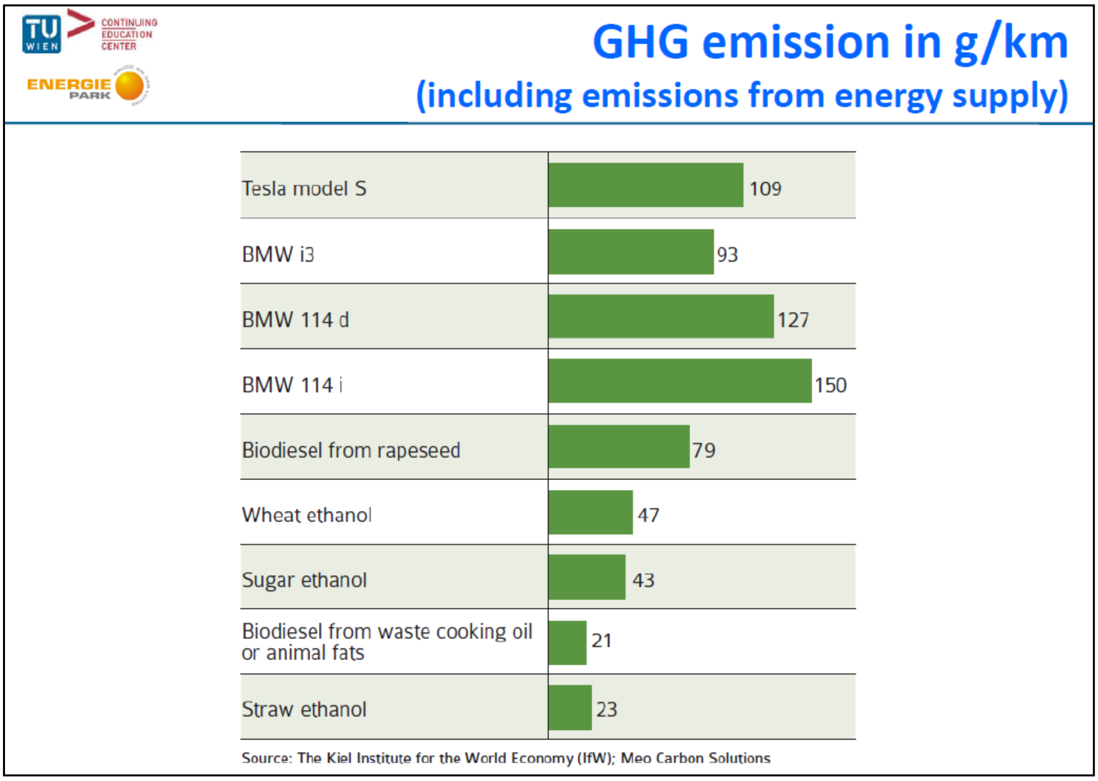


Figure 11. Comparison of GHG emissions from EV and BD [6]

Speaking about the ecological aspects, also the land use change needed for the cultivating of biomass as feedstock and the caused higher soil eutrophication shouldn´t be forgotten. But in general there are a lot of environmental benefits mentioned in this chapter, so that the way of developing of biofuel technologies, producing and using of biofuels should be kept going.

2.5 Economic appraisal of the selected / proposed applications / installations

The determining factors that have been playing a crucial role in the development of the biodiesel industry in the last years are not from technical but from economic nature, such as the costs of the raw material, BD production costs and its price, the price of the fossil fuels and the taxes to be paid. The biggest cost part is taken by the raw material costs. So accordingly to Zobaa and Bansal (2011) [4] in the case of vegetable oils it is between 70 and 80%. Similar tendency can be observed on the Figure 12 taken from the lecture of professor Mittelbach (2015) where the 10% changes of price of BD, yield of the plant and the price of the feedstock lead to change of profit between 22 and 33%. It shows the huge influence of these main drivers upon the economy of the biodiesel industry. The results of made calculations and analyses of the sensitivity of Net Present Value to the variation of feedstock and BD prices presented later in this work are in compliance with above findings.

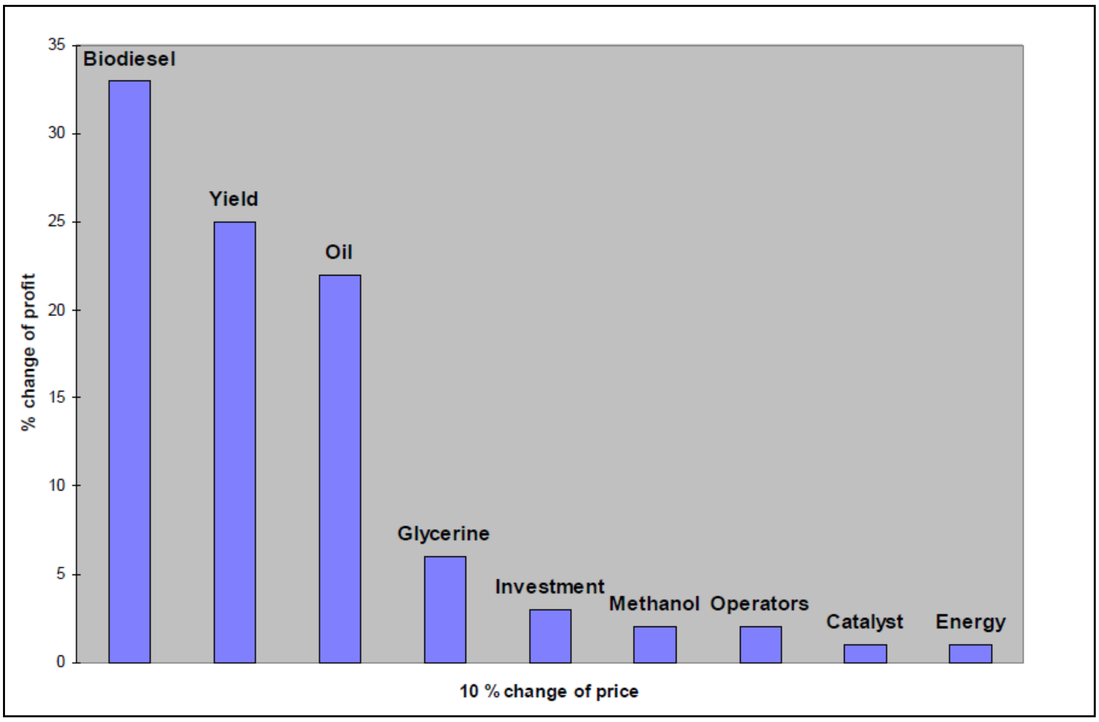


Figure 12. BD Profitability Factors [6]

On the other side, the sale of produced subproducts should not be neglected, too. It is an add-on income, which supports the economy of the BD plant. The main obtained subproduct is glycerine (also shown on the Figure 12 as the forth-main factor).

Although its price[3] has gone down in the last years, glycerine remains the major sub produced source of income. Depending on technology, also other subproducts can be obtained, such as fatty acids used for animal feeding and minerals (not that valuable) used in the fertilizer industry.

As starting point for the economic appraisal of both biodiesel plants was used the idea of Alfred Melamed (2012) [13]. He followed the economic comparison done by Connemann and Fischer (1998) [14] and converted into Euro by Friedrich (2004) [15]. Six different BD plants were compared in their research (Table 4). It´s obtainable there that the investment costs depend much on the type of process used (batch/continuous) and on the capacity [t/a] of the plant.

Table 4. Cost structure of biodiesel plants (Friedrich, 2004) [13]

Plant		**A**	**B**	**C**	**D**	**E**	**F**
Process		batch	batch	cont	batch	cont	cont
Investment	Mio €	1,5	10,2	1,3	12,8	25,5	10,2
Capacity	**t/a**	**2.000**	**15.000**	**8.000**	**75.000**	**125.000**	**80.000**
daily cap	t/d	10	50	20	200	350	250
Oil Quality		ref.deg	ref.deg	crude/ref	ref.deg	ref.deg	crude/ref
Glyc.prep	Content %	60	80/99,5	80	90	92	80/99,7
Personnel		3	8	6	15	20	12
Veg.Oil, ref.deg.		2.100	15.600	8.240	77.250	131.250	82.400
in % of		105%	104%	103%	103%	105%	103%
Biodiesel	t/a	2.000	15.000	8.000	75.000	125.000	75.000
Glycerol	99,5/80/60	0	1.295	783	7.339	12.469	6.953
%of oil. Ref.deg		0%	8%	10%	10%	10%	8%
Fatty acids	80%	80	480	192	1800	5000	1800
Electr. 0,08 €/kWh	kWh/t	105	75	40	60	60	30
Steam 15 €/t	kg/t	650	650	300	600	1200	350
Methanol0,15/0,13 €/kg	kg/t	156	120	120	120	115	115
Catalyst 43/92 €/kg	kg/t	14	10	4	4	3	4
Phosp. acid 38 €/kg	kg/t	43	43	10	10	10	10
Adsorbant 0,6 €/kg	kg/t	0	0	5	0	0	5
Depreciation (10 y)	€/t	77	68	16	17	20	14
Interest 8% (1/2)	€/t	31	27	6	7	8	5
Personnel (40.000 €/p)	€/t	61	22	31	8	7	6
Methanol	€/t	24	18	16	16	15	15
Energy+Chemicals	€/t	48	42	18	22	30	18
Maint 3 %	€/t	23	20	5	5	6	4
Overheads	€/t	38	10	8	5	5	5
Total operating costs	€/t	301	208	99	80	91	67
-Glycerol 637/306 €/t	€/t	0	55	30	30	31	55
-Fatty acids 280 €/t	€/t	11	9	7	7	11	6
+Loss of oil 460 €/t	€/t	23	18	14	14	23	14
Surcharge on oil base	**€/t**	**313**	**162**	**77**	**57**	**73**	**19**

---

[3] Price developing of glycerine in the last 3 years (2016), https://mediathek.fnr.de/grafiken/daten-und-fakten/preise-und-kosten/preise-glycerin-interaktiv.html

Accordingly to the assessment and the table content for the calculations made in current work for the small-scale plant was selected plant B and respectively plant E for the large-scale plant. The figures were compared with the Bulgarian market and found to be similar with the exception of the personal costs since the current average monthly wedge for Burgas accordingly to the National Statistical Institute of Bulgaria is 385 € [66]. Multiplying by 13 months and adding 30% social security amount one gets 6.500 € of cost per person per year.

In order to simplify the calculations for the whole production period of 10 years no price escalation neither for costs nor for revenues was considered (due to the fact that the change of the input material (feedstock) price is related and so coarse balanced with the change of the output product (biodiesel) price. In addition, exactly price predictions for the next 10 years are hardly feasible). Bulgaria is one of the 28 EU countries. Searching for the input and output prices in the Bulgarian database one can see that they are bounded on the EU market. In this calculation were used the currently given prices of vegetable oil and biodiesel obtained from a German statistic (Figure 13) [16] (interesting to be mentioned here is that the Bulgarian currency Lev has still been fixed since 1997 in a ratio 1:1 to the German Mark, although the latter practically does not exist anymore).

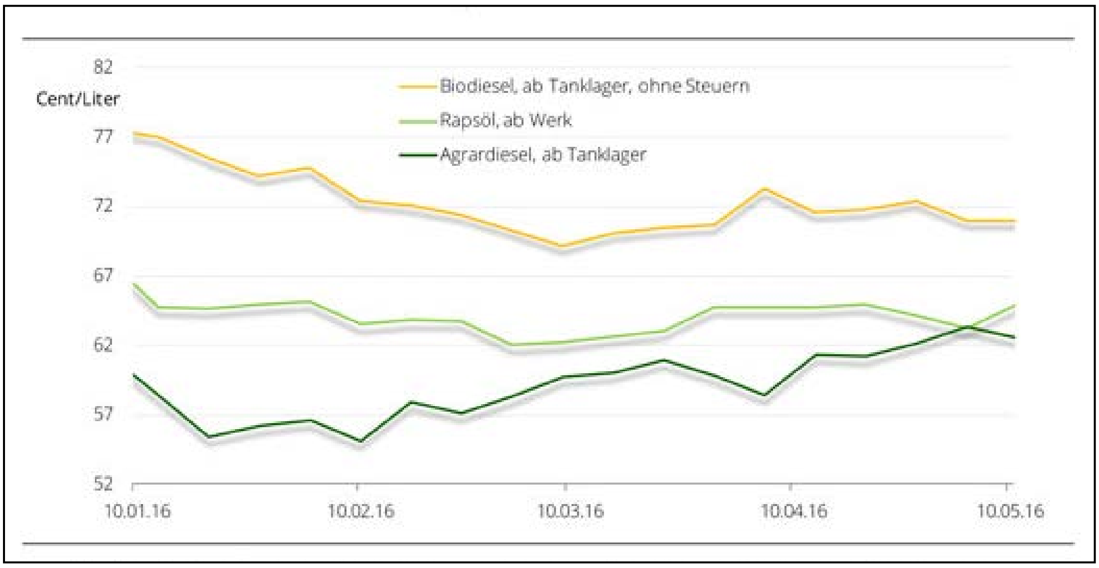


Figure 13. Wholesale prices of biodiesel and rapeseed oil w/o VAT [16]

The prices obtained from the Figure 13 and used in the following calculations (Table 5) are as follow:

Rapeseed oil – 0,64 €/l;   Biodiesel – 0,71 €/l

The UCO price of 0,5 €/l was obtained from the Bulgarian Waste Oil Net company[17]. As already mentioned above, the feedstock costs are the main factor that determines the price of produced biodiesel. This means that the small-scale plant with its Multi Feedstock technology by using of 30% UCO will have lower fuel costs per MWh although its production is more than 13 times less and it has higher investment costs per ton compared to the large-scale plant.

Table 5. Investment calculation for small and large BD plants [OC]

	Small-scale BD plant		**Large-scale BD plant**	
Technology	Multi Feedstock		Single Feedstock	
Process	Batch		Continuous	
Capacity	15.000	t/y	200.000	t/y
Vegetable oil	15.600	t/y	210.000	t/y
Total Investment	8.000.000	€	50.000.000	€
Biodiesel	15.000	t/y	200.000	t/y
Personnel	8	p	30	p
Depreciation in	10	y	10	y
Equity in % of investment	25	%	25	%
Loan in % of investment	75	%	75	%
Term of loan	10	y	10	y
Interest rate of loan	8	%	8	%
Glycerol	1.295	t/y	19.950	t/y
Fatty acids	480	t/y	8.000	t/y
Electricity 0,073 €/kWh	75	kWh/t	60	kWh/t
Steam 15€/t	650	kg/t	1.200	kg/t
Methanol 0.15 / 0.13 €/kg	120	kg/t	115	kg/t
Catalyst 43/92 €/kg	10	kg/t	3	kg/t
Phosph. Acid 38 €/kg	43	kg/t	10	kg/t
Depreciation €/t	68	€/t	20	€/t
Interest 8%	27	€/t	8	€/t
Personnel 6.500 €/p	3,5	€/t	1	€/t
Methanol	18	€/t	15	€/t
Energy+Chemicals	42	€/t	30	€/t
Maintenance 3%	20	€/t	6	€/t
Overheads	10	€/t	5	€/t
Total operating costs	**188,5**	**€/t**	**85**	**€/t**
Glycerol 637/306 €/t	-55	€/t	-31	€/t
Fatty acids 280 €/t	-9	€/t	-11	€/t
Loss of oil 460 €/t	18	€/t	23	€/t
Surcharge on oil base	**142,5**	**€/t**	**66**	**€/t**
Feedstock	0,64	€/l		
Biodiesel	0,71	€/l		
UCO	0,5	€/l		
NPV	**-€ 1.418.528**	**€**	**-€ 22.550.256**	**€**

The economic assessment of both plants was done by calculation[4] of the Net Present Value means the financial value of a project under certain financing conditions right before the time of investment, by using the formula (1) below:

$$NPV = \sum_{t=0}^{T} \frac{C_t}{(1+r)^t} - C_0 \tag{1}$$

with following parameters:

NPV - Net Present Value [€]
T - Investment horizon [y]
T - Year-count
Ct - Cash flow in year t [€]
r - Risk adjusted discount rate / (WACC[5]) [%/year]
C_0 - Initial investment [€]

Unfortunately, both investments showed negative NPV, respectively -€ 1.418.528 for small-scale and -€ 22.550.256 for large-scale biodiesel plant (Table 5). This means that both plants are not rentable with the current market feedstock and biofuel prices and both investments should not be done!

The sensitivity analyses (Figure 14 - Figure 17) show how sensitive indeed the NPV reacts on the price variation of feedstock and biodiesel itself. The current economic research was done with a raw material price of 0,64 €/l. With only 3% less at the amount of 0,62 €/l and remaining on the same BD price level of 0,71 €/l both plants would make break even. However, comparing the feedstock price development (Figure 13) of rapeseed oil during this year but also having in mind the last two years trend, one can see, that the average rapeseed oil price has remained relatively constant by moving up and down around the level of 0,64 €/l. Nevertheless, the situation regarding the BD price deployment looks different. During the last two years it has been going down from 0,77 €/l to 0,71 €/l. And this is from a crucial importance for the economics of both small and large scale BD plants since only a 2% increase of the biodiesel price to a level of 0,724 €/l would make the plants breaking even and coming out of the red.

---

[4] See appendices 1.1-1.2
[5] Weighted Average Cost of Capital

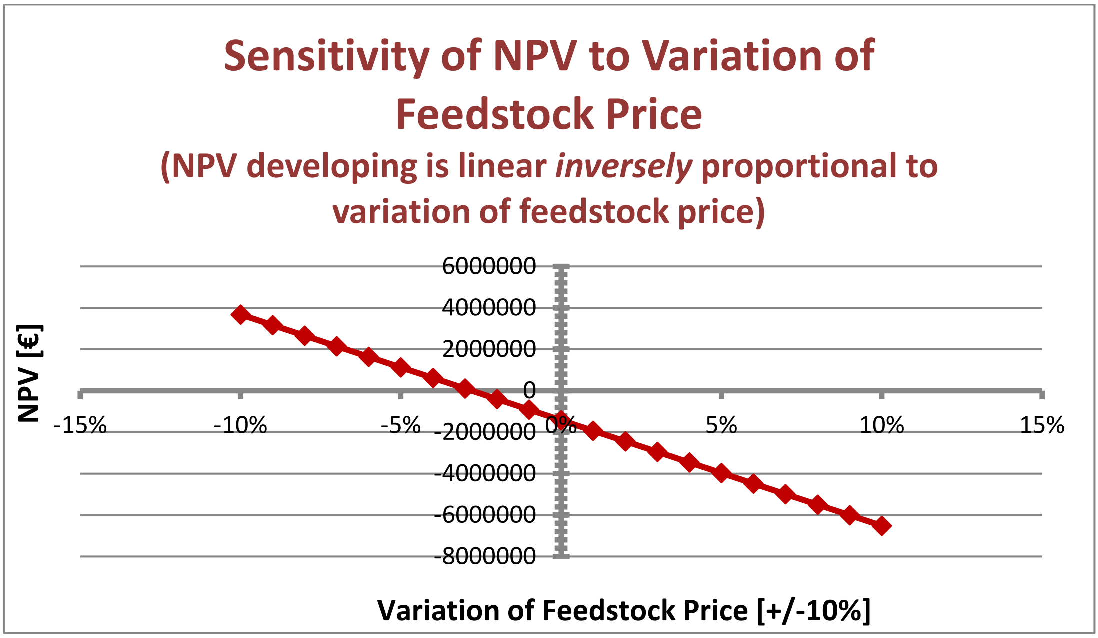


Figure 14. Sensitivity NPV <-> Feedstock price (Small-scale BD plant) [OC]

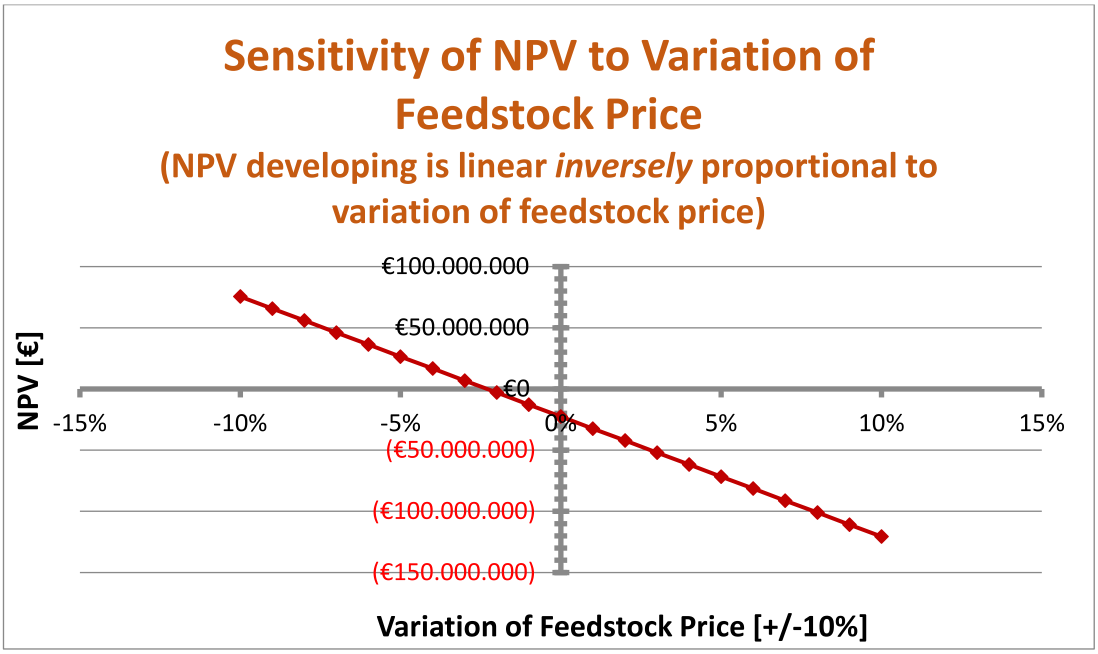


Figure 15. Sensitivity NPV <-> Feedstock price (Large-scale BD plant) [OC]

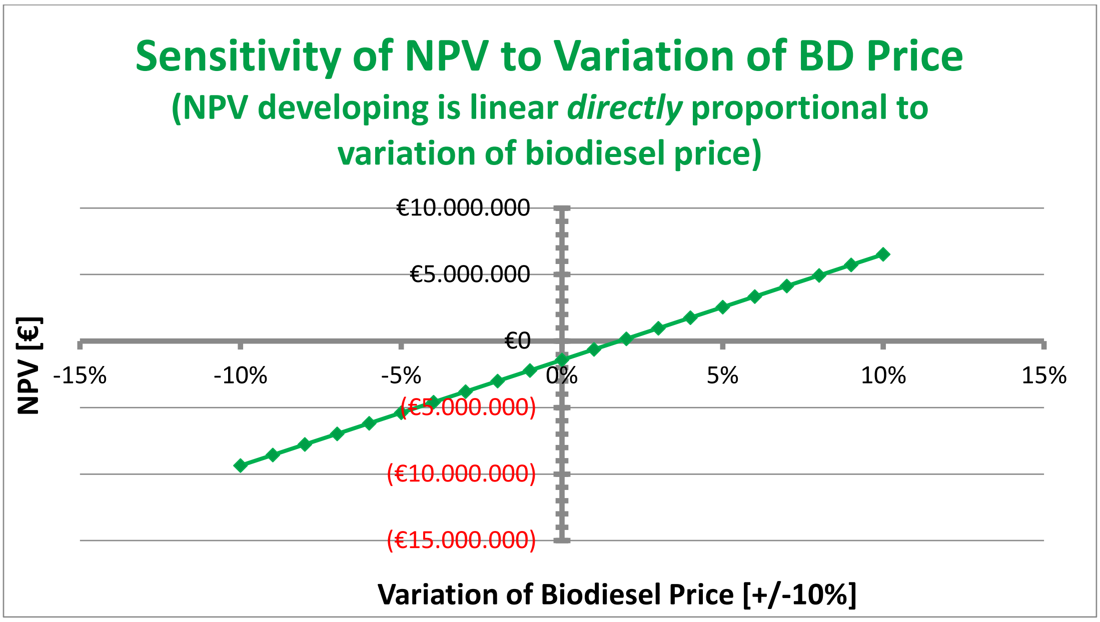


Figure 16. Sensitivity NPV <-> BD price (Small-scale BD plant) [OC]

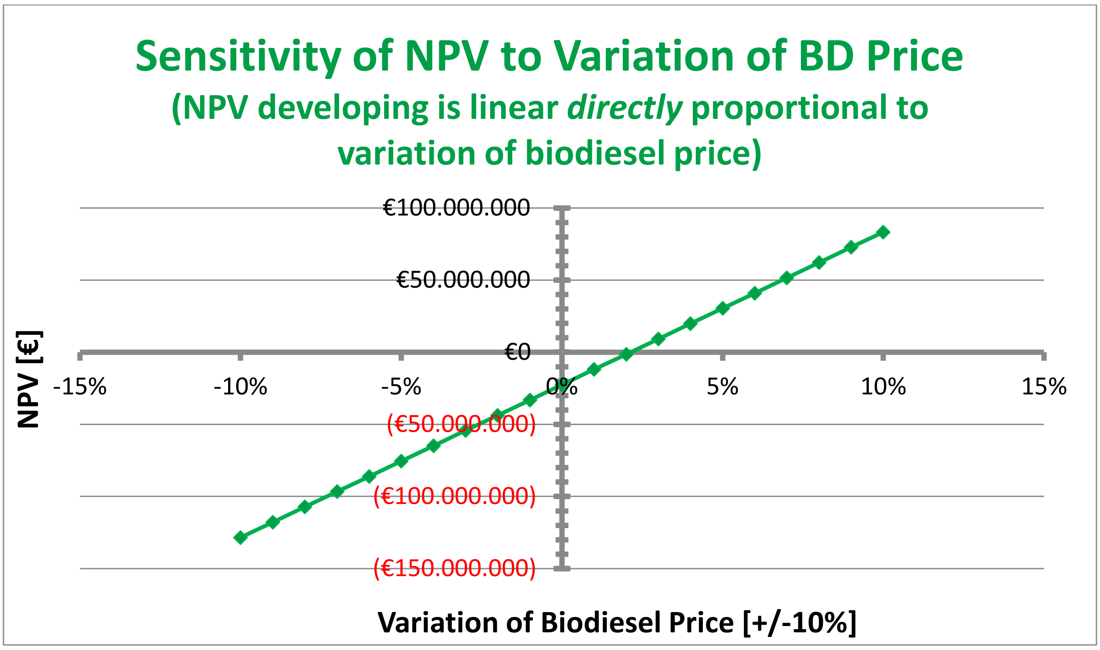
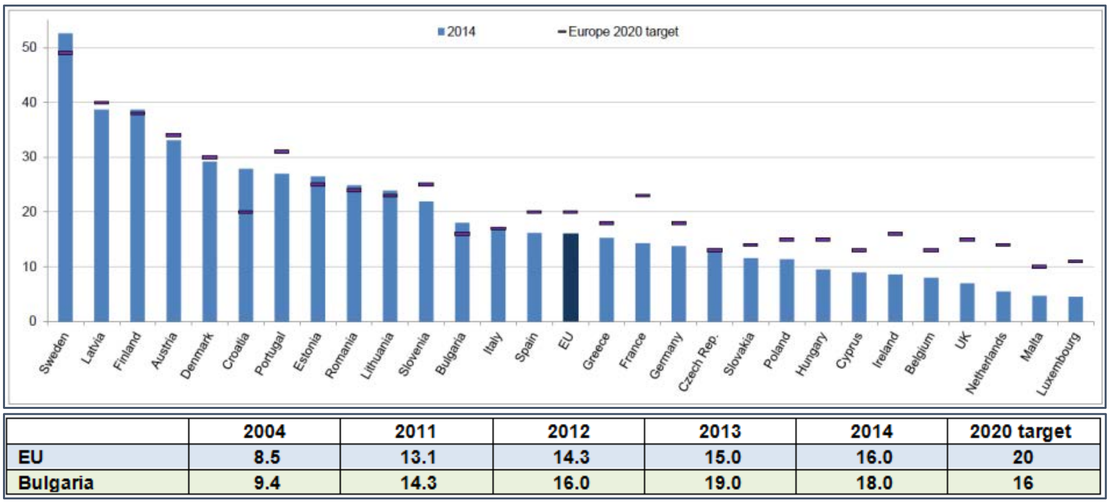


Figure 17. Sensitivity NPV <-> BD price (Large-scale BD plant) [OC]

So what could be done in order to save at least the small-scale BD plant project despite the negative NPV? Firstly, trying to get raw material to a better price may be from non-EU countries. For example there are companies in Belarus (Smorgon, Slutsk), Russia (Barnaul) and Moldova (Chisinau) offering rapeseed oil to a current price of 550 €/t. Of course, there will be supplementary costs for transport, customs duty and storage, but with appropriate long term contracts it could be rentable – here is further precisely research needed. Secondly, increasing the percentage of the UCO in the multi feedstock technology or even switching completely to UCO with appropriate contract with the Bulgarian Waste Oil Net company already mentioned above, but also with local restaurants, catering and fast food chains. Especially during the tourist season in the summer months in the region of Burgas there is a big UCO overproduction that could be used to obtain the oil to an even better price.

Comparing the biodiesel situation in Bulgaria four years ago and now one can see a negative development of this industry. While 2012 there still was an optimistic feeling and profitable production, nowadays, caused by changed market prices and not supporting government decisions (possibly due to the still powerful “fossil fuel” lobby), the BD plants go bankruptcy and accordingly to the Bulgarian BD forum only production for self-consumption remains rentable. For the moment this could be seen as inconsistent with the European directive on the promotion of the use of energy from RES 2009/28/EC, setting until 2020 a part of at least 10% of energy used for transport to be gained from RES (although EV are included). The cancelling of government support for REN generally could also be explained by the fact that Bulgaria has already achieved its 2020 target of 16% in the share of renewables in energy consumption (Figure 18) causing former subsidy to be disposed to other sectors of industry.



	2004	2011	2012	2013	2014	2020 target
EU	8.5	13.1	14.3	15.0	16.0	20
Bulgaria	9.4	14.3	16.0	19.0	18.0	16

Figure 18. Share of energy consumption from RES in the EU-28, 2014 [18]

(in % of gross final energy consumption)

Taking into account the achieved results of this research, a possible decision for the municipality of Burgas could be an installation of a smaller-scale BD plant for supplying the self-consumption of the “BurgasBus” [60] fleet, which contains of 173 busses (2014) and operates the public and rural transport network of Burgas. This company belongs to the municipality of Burgas, which, as already mentioned in the introduction part of this work, is well known in Bulgaria with its continuously implementation of green technologies and further environmental improvements. The overproduction could be distributed to other transport companies in the municipality and neighborhood regions.

3 ASSESSMENT, ANALYSIS AND DISCUSSION OF THE SELECTED SOLAR ENERGY TECHNOLOGIES FOR TRANSPORT

3.1 Method of approach

For comparing the various renewable energy technologies, as objective of the first part of this master thesis, the main calculation steps for determination the equivalent size of the PV and wind power plants were already described in chapter 2.1. As shown there, the annual energy output needed for covering the same service output, which was measured by the same distance driven with diesel and electrical vehicle, was estimated to be 45,35 GWh for the small scale PV power plant and respectively 604,7 GWh for the large one.

The power output of the PV plants will be calculated with the value of the global solar irradiation for the region of Burgas. An appraisal of the environmental impact including GHG savings analysis will be carried out by means of LCA. Finally the economic evaluation will be done like in the BD technology part of this work by calculating of the Net Present Values of the small and large-scale projects.

3.2 Technological overview and description of the selected / proposed applications / installations

The solar radiation received on Earth in 45 minutes only is enough to cover the annual energy demand of the whole world.

Solar cells or photovoltaic (PV) cells are semiconductor elements that based on the PV effect convert the sunlight radiation (Photon) energy directly into electricity (Voltage). The so called photo-electric-effect was firstly discovered in 1839 by the French physicist Edmund Bacquerel but it found its application more than a century later when Bell Lab engineers discovered in 1954 that silicon creates electric charge when is being exposed to sunlight radiation. Soon PV cells were already used for electricity supply of satellites and smaller devices like electronic watches and calculators and found its first terrestrial application in the 1980´s.

The PV hierarchy is shown in Figure 19. The output voltage of a single solar cell is only about 0,6 V. So in order to increase the output voltage many cells are connected in series building a module. In addition, in turn to increase the modules output current, the series strings of PV cells are connected in parallel. Produced on this way, the series and parallel combination of the cells defines the current-voltage output of one module. In order to assemble a PV system with desired current and voltage output one has to connect the modules themselves in series and parallel. These combinations done during the mounting phase of a PV system are called arrays.

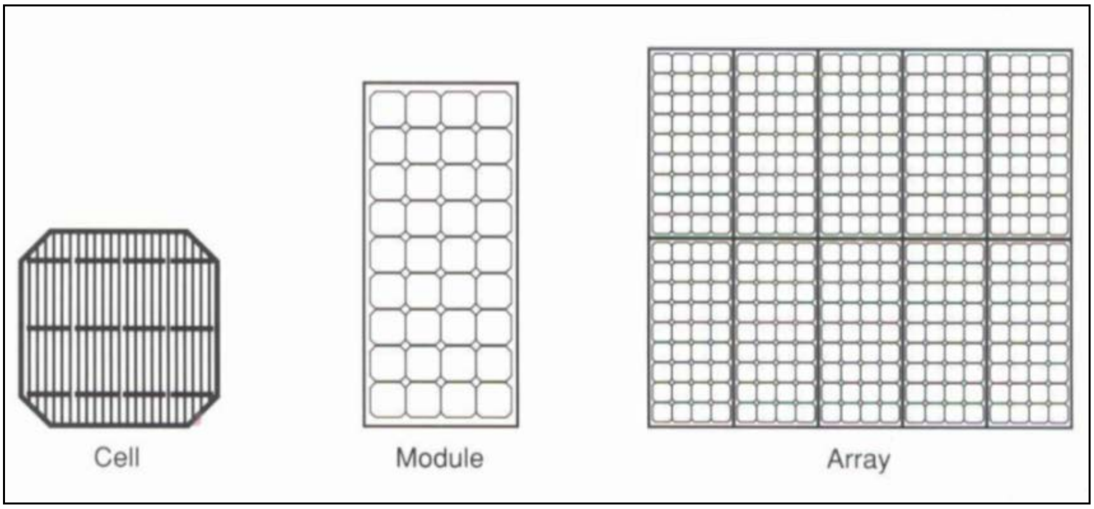


Figure 19. Photovoltaic hierarchy [19]

“*PV cells are generally made either from crystalline silicon, sliced from ingots or castings or from grown ribbons, or thin film, deposited in thin layers on a low cost backing. Thin film technology based on silicon and other materials is expected to gain a by far larger share of the PV market in the future. This technology offers several advantages such as low material consumption, low weight and a smooth visual appearance. Crystalline silicon is still the mainstay of most power modules. Although in some technical parameters not the ideal material for solar cells, it has the benefit of being widely available, well understood and uses the same technology developed for the electronics industry. Efficiencies of significantly more than 20% have been obtained with silicon cells in the laboratory, but production cells are currently averaging 13-17% efficiency. The theoretical limit for crystalline modules approaches 30%.”* [20].

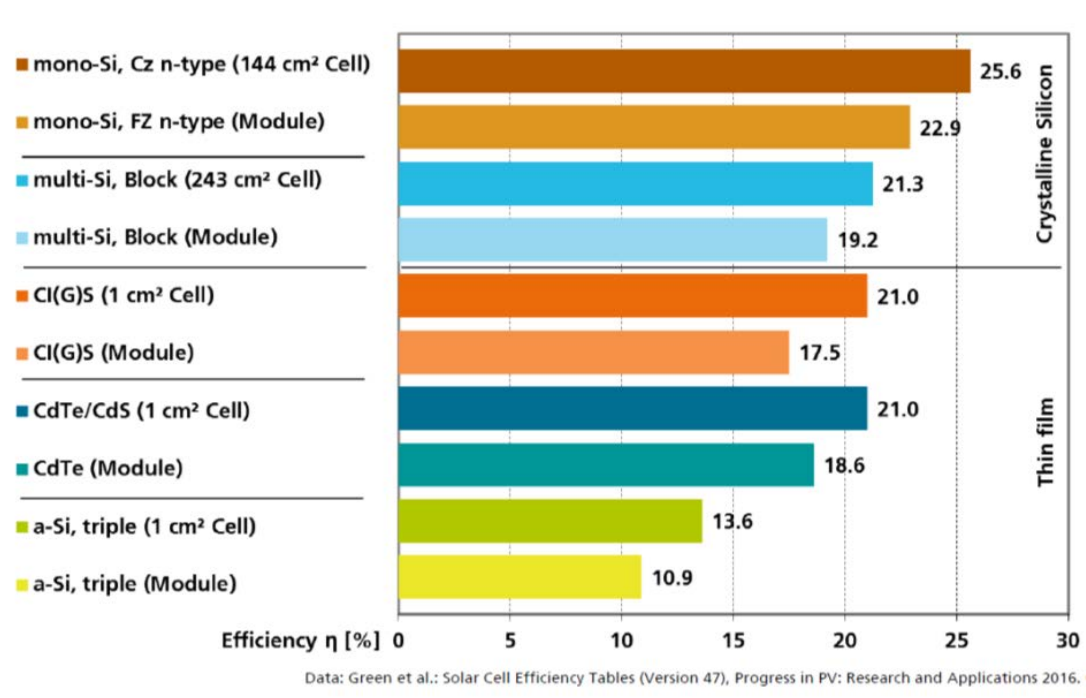
There are two main most economic types of PV modules on the market that differ in the type of silicon they are made of poly- and monocrystalline:

- Monocrystalline silicon wafer are 200 µm thin slides cut from single-crystal boules of grown silicon. Their color is bluish black. The PV modules made out of it have meantime high efficiency of almost 23 % (Figure 20), a proven long live and higher temperature resistance, but are higher in price.

- Poly- or Multicrystalline silicon wafer are thin slides cut from a block of multiple crystal silicon. Their color is usually blue. The PV modules made out of it have lower efficiency of about 18,5 % (laboratory values, Figure 20) but are less expensive.

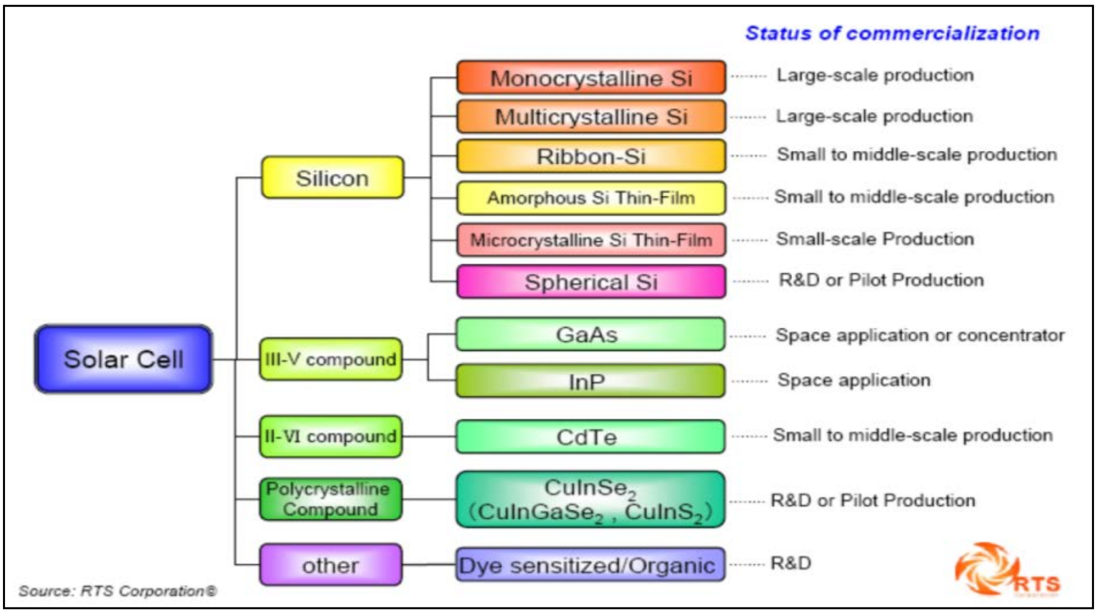
There are also other types of solar cells made of different materials (Figure 21) such as the III-V semiconductor Gallium Arsenide (GaAs) with very high efficiency of up to 30 %, the amorphous Silicon (a-Si), the thin-film polycrystalline materials Copper Indium Diselenide (CuInSe2 or CIS) and Cadmium Telluride (CdTe). They have different price and efficiency (Figure 20) values but will not be presented in detail in this work since these modules are produced in a small to middle scale range and will not be used in the both PV plant projects.

In the research field, the newest solar cells, to see under "other" in Figure 21, are being made from a variety of new materials, including solar inks using conventional printing press technologies, solar dyes, and conductive plastics. Some new solar cells use plastic lenses or mirrors to concentrate sunlight onto a very small piece of high efficiency PV material [22].



Data: Green et al.: Solar Cell Efficiency Tables (Version 47), Progress in PV: Research and Applications 2016.

Figure 20. Current PV cell efficiencies (research and applications 2016) [21]



Source: RTS Corporation©

Figure 21. Diversification of solar cells in the market [19]

Due to the relatively huge energy production capacity of both PV power plants and the fact that the monocrystalline silicon solar panels have higher power output from the same area covered by multi crystalline ones, the mono crystalline technology will be chosen for both projects. The temperature in the region of Burgas can rise in summer up to 40° C and above. Well known is the negative impact of the higher temperatures on the efficiency of the panels – the output voltage UF of the solar cells strongly decreases, which causes running low of the MPP (Maximum Power Point) and respectively declining of the energy yield. Therefore, the higher heat resistance of the monocrystalline silicon panels mentioned above is another heavy argument for selecting them in these projects.

Increasing the energy yield of a solar power plant could be also achieved by using the so-called tracking system. Here the PV panels are mounted on motorized stages, which follow the moving of the sun in both X- and Y-axis to guarantee the maximum gain of the solar irradiation during the completely sun-shining period of the day. However, taking into account the high investment and maintenance cost of such tracking systems especially for larger PV plants like the both brought out here, and comparatively high yearly solar insulation value of about 1.450 kWh/m² (and even higher accordingly to PVGIS) for the region of Burgas (Figure 22) (compared to 1.100 kWh/m² in Vienna), which leads to higher yield even without following position of the sun, tracking systems will not be integrated into these projects.

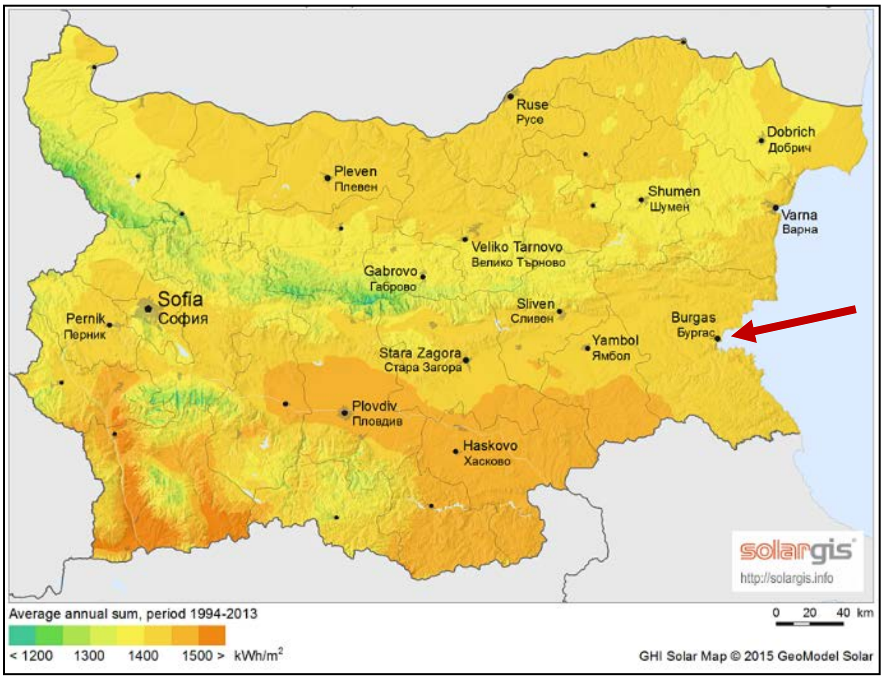
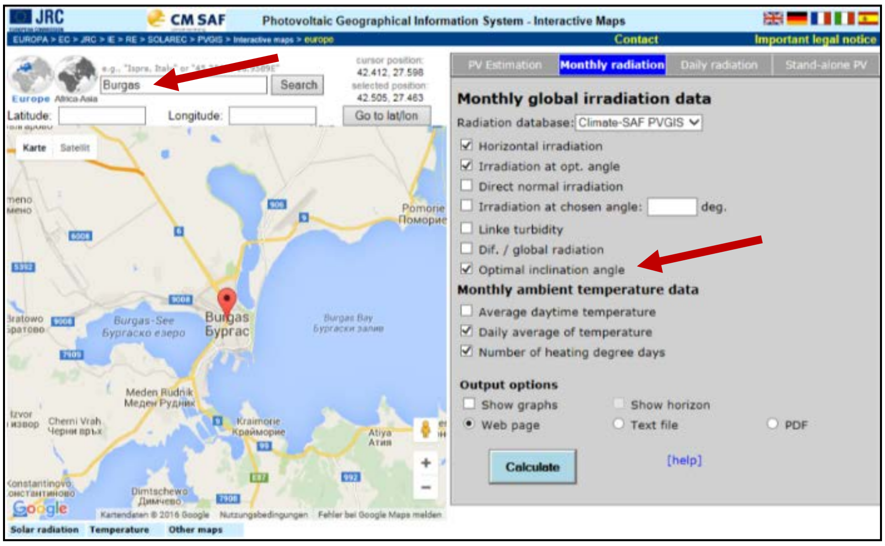


Figure 22. Global Horizontal Irradiation (GHI) Bulgaria [23]

3.3 *Technological and energetic appraisal of the selected / proposed applications / installations*

The performance of both PV plants in the region of Burgas was estimated by using of the free available Photovoltaic Geographical Information System (PVGIS) calculation app (Figure 23). The monthly solar irradiation was obtained accordingly to the PVGIS database and calculation. It showed that the optimal inclination of the solar panels



Burgas

cursor position:
42.412, 27.598
selected position:
42.505, 27.463

Latitude: Longitude:

Monthly global irradiation data

Radiation database: Climate-SAF PVGIS

☑ Horizontal irradiation
☑ Irradiation at opt. angle
☐ Direct normal irradiation
☐ Irradiation at chosen angle: deg.
☐ Linke turbidity
☐ Dif. / global radiation
☑ Optimal inclination angle

Monthly ambient temperature data

☐ Average daytime temperature
☑ Daily average of temperature
☑ Number of heating degree days

Output options

☐ Show graphs ☐ Show horizon
● Web page ○ Text file ○ PDF

Figure 23. Calc. of monthly solar radiation at optimal inclination angle for Burgas [24]

should be 32° and that the average irradiation on this optimally inclined plane is expected to be 4.590 Wh/m²/day (Figure 24), what respectively means 1.675,35 kWh/m²/year.

In order to define the Full Load Hours (FLH) of a PV power plant the calculated annual irradiation has firstly to be divided by the irradiance [W/m²], which is the power of the incident solar radiance per m². This value can be led out from the solar constant (1.367 W/m², the radiation received per square meter on the top of the atmosphere). By going through the atmosphere the power of the sun light reduces and on the earth surface decreases to a value of approximately 1.000 W/m². On this way the number of **FLH** was determined to **1.675,35 [h/year]**.

Already knowing the FLH and the yearly energy generation of the PV plants – **45,35 GWh** for the small and **604,7 GWh** for the big one, is now possible to calculate the needed nominal power output of the system.

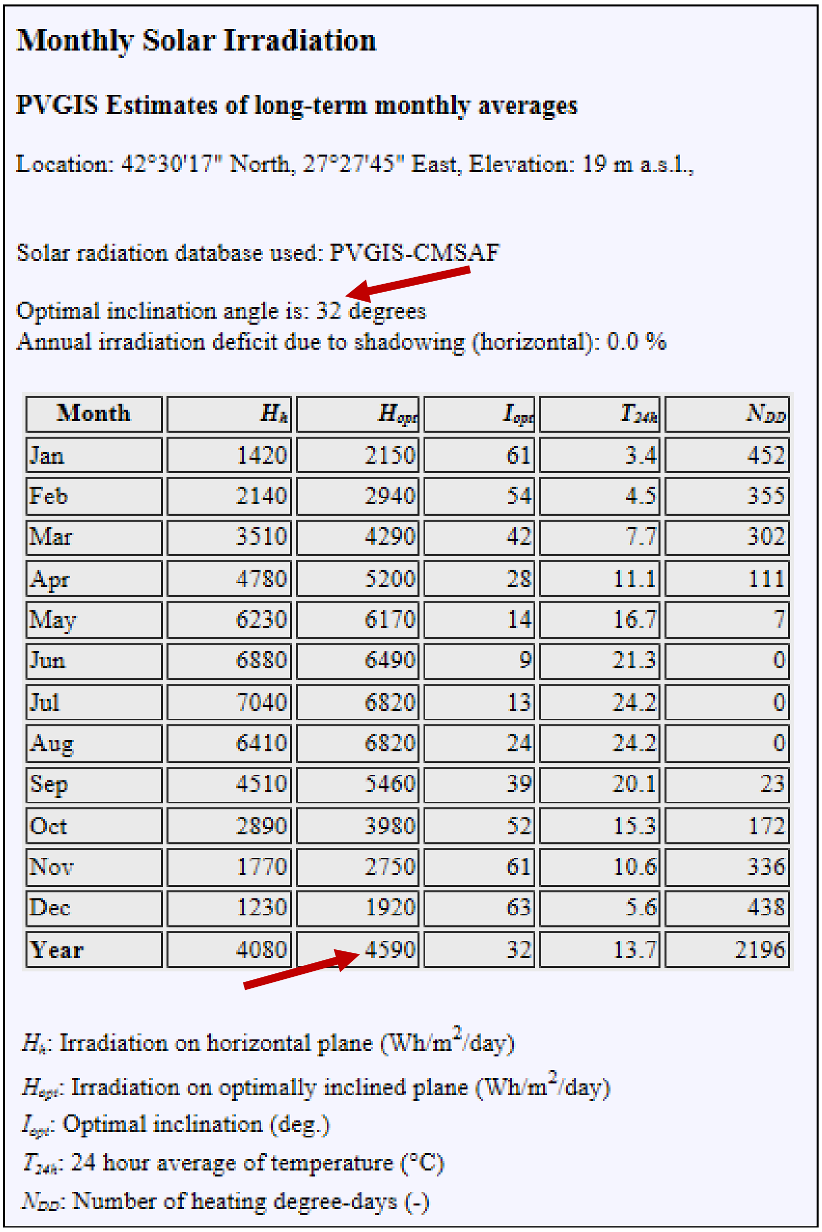
$$Energy\ Generation\ =\ FLH * Power\quad [kWh] \tag{2}$$

This formula (2) would apply in case of a 100% efficiency of the PV systems but there are always losses available. Therefore, one important factor, quantifying the impact of losses on the rated output, has to be added here, called performance ratio (PR) of the system: *"The PR is an internationally introduced measure for the degree of utilization of an entire PV system. It indicates the overall effect of losses on the PV system's rated output due to array temperature, incomplete utilization of the irradiation, and system component inefficiencies or failures. The PR is defined in IEC 61724 as the ratio of final PV system yield (Yf) to so-called reference yield (Yr)"* [20]. It is practically not possible to avoid losses per 100% but the idea is to minimize them and making the system more efficient. High performance PV plants can achieve PR values up to 80% [25]. After adding the influence of the losses characterized by the PR of the PV system, the enhanced formula (2) looks as follow:

$$\boldsymbol{Energy\ Generation\ =\ FLH * Power * PR\quad [kWh]} \tag{3}$$

or

$$\boldsymbol{Power\ = (Energy\ Generation)/(FLH\ *\ PR)\quad [kW]} \tag{4}$$



Monthly Solar Irradiation

PVGIS Estimates of long-term monthly averages

Location: 42°30'17" North, 27°27'45" East, Elevation: 19 m a.s.l.,

Solar radiation database used: PVGIS-CMSAF

Optimal inclination angle is: 32 degrees
Annual irradiation deficit due to shadowing (horizontal): 0.0 %

Month	H_h	H_{opt}	I_{opt}	T_{24h}	N_{DD}
Jan	1420	2150	61	3.4	452
Feb	2140	2940	54	4.5	355
Mar	3510	4290	42	7.7	302
Apr	4780	5200	28	11.1	111
May	6230	6170	14	16.7	7
Jun	6880	6490	9	21.3	0
Jul	7040	6820	13	24.2	0
Aug	6410	6820	24	24.2	0
Sep	4510	5460	39	20.1	23
Oct	2890	3980	52	15.3	172
Nov	1770	2750	61	10.6	336
Dec	1230	1920	63	5.6	438
Year	4080	4590	32	13.7	2196

H_h: Irradiation on horizontal plane (Wh/m^2/day)

H_{opt}: Irradiation on optimally inclined plane (Wh/m^2/day)

I_{opt}: Optimal inclination (deg.)

T_{24h}: 24 hour average of temperature (°C)

N_{DD}: Number of heating degree-days (-)

Figure 24. Monthly solar irradiation at optimal inclination angle for Burgas [24]

In the current calculation was assumed a performance ratio of 75% for both systems. Having all the needed values it´s now possible to calculate the power of the both PV plants:

- Small PV plant:

$$\boldsymbol{Power(small)} = \mathbf{45,35}\ [\boldsymbol{GWh}]/(\mathbf{1.675,35}\ [\boldsymbol{h}] * \mathbf{75}\ [\%]\ ) = \mathbf{36.092,3}\ [\boldsymbol{kW}] \qquad (1)$$

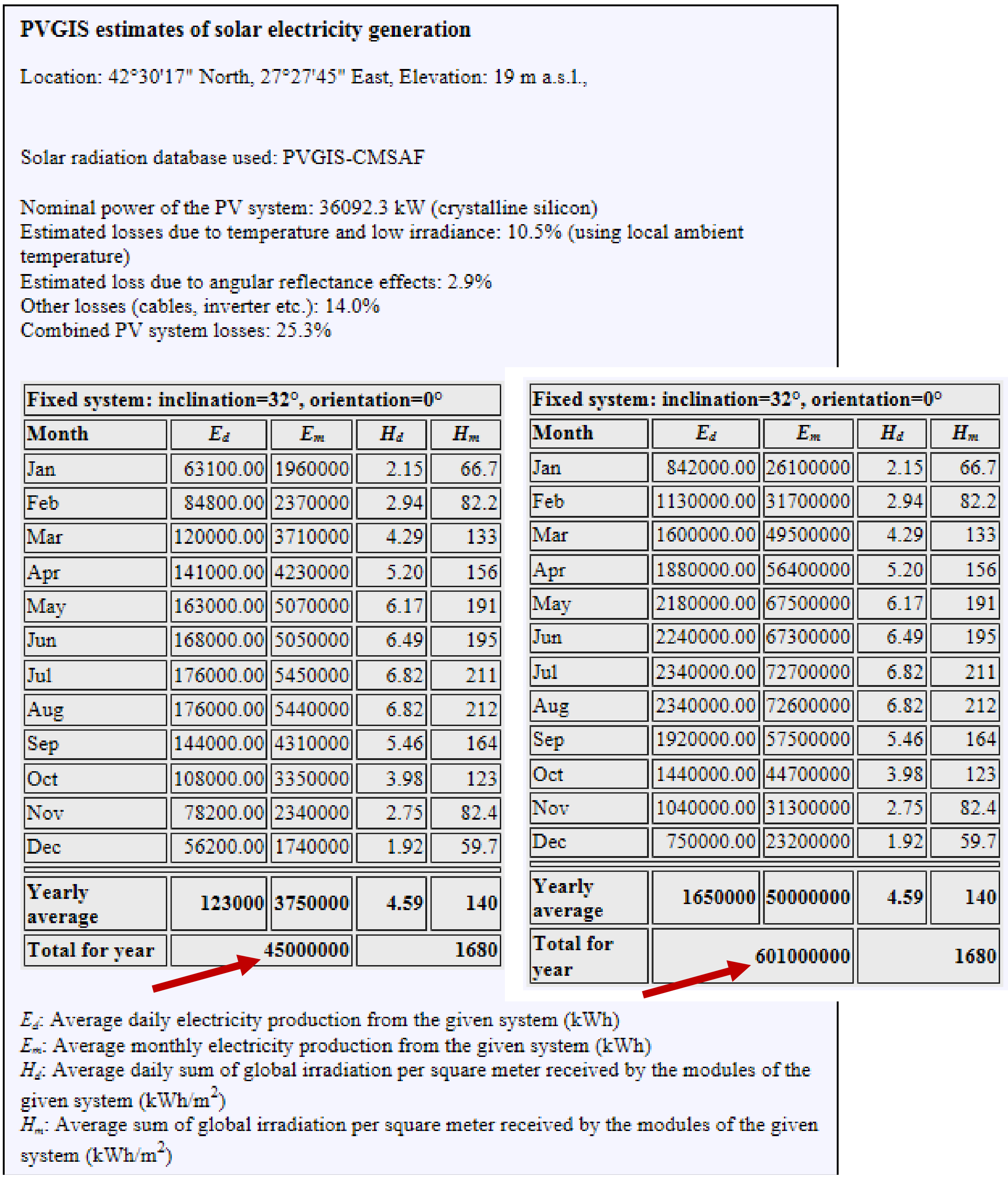
- Large PV plant:

$$\boldsymbol{Power(large)} = \mathbf{604,7}\ [\boldsymbol{GWh}]/(\mathbf{1.675,35}\ [\boldsymbol{h}] * \mathbf{75}\ [\%]\ ) = \mathbf{481.257,46}\ [\boldsymbol{kW}] \qquad (2)$$

After entering the obtained values for nominal power of the PV systems into the PVGIS estimation tool for further calculation (Figure 25) following results for yearly energy generations were achieved:

$\boldsymbol{E\ year\ (small)} = 45\ [GWh]$ and $\boldsymbol{E\ year\ (large)} = 601\ [GWh]$

Both results confirm the values for yearly energy generation of the PV plants calculated in chapter 2.1. There are only very small, less than 1 %, deviations observed (-0,77 % for the small PV plant and -0,61 % for the large one).



PVGIS estimates of solar electricity generation

Location: 42°30'17" North, 27°27'45" East, Elevation: 19 m a.s.l.,

Solar radiation database used: PVGIS-CMSAF

Nominal power of the PV system: 36092.3 kW (crystalline silicon)
Estimated losses due to temperature and low irradiance: 10.5% (using local ambient temperature)
Estimated loss due to angular reflectance effects: 2.9%
Other losses (cables, inverter etc.): 14.0%
Combined PV system losses: 25.3%

Fixed system: inclination=32°, orientation=0°

Month	E_d	E_m	H_d	H_m
Jan	63100.00	1960000	2.15	66.7
Feb	84800.00	2370000	2.94	82.2
Mar	120000.00	3710000	4.29	133
Apr	141000.00	4230000	5.20	156
May	163000.00	5070000	6.17	191
Jun	168000.00	5050000	6.49	195
Jul	176000.00	5450000	6.82	211
Aug	176000.00	5440000	6.82	212
Sep	144000.00	4310000	5.46	164
Oct	108000.00	3350000	3.98	123
Nov	78200.00	2340000	2.75	82.4
Dec	56200.00	1740000	1.92	59.7
Yearly average	**123000**	**3750000**	**4.59**	**140**
Total for year	**45000000**		**1680**	

Fixed system: inclination=32°, orientation=0°

Month	E_d	E_m	H_d	H_m
Jan	842000.00	26100000	2.15	66.7
Feb	1130000.00	31700000	2.94	82.2
Mar	1600000.00	49500000	4.29	133
Apr	1880000.00	56400000	5.20	156
May	2180000.00	67500000	6.17	191
Jun	2240000.00	67300000	6.49	195
Jul	2340000.00	72700000	6.82	211
Aug	2340000.00	72600000	6.82	212
Sep	1920000.00	57500000	5.46	164
Oct	1440000.00	44700000	3.98	123
Nov	1040000.00	31300000	2.75	82.4
Dec	750000.00	23200000	1.92	59.7
Yearly average	**1650000**	**50000000**	**4.59**	**140**
Total for year	**601000000**		**1680**	

E_d: Average daily electricity production from the given system (kWh)
E_m: Average monthly electricity production from the given system (kWh)
H_d: Average daily sum of global irradiation per square meter received by the modules of the given system (kWh/m^2)
H_m: Average sum of global irradiation per square meter received by the modules of the given system (kWh/m^2)

Figure 25. PVGIS estimates of solar electricity generation [24]

From both tables shown on Figure 24 Figure 25 can also be gathered the monthly values for solar irradiation and respectively electricity generation for the considered small and large scale PV plants in the region of Burgas. These values are understandably high in the summer months Mai-August and low during the winter period.

The daily and seasonally intermittency of electricity generated by PV (and wind power) plants raises up the question of storage the excess energy in the times of overproducing. Batteries are the most common method used for storage of the surplus energy. Pumping of water upwards, producing of hydrogen (H2) by splitting the water molecules through electrolysis or Power-to-Gas technology are other methods for storage used nowadays. Interesting to be shortly mentioned here are some new storage technologies especially suitable for sea coast regions like Burgas and partly already applied in Germany and Canada, like underwater using of spheres made of concrete (Figure 26) or special nylon balloons (Figure 27), both based on using the water pressure force. The energy is stored by pumping of water out of the concrete balls in the first method and pumping of air into the balloons in the second. The energy generation out of the stored amount is realized in the first technique by small turbines mounted atop of each ball and driven by flowed in water. In the second technique, onshore turbines are driven by stored compressed air.

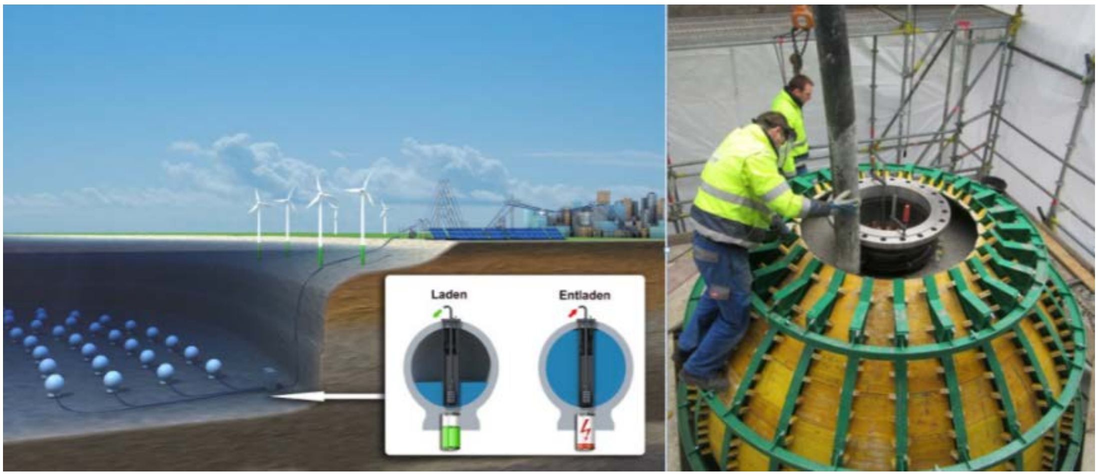


Figure 26. Storage of energy in concrete balls on the see ground in Germany [26]

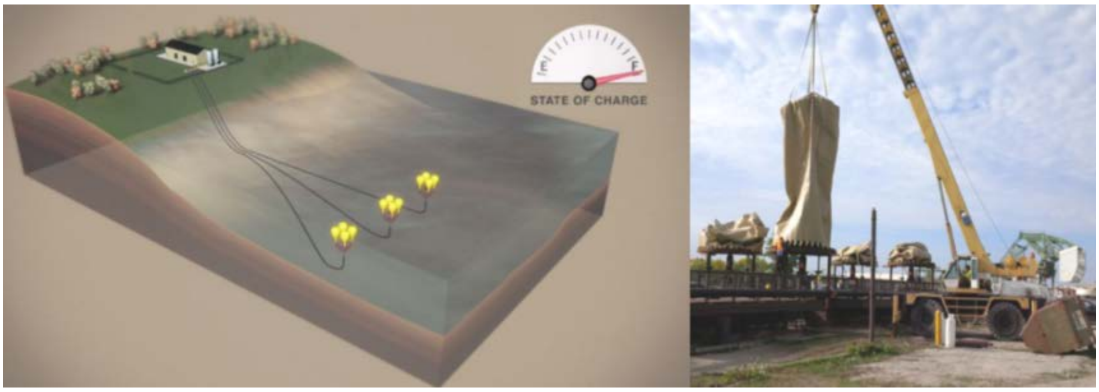


Figure 27. Hydrostor - storage of energy in nylon balloons in Ontario Lake,Canada [26]

In addition, there is a new membrane separating technology invented by the group of Prof. Michael Harasek from the Institute of Chemical Engineering at the TU Wien. It enables on the one hand combination of biogas with Power-to-Gas plants (Figure 28) and on the other, energy efficient transportation of through electrolysis produced H2 in the existing gas grid and directly use of the hydrogen with purity of 99,97 % for electricity production in fuel cells (Figure 29) [27, 28].

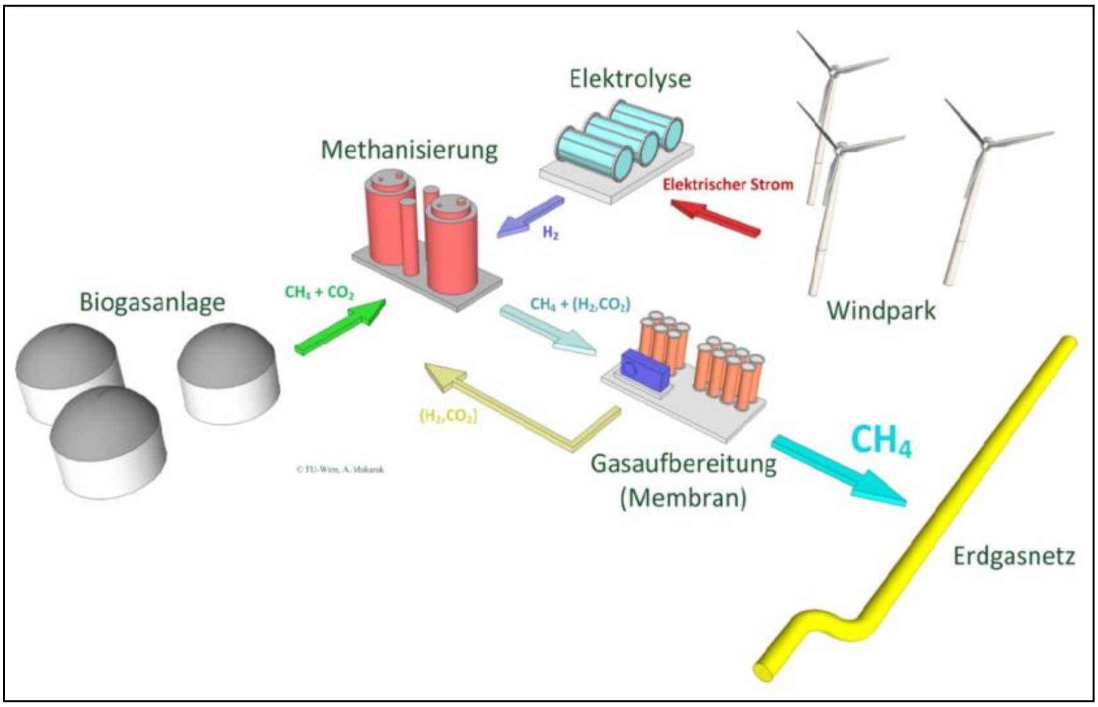


Figure 28. Flow chart of the power-to-gas system developed at TU Wien [27]

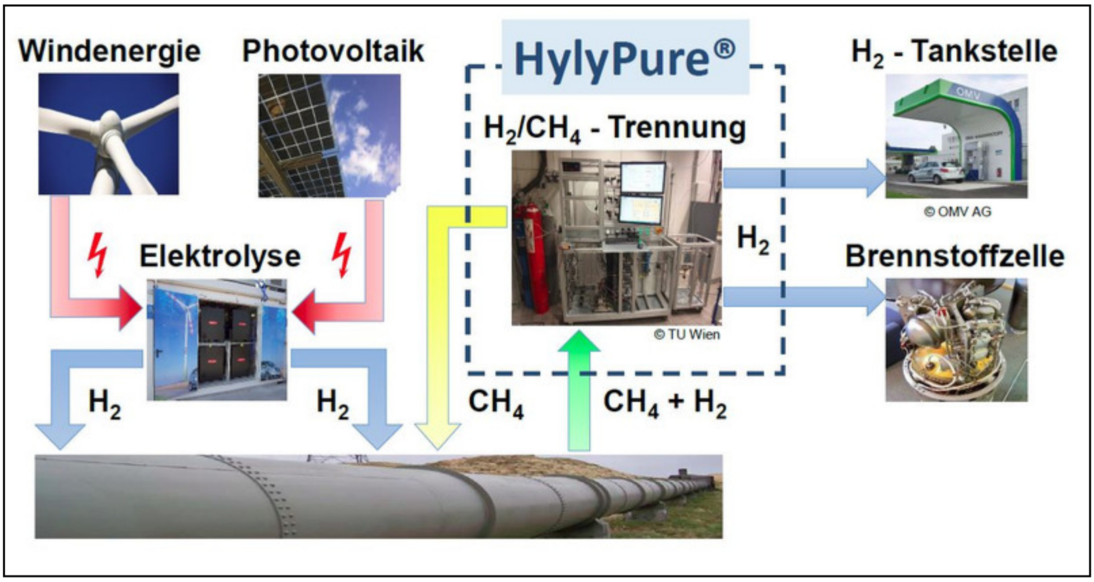


Figure 29. Supply of green hydrogen by means of HylyPure® developed at TU Wien [28]

Because of relatively high investment costs and not attractive Feed In Tariffs (FIT) in Bulgaria storage systems should not be implemented. However, especially in the case of the large-scale PV plant, eventually combined with a wind power plant and appropriate financial support from the EU, a later utilization of some of the above-mentioned technologies could be conceivable.

Being not only a student but also an employee at the Vienna University of Technology (TU Wien), the author would like to point one more innovation, named Heliofloat. The group of Prof. Markus Haider, from the Institute for Lightweight Design and Structural Biomechanics, developed lightweight constructions (Figure 30 and Figure 31) that create new space for solar energy out on the water. The hundred meters long platforms remain steady and stable even in rough sea weather. Besides solar power plant application, Heliofloat offers new possibilities for desalination plants and biomass extraction processes for salt water or even for protecting lakes against drying up in hot regions. At the same time, the platforms allow sunlight to penetrate through to the water, ensuring that the aquatic ecosystems are not negatively impacted. Heliofloat was presented to the public at the Hanover trade fair 2016 [29]. Especially for the coast located Burgas this could be a good technological solution in the future.

Figure 30. Heliofloat – a floating lightweight platform for PV power plants [29]

Figure 31. Heliofloat - offshore platforms for solar power plants [29]

3.4 Ecological appraisal of the selected / proposed applications / installations

The production of PV modules has shown a huge increase in the last 20 years growing up from 80 MWp in 1995 to 46.000 MWp in 2014 [20]. In this period has been observed a continuing conversion efficiency growth of the PV cells and reduction of electricity use for production of the modules. Efforts have also been made in reducing the thickness of silicon wafer used in PV modules to save expensive high-grade silicon materials. This impressive growth and the big potential of PV as a RES make the analysis of their environmental impact by Life Cycle Assessment (from “cradle” to “grave” analysis) very important. Figure 32 below displays the process flow how for PV panels the life cycle starts with the extraction of raw materials (cradle) and ends with the disposal (grave) or reuse, recycling and recovery (cradle).

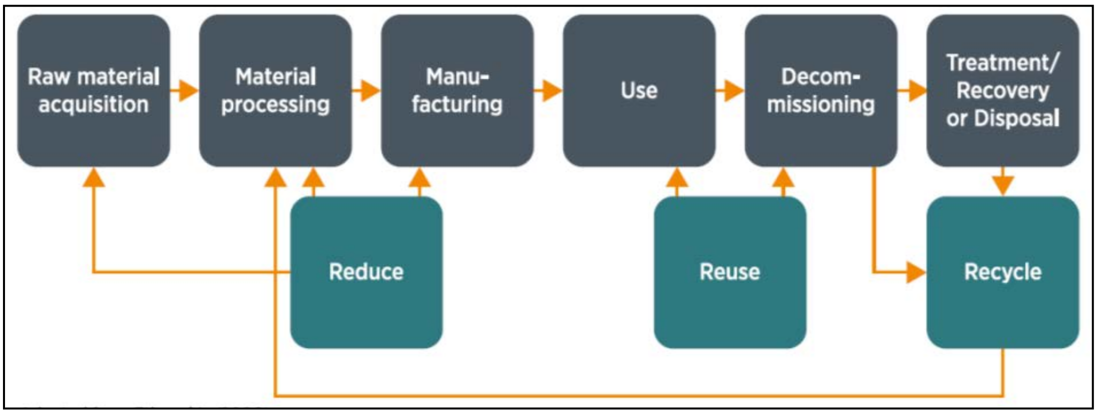


Figure 32. Process flow diagram of the life cycle stages for PV panels [31]

The LCA for PV systems is based on the determination of the Energy Payback Time (EPBT) and life cycle greenhouse gas emissions. The EPBT describes the period needed for a renewable energy system to generate the same amount of energy that was used for producing of the system itself [20]. The EPBT is determined by the insolation strength in the mounting area, the conversion efficiency of the PV system and the technology applied for producing the modules. In areas with higher solar irradiation values the EPBT decrease due to higher amount of generated electricity. And vice versa the EPBT increase by applying of technologies for producing of modules with higher efficiency due to increased energy demand (Figure 33).

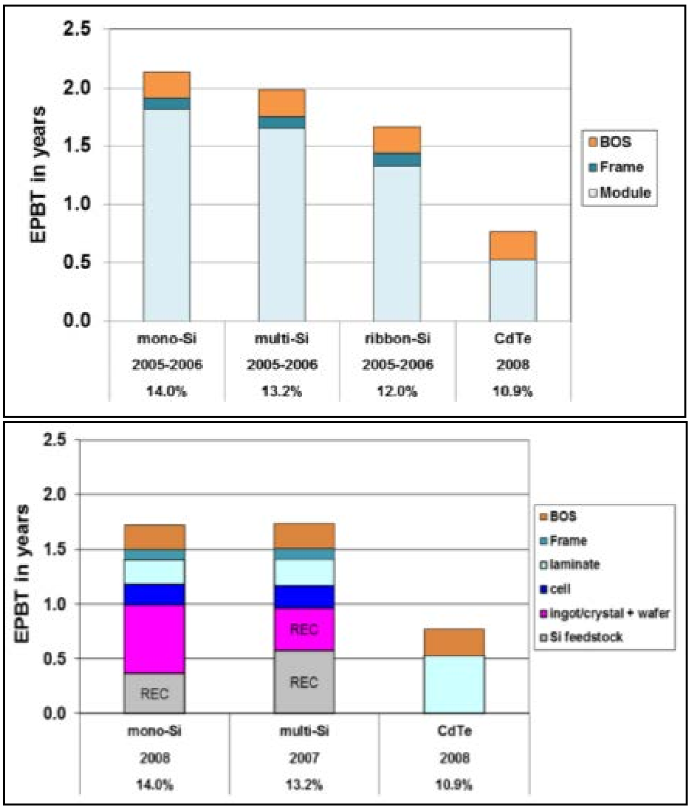
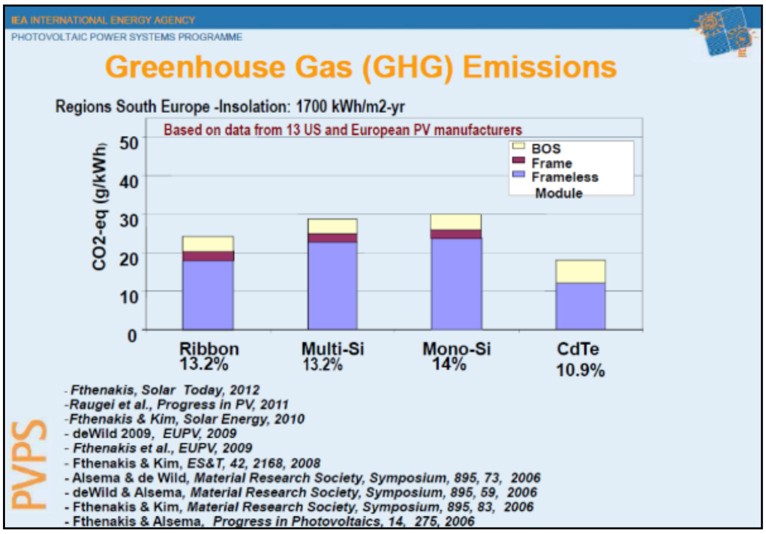


Figure 33. EPBT of rooftop mounted PV systems (2005-2008) [32]

The graphs (Figure 33, Figure 34) are based on Southern European irradiation of 1.700 kWh/m²/year and performance ratio of 0,75 [32]. The solar irradiation of Burgas obtained from the PVGIS calculation tool is with its 1.675,35 kWh/m²/year very closed to this value (see chapter 3.3). In addition, the assumed performance ratio is the same, so that the data from Figure 34 will be used one-to-one for obtaining the GHG emission savings of both PV power plants.



IEA INTERNATIONAL ENERGY AGENCY
PHOTOVOLTAIC POWER SYSTEMS PROGRAMME

Greenhouse Gas (GHG) Emissions

Regions South Europe -Insolation: 1700 kWh/m2-yr

Based on data from 13 US and European PV manufacturers

- *Fthenakis, Solar Today, 2012*
-*Raugei et al., Progress in PV, 2011*
-*Fthenakis & Kim, Solar Energy, 2010*
- deWild 2009, *EUPV, 2009*
- *Fthenakis et al., EUPV, 2009*
- Fthenakis & Kim, *ES&T, 42, 2168, 2008*
- Alsema & de Wild, *Material Research Society, Symposium, 895, 73, 2006*
- deWild & Alsema, *Material Research Society, Symposium, 895, 59, 2006*
- Fthenakis & Kim, *Material Research Society, Symposium, 895, 83, 2006*
- Fthenakis & Alsema, *Progress in Photovoltaics, 14, 275, 2006*

Figure 34. Life cycle GHG emissions of PV systems [20]

As explained in chapter 3.2, mono-Si modules will be used in both plants. According to Figure 34 the GHG emissions for this technology are 30 g/kWh of CO2 equivalent. This leads to following results:

- Small PV plant:

$$GHG\ emis.(small) = 45{,}35\ [GWh] * 30\ [g\ CO2\ eq/kWh] = 1.360{,}5\ [t\ CO2\ eq] \qquad (3)$$

- Large PV plant:

$$GHG\ emis.(large) = 604{,}7\ [GWh] * 30\ [g\ CO2\ eq/kWh] = 18.141\ [t\ CO2\ eq] \qquad (4)$$

Compared with BD plant the PV plant is much more environmental friendly. Having into account the GHG emissions of 45,6 [g CO2-eq/MJ] means 164,16 [g CO2-eq/kWh][6] for rape seed BD (Figure 7) and compare them with the 30 [g CO2-eq/kWh] for mono-Si system one can see the 5,5 times less emissions on the account of PV technology. Going further and using the energy consumption data of EV (15,5 kWh/100 km) and BD car (46 kWh/100 km) (see chapter 2.1) is visible that the EV, charged with PV produced electricity, is *over 16 times more ecological friendly* than the BD car:

- Greenhouse gas emissions of EV:

$$GHG(EV) = 15{,}5\ [kWh/100km] * 30\ [g\ CO2\ eq/kWh] = 465\ [g\ CO2\ eq/100km] \qquad (5)$$

- Greenhouse gas emissions of BD driven car:

$$GHG\ (BD) = 46\ [kWh] * 164{,}16\ [g\ CO2\ eq/kWh] = 7.551{,}4\ [g\ CO2\ eq/100km] \qquad (6)$$

Another environmental impact could be the land use change (LUC) which especially in the case of large scale BD, PV and wind power plants should be taken into account but will not be considered in this work.

There is also one more important ecological factor, which should be paid attention to in the near future. At the present, there is hardly any module waste, but the live time of the PV modules is assumed to be about 25 years. This means that after some years a huge amount of end-of-life PV components can be expected all over the world. Their recycling should have as less environmental impact as possible. So new steps are being implemented now in the waste management of the life cycle of PV components – firstly reducing of material and energy demand during production, then further

---

[6] 1 kWh = 3,6 MJ

reusing of old components and only then, as least preferred step, recycling of the left amount of real waste that is no more possible to be reused (Figure 32, Figure 35).

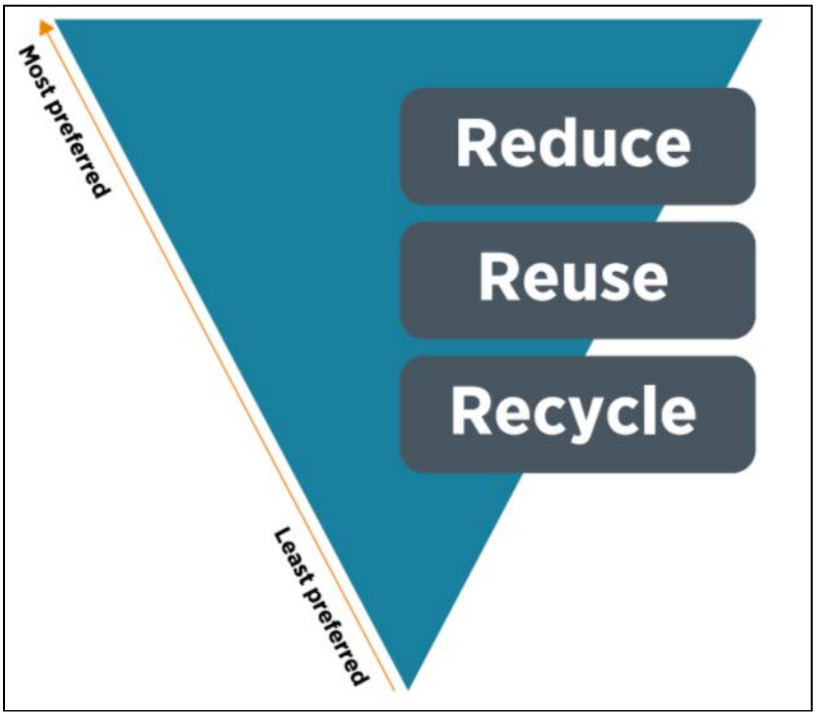


Figure 35. Preferred options for PV waste management [31]

3.5 Economic appraisal of the selected / proposed applications / installations

For the economic analysis of the PV plants will be used the same calculation sheet like in BD (chapter 2.5) adapted to the PV technology with its parameters (Table 6). Taking into account the current average end-customer price of 1.270 €/kWp for installed rooftop PV systems up to 100 kWp in Germany (Figure 36) and the installation cost of 860 €/kWp for Bulgaria, obtained from the paper of Velinov and Stefanov from the Bulgarian University of Mining and Geology in Sofia [33], following assumption for the PV installation cost per kW for the region of Burgas have been made:

- Small-scale PV plant: 1.100 €/kWp
- Large-scale PV plant: 1.000 €/kWp

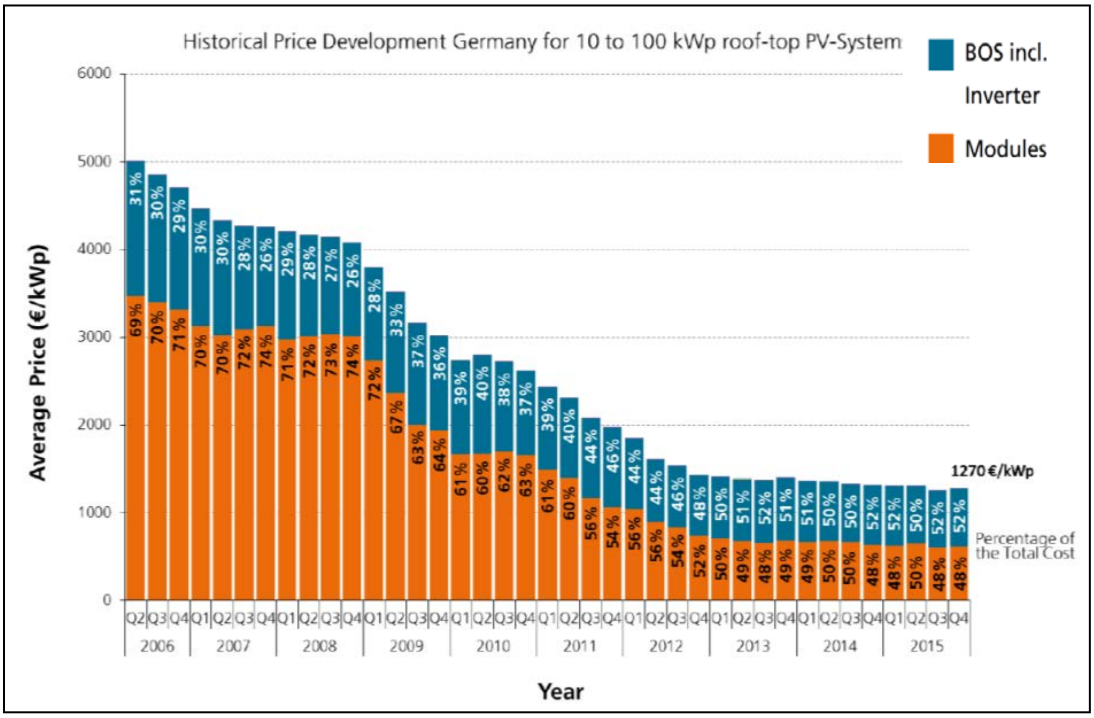


Figure 36. Development of aver. end-customer price for installed roof PV systems [21]

Unfortunately, the financial support of larger PV plants has been lowered more and more in the last years in Bulgaria. With the beginning of 2014 a new state fee, applicable for PV and wind power plants, was established in Bulgaria. This state fee is equal to:

“FIT x QEP x 20 %, where “QEP” means the quantity of electricity, purchased from a producer” [34]. Moreover, the restrictions didn´t stop. While in 2013 the FIT for solar systems were still between 0,082-0,181 €/kWh, depended on installed capacity [35], so due to the RES decision (No. C-24 from 30. June 2015) of the Bulgarian Energy and Water Regulatory Commission, FIT can be applied for period of 20 years but only for roof-top and facade-integrated PV systems up to 30 kWp:

“ • up to 5 kWp: BGN 228,00 per MWh excl. VAT (about 0,108 € per kWh) with 1.460 hours on average per year

• 5- 30 kWp: BGN 211,71 per MWh excl. VAT (about 0,104 € per kWh) with 1.460 hours on average per year” [35].

For both PV plants observed in this work the above-mentioned facts mean that no FIT can be obtained. The only positive conclusion – no FIT, no state fee. The produced electricity can be sailed to a very low price of 0,03 €/kWh only. In addition there are large grid access and transmission taxes to be paid – 7,35 €/MWh yearly [36]. The sale price of the by PV produced electricity is already on a very low level and the taxes are already relatively high, so that the investment calculation will be theoretically done with the same amounts for the whole period, due to assumed low changes. The PV modules lifetime of 25 years defines the longer depreciation period (compared to the 10 years of BD plant). All other relevant data were obtained from literature research and expert interviews [37].

Table 6. Investment calculation for small and large PV plants [OC]

	Small-scale PV plant		Large-scale PV plant	
Technology	Monocristalline		Monocristalline	
System	Ground mounted		Ground mounted	
Power	36,09	MW	481,25	MW
FLH	1.675	h/y	1.675	h/y
Energy production	45,35	GW	604,7	GW
Investment Cost per kW	1.100	€/kW	1.000	€/kW
Total Investment	€ 39.699.000	€	481.250.000	€
Depreciation in	25	y	25	y
Equity in % of investment	25	%	25	%
Loan in % of investment	75	%	75	%
Term of loan	25	y	25	y
Interest rate of loan	8	%	8	%
Electricity sale price (No FIT)	0,030	€/kWh	0,030	€/kWh
Grid connection 1,25 €/MWh	€ 56.688	€	€ 755.875	€
Grid access&transm. 7,35 €/Mwhy	€ 333.323	€/y	4.444.545	€/y
Land per MW	25.000	m²/MW	25.000	m²/MW
Land m²	902.250	m²	12.031.250	m²
Land (to buy) price per Dekar	500	€/daa	500	€/daa
Total land price	451.125	€	6.015.625	€
Personnel	8	p	30	p
Total pers. cost 6.500 €/py + 2%/y	1.665.576	€	6.245.908	€
Maintenance 0,6% of investm.	€ 238.194	€/y	€ 2.887.500	€/y
Insurance 0,6% of investm.	€ 238.194	€/y	€ 2.887.500	€/y
NPV	**-€ 34.986.308**	**€**	**-€ 405.933.178**	**€**

The economic assessment of both plants was done on the same way like for BD plants in chapter 2.5 by calculation[7] of the Net Present Value. Unfortunately, also here both investments showed negative NPV (Table 6). Here even in a higher range when comparing the ratio investment/NPV of BD and PV plants.

Without FIT for PV plants above 30 kWp in Bulgaria since 2015, the electricity sale price has to be more as triple as higher (0,1023 €/kWh for the small and 0,0929 €/kWh

---

[7] See appendices 2.1-2.4

for the large PV plant) as the current one (0,030 €/kWh) in order to operate just above the break-even (see sensitivity analysis on Figure 37 and Figure 38). This higher electricity sale´s price level could be observed 3 years ago, but due to the mentioned resolution of the Bulgarian Energy and Water Regulatory Commission is no more available. Therefore, every investment into such PV plants in Bulgaria is now highly not recommendable. The world largest PV plant, “Agua Caliente” in the Arizona desert in USA, has 5,2 million solar modules and power of 290 MW. The 481 MW large PV project observed in this work, even if the NPV were positive, is practically not feasible for the region of Burgas due to such a huge needed investment in the economic poorest EU country Bulgaria.

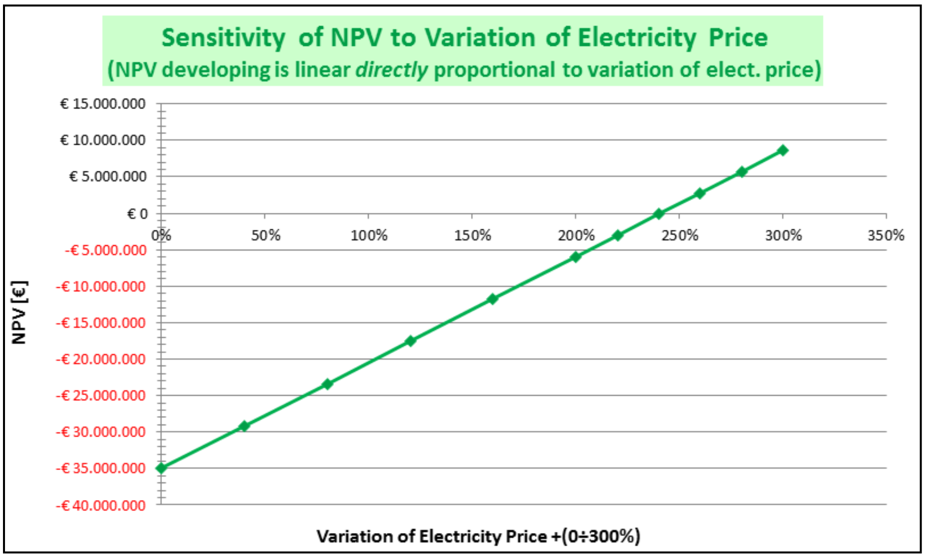


Figure 37. Sensitivity NPV <-> electricity price (Small-scale PV plant) [OC]

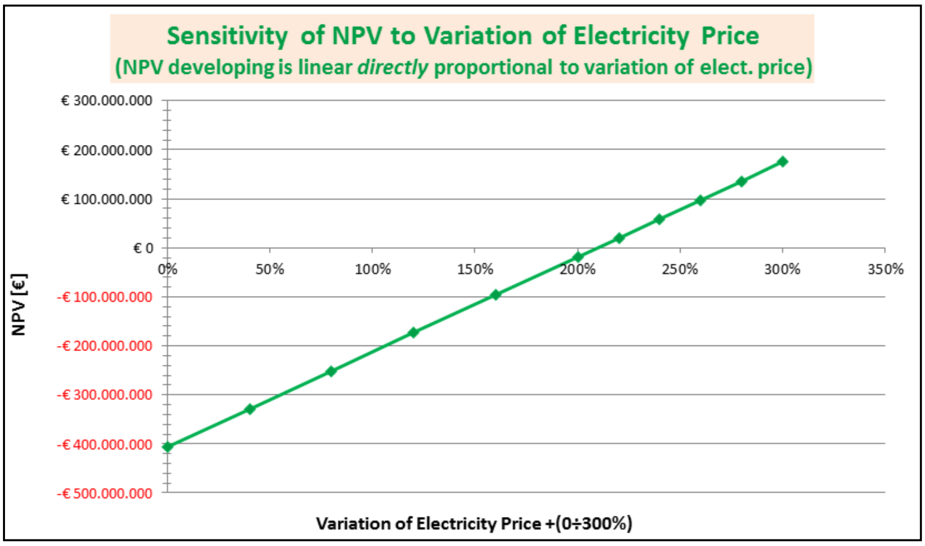


Figure 38. Sensitivity NPV <-> electricity price (Large-scale PV plant) [OC]

Comparing both BD and PV technologies for transport fuel production in the area of Burgas and having in mind the current legal and market price situation, investments cannot be recommended for anyone of the observed plants for now.

4 ASSESSMENT, ANALYSIS AND DISCUSSION OF THE SELECTED WIND ENERGY TECHNOLOGIES FOR TRANSPORT

4.1 Method of approach

For comparing the various renewable energy technologies, as objective of the first part of this master thesis, the main calculation steps for determination the equivalent size of the PV and wind power plants were already described in chapter 2.1. As shown there the annual energy output needed for covering the same service output, which was measured by the same distance driven with diesel and electrical vehicle, was estimated to be 45,35 GWh for the small-scale PV and wind power plants and respectively 604,7 GWh for the large ones.

The power output of the wind power plants will be calculated after analysis of the wind conditions in the region of Burgas. An appraisal of the environmental impact will be carried out by means of LCA including GHG savings analysis and compared with other technologies. And finally the economic evaluation will be done like in the other both fuel production methods, observed in this work, by calculating of the Net Present Values of the small and large scale projects. Data have been obtained through literature research and interviews with Tsalo Parvanov [37], a chef engineer working for years in the area of REN in Bulgaria and abroad.

4.2 Technological overview and description of the selected / proposed applications / installations

For thousands of years wind power has been used as an energy source for sailing and milling grains. The first usage of wind energy for electricity generation dates back to the 19th century, but the low price of fossil fuels at that time made it economically not attractive and caused stopping of further developments. Only 1973, forced by the world oil crisis, researches were put into action again and since the end of the 90s wind power has been taking an important part in the area of REN. Wind turbine technologies were developed in the whole world, especially in countries like Denmark, Germany and Spain. Moreover, while in the early 80s turbines began to appear with rotor diameters of 10-15 meters and rated power of 10-60 kW, so nowadays the offshore wind turbines have rotor spans over 140 m. and generators rated above 7 MW. A wind energy conversion system (WECS) consists of rotor, a gearbox (not always as there are gearless models too), a generator and power electronics with converter and control system (Figure 39). Power is transferred from the wind to the rotor, then passes through the gearbox, generator and power electronics until it finally gets fed into the electrical grid. There are different types of WECS but they all are based on the principle of converting the kinetic energy of the wind into electricity. According to the orientation of the rotation axis to the wind direction the wind turbines are divided into two categories: vertical axis wind turbine (VAWT) and horizontal axis wind turbine (HAWT). Typical VAWT are Savonius, Darrieus, H-rotor and Giromill turbines [38] with following advantages: easy maintenance for ground mounted generator and gearbox, utilization of wind from any direction and simple blade design and low cost of fabrication. But they have also some disadvantages, such as not self-starting, thus, the generator has to run as a motor at start, lower efficiency and difficulty in controlling blade over-speed. So the most common design of modern turbines became to be based on the horizontal axis principle. In this case, turbines are mounted on towers in order to catch stronger winds, respectively to harness more energy. The rotors here could be with one, two (for power up to 200 kW) or three blades. The three blades rotors are with about 95% the most common system due to lower noise level and better stability and efficiency. Depending on the positioning of the rotor to the wind, HAWT can be built with Luv- (upwind oriented rotors) and Lee- (downwind oriented rotors) [38]. The advantages of the horizontal turbines are the higher efficiency, the ability to turn the blades and the lower cost-to-power ratio. Although HAWT is the most widespread technology, there are also some disadvantages, such as difficult access for servicing, since the turbines are raised on towers and more complex design required for catching or going out of the wind [4]. A plant of many wind turbines builds so-called “wind farms”. They can be located

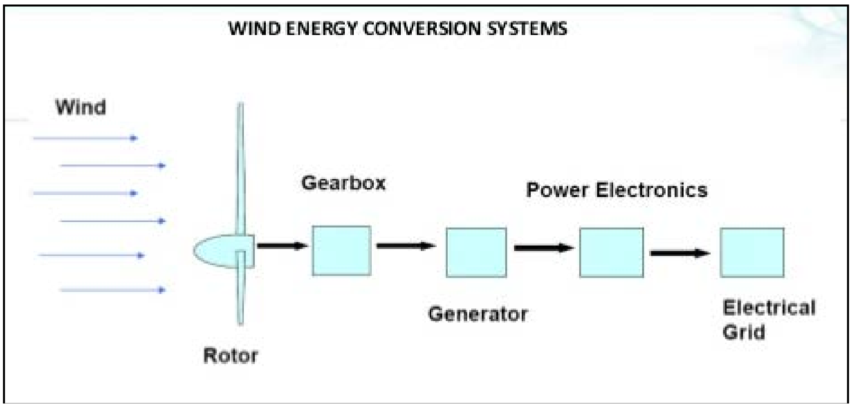


Figure 39. Wind Energy Conversion System (WECS) [39]

onshore with turbines in the range of 2-3 MW and offshore with generator´s power already above 7 MW. Turbine performance depends on wind velocity and turbulence, tower height, span of the rotor blades and air density. Therefore, it is important to know the specific potential of the region chosen for installing the wind facility, and the conditions under which this potential has been obtained [40].

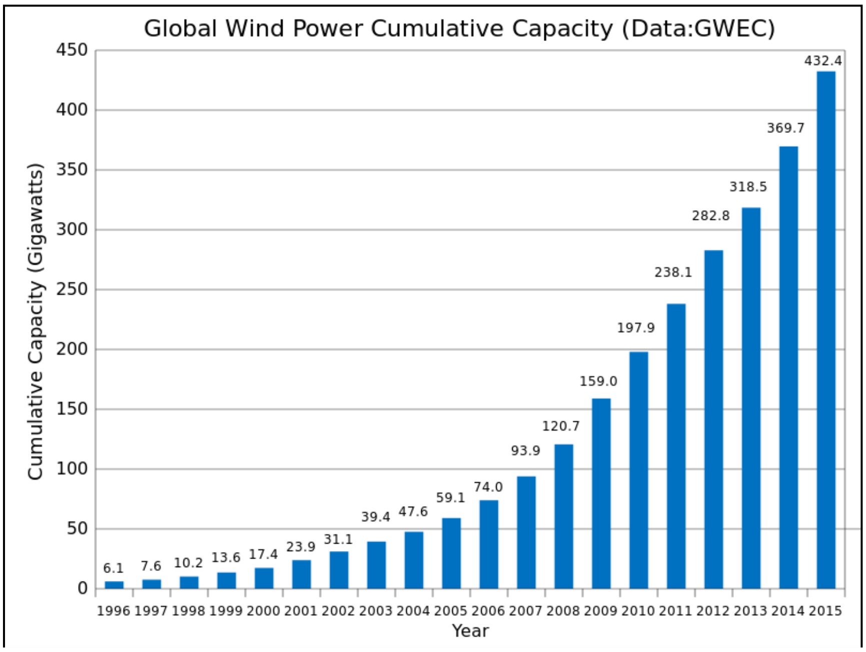


Figure 40. Global Wind Power Cumulative Capacity [GWEC, 2016]

A huge progress in the installed wind power capacity has been observed in the last 10 years. According to the Global Wind Energy Council (GWEC), the worldwide installed wind power capacity has increased from 6,1 GW in 1996 to 432,4 GW by the end of 2015 and raised by 17% compared to the previous year (Figure 40). Wind power's share of worldwide electricity usage at the end of 2014 was 3,1% [41] and should increase up to 18% by 2050 [42].

And how does the wind energy situation in Bulgaria look like? “*Studies show that due to its geographical location Bulgaria is with a favorable wind potential. The fully marine eastern border of the country* (the region were Burgas is located) *determines the invasion of the sea breeze up to 40 km inland. On the other hand, the western part includes many hilly and mountainous terrains in which the total wind resource is greater than those in the flat eastern part.*” [43] (Figure 41).

According to the European Wind Energy Agency (EWEA) up to 2012 large-scale prospects for wind energy development had spurred the construction of numerous wind farms, making Bulgaria one of the fastest-growing wind energy producers in the world at that time. But since 2012 the country has added very little and in the last two years no one new wind energy capacity as evidenced by the EWEA and Bulgarian Wind Energy Association (BWEA) statistical data below (Table 7 and Figure 42).

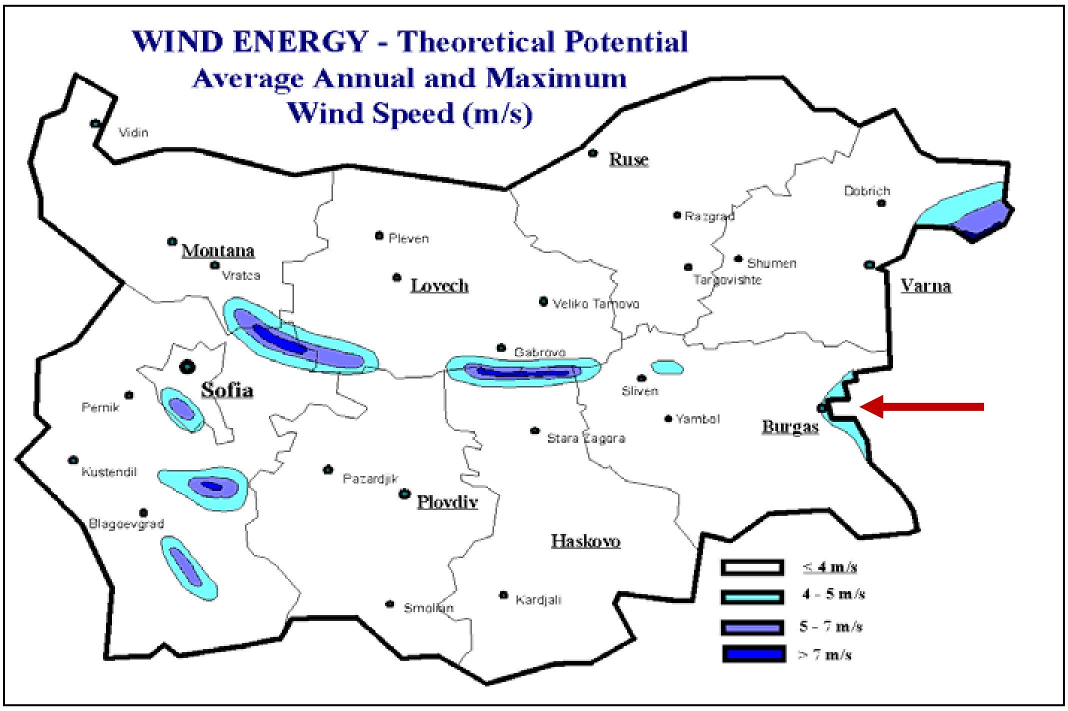
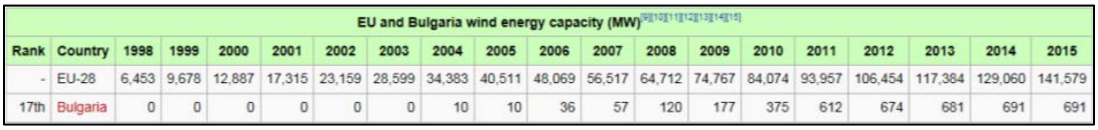


Figure 41. Wind energy potential in Bulgaria [40]

Table 7. Comparison of installed wind energy capacity in EU and Bulgaria [44]



EU and Bulgaria wind energy capacity (MW)[9][10][11][12][13][14][15]

Rank	Country	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
-	EU-28	6,453	9,678	12,887	17,315	23,159	28,599	34,383	40,511	48,069	56,517	64,712	74,767	84,074	93,957	106,454	117,384	129,060	141,579
17th	Bulgaria	0	0	0	0	0	0	10	10	36	57	120	177	375	612	674	681	691	691

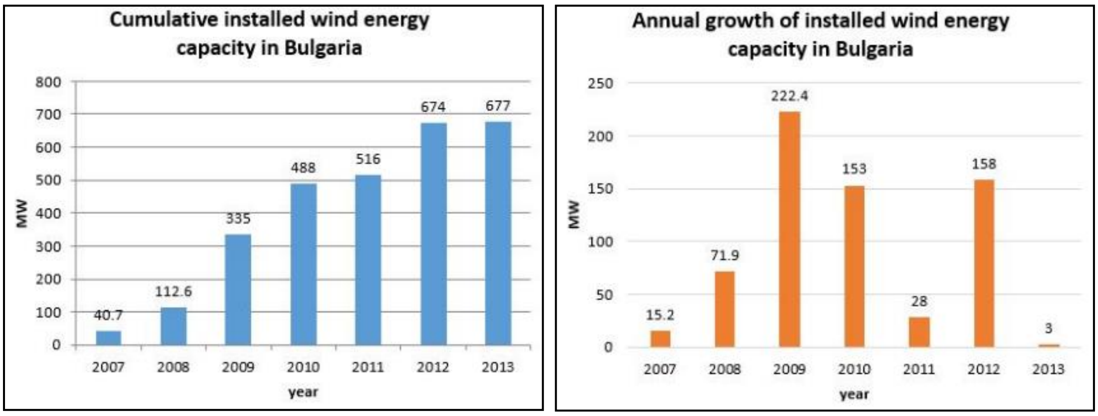


Figure 42. Wind energy in Bulgaria – cumulative installed and annual growth [45]

In the year 2015, electricity generated by wind turbines in Bulgaria is 1.436 GWh that is 3% of the total yearly produced electricity in the country [46].

4.3 Technological and energetic appraisal of the selected / proposed applications / installations

At the beginning of this chapter it´s important to be mentioned that the theoretical power contained in the wind depends among air density and area covered by the rotated rotor blades, much more from the cubed value of the wind velocity, to which it is directly proportional (Figure 43).

$$p_{th} = \frac{\rho}{2} A v^3$$

p_{th}	Theoretical power (in watts) contained in the wind
ρ	Air density (kg/m³), the air density is dependent on air pressure and temperature
A	Vertical surface or rotor swept area (m²) at right-angles (90°) to the wind
V	Flow speed of the wind (m/s)

Figure 43. Theoretical power of the wind [47]

Capturing all the energy of the wind passing through the area swept by the rotor blades is practically impossible, as this would mean that the wind after running through the turbine must immediately stop. Albert Betz, a German physicist and a pioneer of wind turbine technology, has indicated in 1919 the maximum power that can be extracted from the wind, independent of the design of a wind turbine in open flow. According to Betz's law, no turbine is able to capture more than 59,26% of the wind kinetic energy. The factor 0,593 (16/27) is known as Betz's coefficient Cp. However, there are also other factors, which decrease the efficiency, such as friction and drag of the rotor and losses in the gearbox, generator and power electronics (Figure 39). Practical utility-scale wind turbines achieve at peak 75% to 80% of the Betz limit, what means maximal efficiency of about 45% [49].

Detailed view of the connection between generated power and wind speed is given by a graph for each turbine. The power curves give an overview how much wind power per square meter of the rotor´s swept area is available and practically and theoretically obtainable by turbine from the at defined wind speed range (Figure 44).

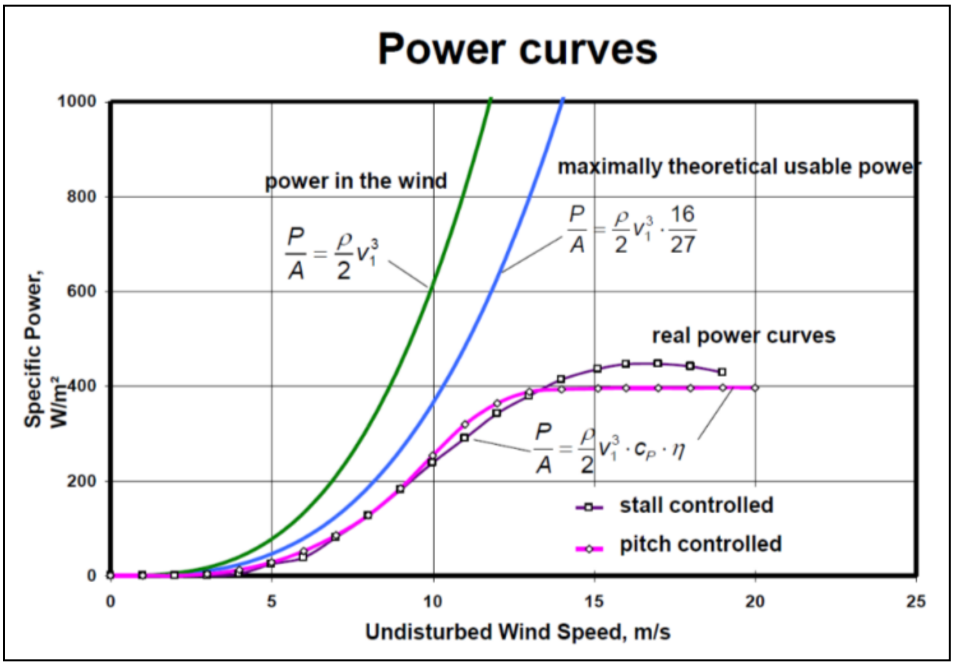
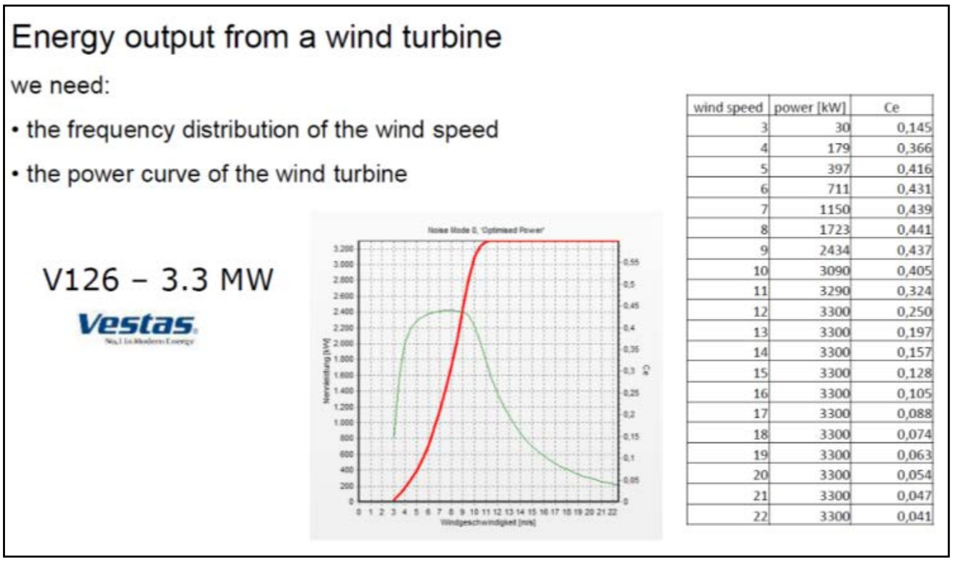


Figure 44. Power curves of wind turbines [48]

At the pre-beginning stadium of a wind power harvesting project precise measurements of the wind velocity and its frequency distribution for the chosen location have to be done with duration of at least one year or such already existing exactly data obtained from appropriate organisations. Then by having this data and the power curve of the intended wind turbine to be used, the expected annual electricity yield can be calculated (Figure 45, Figure 46).



Energy output from a wind turbine

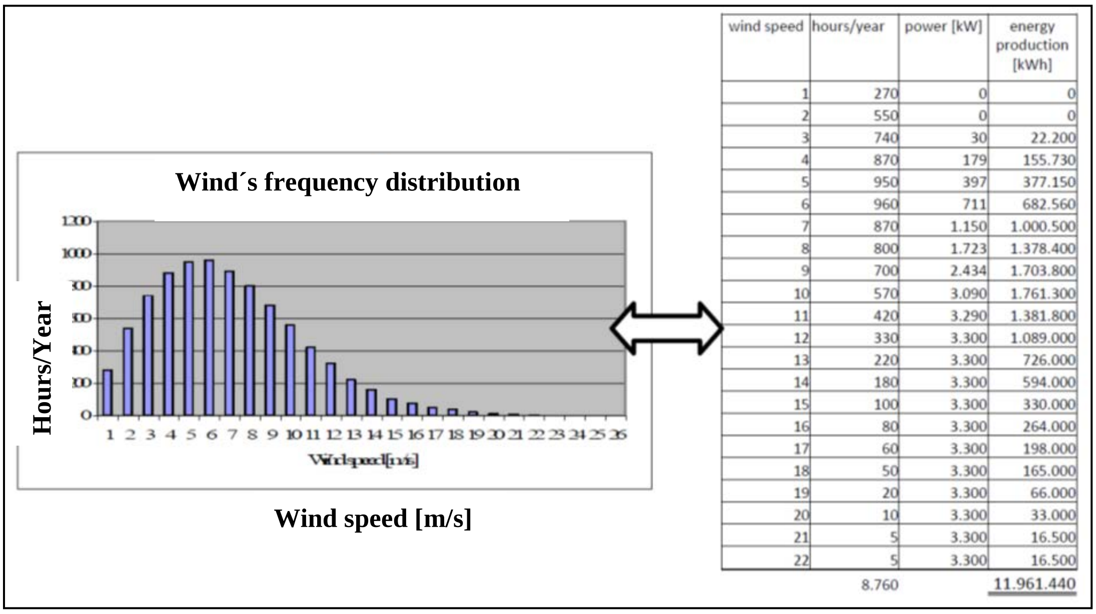
we need:

- the frequency distribution of the wind speed
- the power curve of the wind turbine

V126 – 3.3 MW

wind speed	power [kW]	Ce
3	30	0,145
4	179	0,366
5	397	0,416
6	711	0,431
7	1150	0,439
8	1723	0,441
9	2434	0,437
10	3090	0,405
11	3290	0,324
12	3300	0,250
13	3300	0,197
14	3300	0,157
15	3300	0,128
16	3300	0,105
17	3300	0,088
18	3300	0,074
19	3300	0,063
20	3300	0,054
21	3300	0,047
22	3300	0,041

Figure 45. Energy output from WT Vestas V126 – 3,3 MW [50]



wind speed	hours/year	power [kW]	energy production [kWh]
1	270	0	0
2	550	0	0
3	740	30	22.200
4	870	179	155.730
5	950	397	377.150
6	960	711	682.560
7	870	1.150	1.000.500
8	800	1.723	1.378.400
9	700	2.434	1.703.800
10	570	3.090	1.761.300
11	420	3.290	1.381.800
12	330	3.300	1.089.000
13	220	3.300	726.000
14	180	3.300	594.000
15	100	3.300	330.000
16	80	3.300	264.000
17	60	3.300	198.000
18	50	3.300	165.000
19	20	3.300	66.000
20	10	3.300	33.000
21	5	3.300	16.500
22	5	3.300	16.500
	8.760		11.961.440

Figure 46. Wind´s frequency distribution [50]

For the coarse calculations made in this work will be used the data from Figure 39, performed by 119 weather stations in Bulgaria, registered wind speed and direction through a period of 30 years [40]. According to this, the annual mean speed for the coast region of Burgas, measured in height of 10 m, is between 4-5 m/s. The selected turbines will be V90-3.0 MW [53] from the well-known Danish company Vestas. Its power curve is shown on Figure 47. The reason for choosing them is that 52 such turbines have already well approved themselves, being utilised since 2010 in the Bulgarian´s largest wind farm “Saint Nikola” with 156 MW total nominal power [51], located near to Varna, also on the Bulgarian´s Black Sea coast.

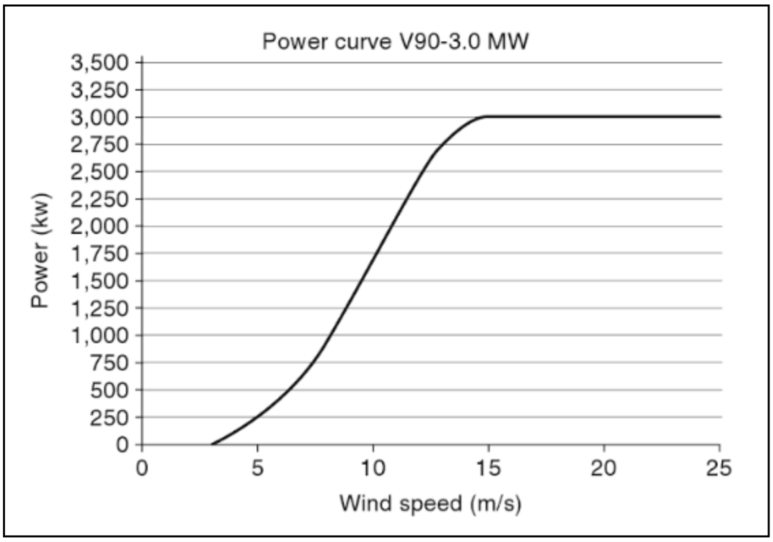


Figure 47. Power curve for Vestas V90-3.0 MW turbine [52]

By applying the formula from Figure 43 for the theoretical power contained in the wind and multiplying it with the power coefficient Cp that “*represents the aerodynamic efficiency of the rotor … and for large modern wind turbines is normally in the range 0,4 – 0,5*” [52], following value for the power that can be extracted by V90-3.0 MW from the wind in the region of Burgas is calculated as shown below. Air density *p* is dependent on air pressure and temperature. At sea level and at 15° C air has a density of approximately 1.225 kg/m³ [8]. The annual average temperature for Burgas is given with 17,2° C[9], so that taking into account the reduction table[10] *p* was assumed to an average value of 1.217 kg/m³. The area swept by the rotor blades of V90-3.0 MW is 6.362 m² [53]. As the wind speed data in Figure 39 is given for the height of 10 m a conversion to the real value in the hub height of 80 m for WT V90-3.0 MW was carried out by using the Volker-Quaschning SW-tool [54]. On this way was obtained the wind speed of 6,11 m/s.

$$\boldsymbol{P} = \frac{\mathbf{1{,}217}\ \left[\frac{kg}{m^3}\right] * \mathbf{6.362}\ [m^2] * \mathbf{6{,}11^3}\ \left[\frac{m}{s}\right] * \mathbf{0{,}4}}{\mathbf{2}} = \mathbf{353{,}2}\ [\boldsymbol{kW}] \tag{7}$$

The same result is coarse obtainable from the power curve of this turbine on Figure 47. This calculation shows that in the region of Burgas at mean wind speed of 6,11 m/s with the wind turbine V90-3.0 MW only less than **12% load rate** (percentage of the rated turbine power) can be achieved. If the wind velocity would increase with less than 1 m/s to 7 m/s then already over half megawatt can be produced. This indicates the large impact of the wind speed. Making the same calculation with a smaller turbine such as Mitsubishi MWT-1000A[11] with 1 MW power, swept area of 2.960 m² and hub height of 69 m (which leads to an wind speed of 6 m/s [54]), in use in some other wind farms in Bulgaria, one can see that only 155,6 kW could be extracted. Since other wind energy producers, such as the “Saint Nicola” 156 MW wind farm [51], also located on the Bulgarian coast has been using the Vestas V90-3.0 MW turbines, this model remains as selected in current work.

For further proceeding the possible full load hours has to be determined. As already presented in Table 7 the cumulative installed wind energy capacity in Bulgaria in 2015 was 691 MW. They generated 1.436 GWh of electricity [46]. So the mean amount of FLH for Bulgaria´s installed wind capacity can be calculated as follow:

---

[8] https://en.wikipedia.org/wiki/Density_of_air

[9] http://www.asen.iliev.name/weather/almanac.htm

[10] http://hvac-eco.com/bg/hvac-manual/27-air-properties.html

[11] http://en.wind-turbine-models.com/turbines/608-mitsubishi-mwt-1000a

$$\boldsymbol{FLH = \frac{Annual\ Energy\ Production\ [GWh]}{Installed\ power\ capacity\ [GW]} = \frac{1436\ [GWh]}{0{,}691\ [GW]} = 2078\ [h]} \quad (8)$$

Further estimation in this work will be based on the above calculated value of FLH. When the FLH is divided by the amount of hours in a year (8.760 h) one can get the capacity factor of the installed power capacity. In the above case the capacity factor is 2.078 / 8.760 = 23,7%. By coincidence the installed wind power in Bulgaria shows the same value as the mean capacity factor for installed wind power in EU-28 [46].

As described in the BD part of this work (chapter 2.1) the annual energy output needed for covering the same service output, which was measured by the same distance driven with diesel and electrical vehicle, was calculated to be 45,35 GWh for the small scale PV and wind power plants and respectively 604,7 GWh for the large ones. Knowing the annual energy needed to be generated and the FLH now is possible to compute the total power required for producing this electricity by using the formula (5) below:

$$\boldsymbol{Power = E/FLH \quad [kW]} \quad (5)$$

Consequently for the

- Small-scale wind farm:

$$\boldsymbol{Power(small) = (45,35\ [GWh])/(2.078\ [h]) = 21,82\ [MW]} \quad (9)$$

and respectively for the

- Large-scale wind farm:

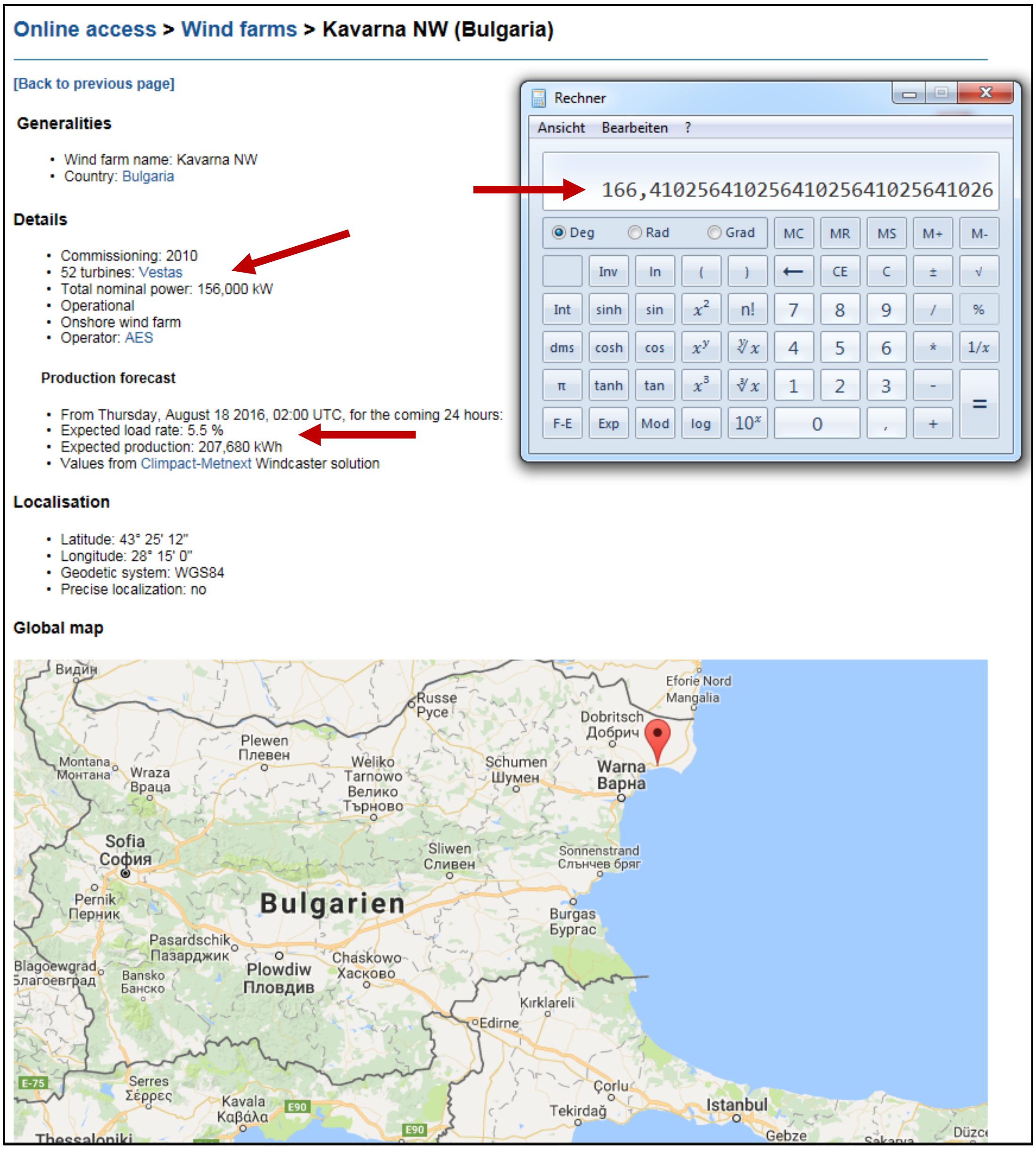
$$\boldsymbol{Power(large) = (604,7\ [GWh])/(2.078\ [h]) = 291\ [MW]} \quad (10)$$

were calculated.

By dividing above estimated total power values through the power that can be achieved with one turbine (**353,2 kW**) one gets the numbers of turbines required in both wind farms:

Number of turbines in the **Small-scale** wind farm: $\frac{\mathbf{21{,}82}\ [MW]}{\mathbf{353{,}2}\ [kW]} = \mathbf{62\ turbines}$ (11)

Number of turbines in the **Large-scale** wind farm: $\frac{\mathbf{291}\ [MW]}{\mathbf{353{,}2}\ [kW]} = \mathbf{824\ turbines}$ (12)



Online access > Wind farms > Kavarna NW (Bulgaria)

[Back to previous page]

Generalities

- Wind farm name: Kavarna NW
- Country: Bulgaria

Details

- Commissioning: 2010
- 52 turbines: Vestas
- Total nominal power: 156,000 kW
- Operational
- Onshore wind farm
- Operator: AES

Production forecast

- From Thursday, August 18 2016, 02:00 UTC, for the coming 24 hours:
- Expected load rate: 5.5 %
- Expected production: 207,680 kWh
- Values from Climpact-Metnext Windcaster solution

Localisation

- Latitude: 43° 25' 12"
- Longitude: 28° 15' 0"
- Geodetic system: WGS84
- Precise localization: no

Global map

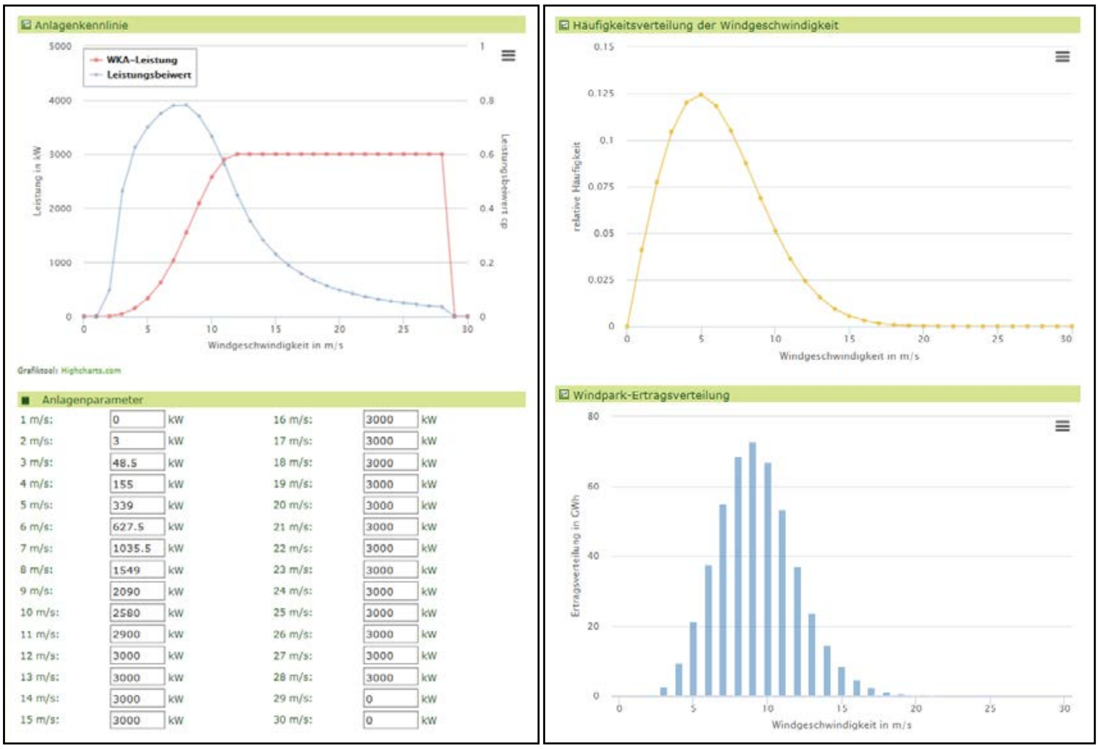
166,41025641025641025641025641026

Figure 48. Production forecast for “St. Nicola” 156 MW wind farm for 18th Aug.2016 [55]

The large-scale quantity of 824 WT in a farm is not realistic in Bulgaria. However, the 62 turbines wind farm, although not that small, is possible. Bulgarian´s largest wind farm “Saint Nicola” (Kavarna NW) mentioned above consists already of 52 Vestas WT V90-3.0 MW. According to the official production forecast (Figure 48) and expected wind velocity of 3,9 m/s (at 10 m height which equates to 5,3 m/s at 80 m hub height [54]) their expected electricity generation for 18th August 2016 was 207.680 kWh. By dividing this value through the number of turbines (52) and the daily amount of hours (24), ones gets **166,4 kW** of power extracted by each turbine from the wind near to

Varna or an expected load rate of only **5,5%** (also due to a lower power coefficient Cp at lower wind speed on the 18.08.2016). This calculation, carried out with real data from existing wind farm, that is also located on the sea coast and utilises the same turbines, just confirms the correctness of the estimations made above for the WT in the region of Burgas (**353,2 kW,** load rate ca. **12%** and average wind speed of **6,11 m/s** at 80 m hub height).

It has to be mentioned here again that this is only a coarse calculation. Especially having in mind that the wind speed is cubed in the formula, taking an average value can lead to large deviations. The precisely wind frequency distribution method that has to be used for electricity yield pre-calculations in real projects was described on previous pages in this chapter. Such simulated wind distribution is visualized on the Figure 49 below. These results were obtained with the above-mentioned SW-tool by inserting the technical and meteorological data for the small wind farm in Burgas. The power curve and the power coefficient Cp of the used WT Vestas V90-3.0 MW are shown in the left upper part of the figure.



Anlagenparameter

1 m/s:	0	kW	16 m/s:	3000	kW
2 m/s:	3	kW	17 m/s:	3000	kW
3 m/s:	48.5	kW	18 m/s:	3000	kW
4 m/s:	155	kW	19 m/s:	3000	kW
5 m/s:	339	kW	20 m/s:	3000	kW
6 m/s:	627.5	kW	21 m/s:	3000	kW
7 m/s:	1035.5	kW	22 m/s:	3000	kW
8 m/s:	1549	kW	23 m/s:	3000	kW
9 m/s:	2090	kW	24 m/s:	3000	kW
10 m/s:	2580	kW	25 m/s:	3000	kW
11 m/s:	2900	kW	26 m/s:	3000	kW
12 m/s:	3000	kW	27 m/s:	3000	kW
13 m/s:	3000	kW	28 m/s:	3000	kW
14 m/s:	3000	kW	29 m/s:	0	kW
15 m/s:	3000	kW	30 m/s:	0	kW

Figure 49. Power curve, coefficient Cp and wind distrib. for the small farm Burgas [54]

Some innovative energy storage technologies were described in chapter 3.3. As mentioned in the PV part of this work due to relatively high investment costs and not attractive FIT in Bulgaria storage systems should not be implemented. However, the seasonally weather conditions can be really helpful for supporting the constant energy supply. The wind on the Black Sea coast in Burgas is relatively week during the summer months July-August and strong in February-March. The intensity and duration of the sunshine is exactly other way around. This fact means that both electricity-generating methods can very well complete each other by producing more electricity from the wind energy in winter and from the sun in summer.

4.4 Ecological appraisal of the selected / proposed applications / installations

The environmental value of by wind power plants generated electricity can be seen as the decreasing of GHG emissions that would have been caused by a fossil fuel power plant generating the same amount of electricity. The directly emissions impact is near to zero but as already shown in the BD and PV parts of this work, the whole life cycle of the wind power systems has to be taken into consideration. The life cycle chart flows on Figure 50 and Figure 51 prepared by the Danish company Vestas whose turbines are used in this project work display the potential environmental impact of a wind power plant. It is obvious how many steps besides operation contribute to the whole impact and causes emissions to air, water and land.

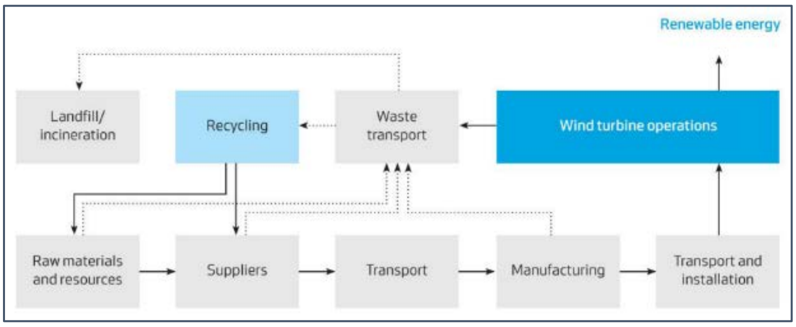


Figure 50. Life cycle of the wind power plant [56]

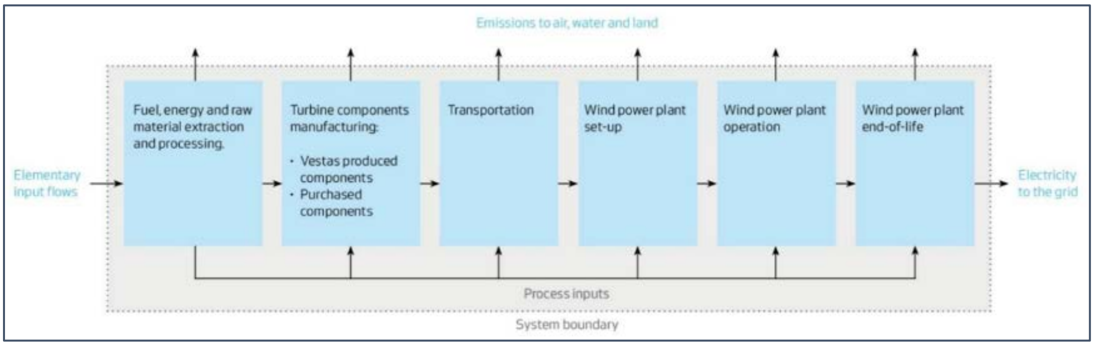


Figure 51. LCA for a 90MW onshore wind power plant of V90-3.0MW turbines [56]

In their assessment, Vestas classifies following potential environmental impacts divided into three groups [57]:

Environmental impacts:

- Global warming
- Ozone-depletion
- Acidification
- Nutrient enrichment (eutrophication)
- Photochemical ozone formation (smog)

Toxicity:

- Human toxicity
- Eco-toxicity

Waste:

- Bulk waste
- Slags and ashes
- Hazardous waste
- Radioactive waste

This Vestas LCA study is based on the V90-3.0 MW model and expresses a realistic site placement. Just to remember, the same WT have been utilized on the Bulgarian coast since 2010 and have been selected for the region of Burgas in this project work. As can be obtained from the Figure 52, the main impact sources are “production total” and “disposal”.

There is no any operation influence and the impact of transport is also that low, compared to the first both factors, that there is no indication for it in this diagram. There are also negative values for disposal, which has to be deducted from the positive columns. The reason is that recycling is applied in a high degree, so that there is a significant quantity of materials ready for new use.

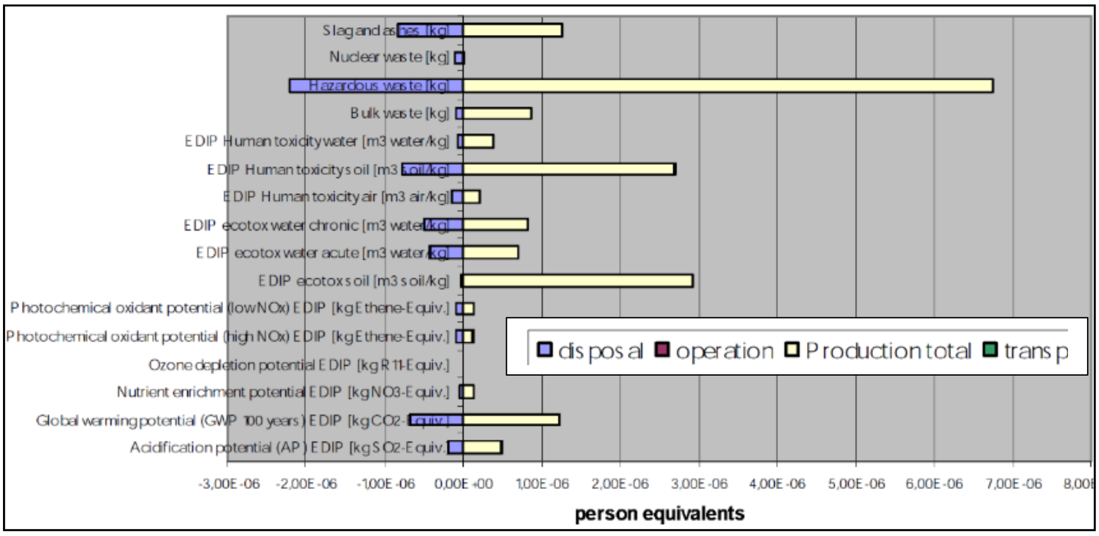


Figure 52. Environmental impacts from 1 kWh generated by V90-3.0 MW, *Onshore* [57]

Just to show the difference to offshore installed WT, on the next diagram (Figure 53) is presented the environmental impact for the same V90-3.0 MW turbines but with offshore location. The influence of operation (due to zinc discharge from the offshore cables during the operation stage) and transport (due to longer distances and heavier components) is already visible here. In general and logically, the eco impact of the onshore wind power plant to the soil is significantly higher and respectively significantly higher is the eco impact of the offshore wind power plant to the water [57].

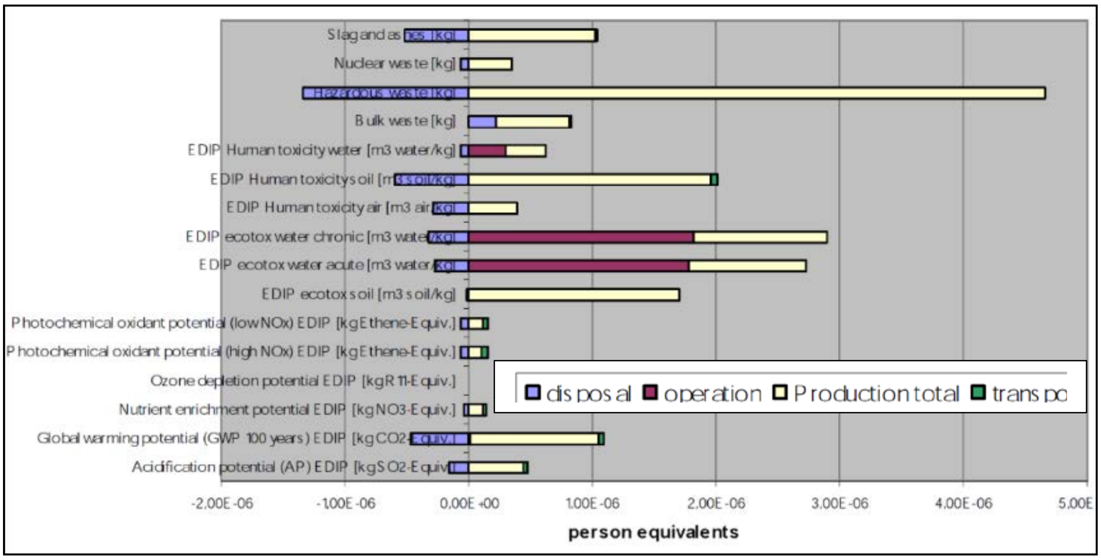


Figure 53. Environmental impacts from 1 kWh generated by V90-3.0 MW, *Offshore* [57]

In order to relate the environmental impacts to the average European electricity generation, Vestas compared 1 kWh electricity from the on- and offshore wind power plants with the average European electricity generation for 1990. As shown in the Figure 54, the environmental impacts of electricity generated by both wind power plants are considerably lower than from European average produced electricity in 1990. Of course, it is not really fair to compare 1 kWh average electricity generated in 1990 with 1 kWh of electricity generated by wind turbines in 2005-2025. However, the comparison is made to visualize the huge order of magnitude and to emphasise the large ecological potential of the clean electricity extracted from the power of the wind [57].

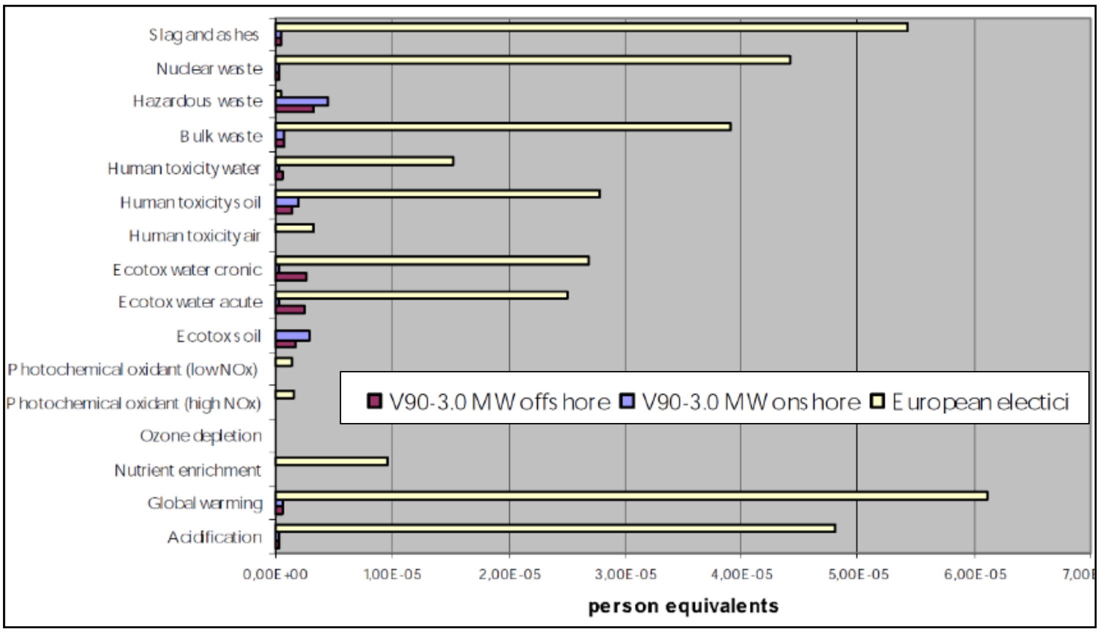


Figure 54. Comparison of 1 kWh generated by V90-3.0 MW and European electricity [57]

The offshore wind turbines produce more electricity than the onshore ones. However, it is more resource demanding to establish offshore wind power plants. These two parameters are almost compensated by each other, so that the global warming potential is nearly the same for offshore and onshore wind power plants per kWh (Figure 52-Figure 55) [57].

Figure 55 shows the potential impacts of global warming per kWh of electricity produced by V90-3.0 MW power plant.

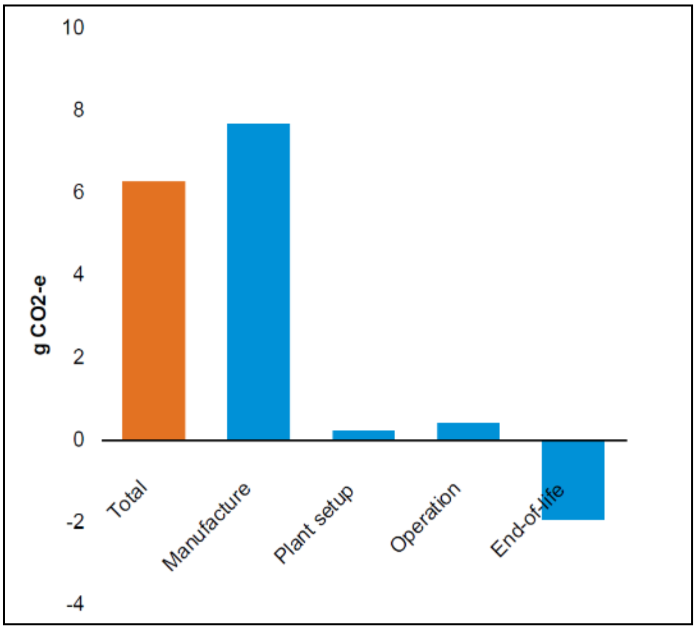


Figure 55. Contribution by life cycle stage to Global warming potential per kWh [56]

According to it, the total CO2-equivalent emission is only 6 g/kWh. This value is much lower than the 504 g/kWh of CO2-e global average emission factor for electricity[12]. "*As with other impact categories, it is the manufacturing stage that dominates the life cycle, with the production of the tower (26%), nacelle (17%), foundations (15%) blades (10%) and cables (7%), being the primary components contributing to this impact category. Vestas production and operations contribute around 7% of the global warming impacts. The end-of-life phase also has a significant contribution (-52%), providing environmental credits associated with avoided metal production of iron, steel, copper and aluminium. The emission to air of carbon dioxide (92%) is the primary contributing substance, which results from the combustion of fuels in production of the turbine raw materials, as well as methane (5%) resulting from steel production. Other lesser contributing substances to global warming potential include the release of sulphur hexafluoride gas to air (1%) from improperly disposed switchgears, and nitrous oxide (1%) from various production processes, including glass fibre production used in the blades*" [56].

As explained in chapter 3.4 the determination of the Energy Payback Time is the other significant part of the LCA. The EPBT also called return-of-energy describes the period for generating the same amount of energy that is required over the whole life

---

[12] https://www.worldsteel.org/dms/internetDocumentList/case-studies/Wind-energy-case-study/document/Wind%20energy%20case%20study.pdf

cycle of the wind plant and among other factors is mainly dependant of the wind speed and FLH. This energy payback period is measured in “months to achieve payback” Alternatively, energy payback may be measured by “number of times payback”, where it shows the number of times more energy the wind plant generates over its lifetime versus the amount consumed during its lifetime. According to Vestas homepage the EPBT for their turbines generally ranges between 5 to 12 months. With the example given there a V112-3.3 MW wind power plant has a payback period of 6,5 months for medium wind conditions[13]. And seen over its life time of 20 years it returns 38 times more energy back to society than it consumed, means that for 1 kWh of invested energy one gets 38 kWh in return (Figure 56). From the same diagram is obtainable that EPBT for gas and coal plants can even not be achieved as for 1 kWh invested in coal one gets back nearly 4 times less[14]. The wind turbine technologies show continuously improvement so that Vestas has significantly enhanced the EPBT of the V112-3.3 MW turbine by around 26% compared to the V112-3.3 MW model from 2010 [58]. In comparison with an equivalent PV power plant, the return-on-energy of this WT plant is almost 5 times more.

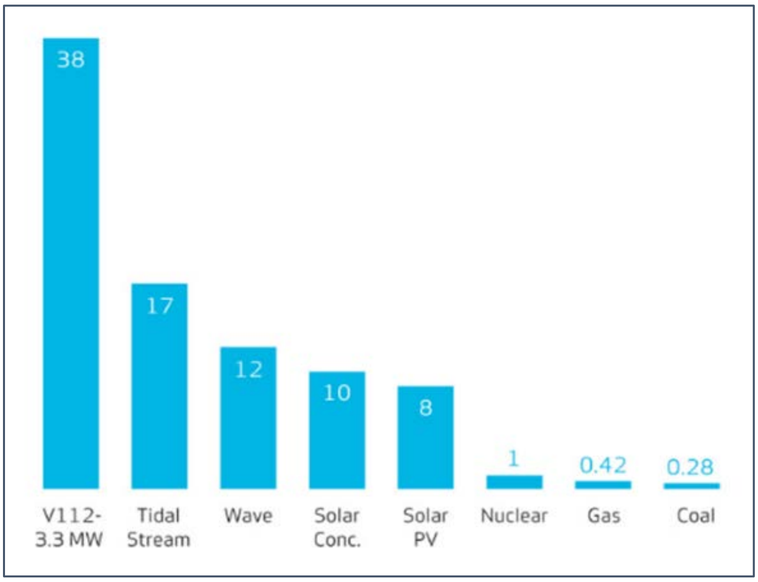


Figure 56. EPBT in “number of times payback” for REN and others [58]

In the region of Burgas V90-3.0 MW turbines will be used. According to Vestas the breakeven time of the onshore V90-3.0 MW is 6,7 months for high wind conditions[15] and 8.3 months for medium wind. The same expressed in “number of times payback”

---

[13] 8 m/s [56]
[14] http://www.worldcoal.org/environmental-protection
[15] 9,2 m/s [56]

means that the wind plant will return 36 times at high wind and 29 times at medium wind more energy back to society than it consumes over the plant life cycle of 20 years [56]. With the lower wind conditions on the Bulgarian coast, respectively less electricity generation, the EPBT of the plants with the same turbine is expected to be longer.

When planning a wind farm an important part is also an assessment of the location and the surrounding environment. In many countries environmental and social impact assessments are required by law or by the international financial institutions which support the projects. These environmental and social assessments typically consider direct and indirect impacts such as:

- Landscape and visual impressions
- Flora
- Fauna (e.g. birds and bats)
- Noise
- Shadows

And the social aspects themselves identify issues such as:

- Community engagement and development
- Land rights
- Local employment and livelihoods including job creation
- Cultural heritage
- Community health and safety [58]

4.5 Economic appraisal of the selected / proposed applications / installations

For the economic analysis of the PV plants will be used the same calculation sheet like in PV (chapter 3.5) adapted to the wind power technology with its parameters (Table 7). As calculated in chapter 4.2 the relatively week wind speed conditions in the region of Burgas lead to a lower load factor of the wind turbines. This means, as shown before, that for generating of the same amount of energy produced with the BD and PV plants, a high number of turbines is required, namely 62 for the small wind farm and accordingly 824 for the large one. By comparing the data given for wind power project cost in the script of Matthias Neubauer [50] and adapting it to the Bulgarian conditions [46] were assumed cost of 1.000.000 €/MW per turbine nominal power for the small wind farm respectively 800.000 €/MW per turbine nominal power for the large one. The FIT for wind farms in Bulgaria is provided for 12 years but at a price of 0,075 €/kWh only at sinks after this period to the humble 0,03 €/kWh [46]. The grid prices remain the same like for PV plants [36]. For the calculation of required area per installed wind turbine will be used the rough rule of thumb defining for distance in main wind direction at least 5 rotor diameters and perpendicular to it at least 3 rotor diameters [50]. The investment horizon is fixed to the officially given wind turbine life time of 20 years. All other relevant data were obtained from literature research and interview with Tsalo Parvanov [37].

Table 8. Investment calculation for small and large PV plants [OC]

	Small-scale wind farm		**Large-scale wind farm**	
Region	Burgas, onshore		Burgas, onshore	
Wind turbines Vestas V90-3.0MW	62		824	
Total nominal power	186	MW	2.472	MW
FLH	2.078	h/y	2.078	h/y
Energy production	45,35	GW	604,7	GW
Investment cost per MW	1.000.000	€/MW	800.000	€/MW
Total Investment	€ 186.000.000	€	1.977.600.000	€
Depreciation in	20	y	20	y
Equity in % of investment	25	%	25	%
Loan in % of investment	75	%	75	%
Term of loan	20	y	20	y
Interest rate of loan	8	%	8	%
FIT (12 years)	0,075	€/kWh	0,075	€/kWh
Electricity sale price (No FIT)	0,030	€/kWh	0,030	€/kWh
Grid connection 1,25 €/MWh	€ 56.688	€	€ 755.875	€
Grid access&transm. 7,35 €/Mwhy	€ 333.323	€/y	4.444.545	€/y
Land per turbine (5ø*3ø) = 12,15 ha	12,15	ha	12,15	ha
Land	753,30	ha	10.011,60	ha
Land (to buy) price per hectare	5000	€/ha	5000	€/ha
Total land price	3.766.500	€	50.058.000	€
Personnel	20	p	50	p
Total pers. cost 6.500 €/py + 2%/y	3.158.658	€	7.896.645	€
Maintenance 2% of investm.	€ 3.720.000	€/y	€ 39.552.000	€/y
Insurance 0,6% of investm.	€ 1.116.000	€/y	€ 11.865.600	€/y
NPV	**-€ 213.315.434**	**€**	**-€ 2.197.387.444**	**€**

Unfortunately, also here both investments showed negative Net Present Value[16] even in a much higher range compared to the BD and PV power plants (Tables 5,6 and 8). Since the negative value is much too high NPV sensitive analysis will not be carried out here. The big amount of required turbines causes huge investment cost. By

---

[16] See appendices 3.1-3.2

increasing the wind speed with 3 m/s the load factor gets higher and the number of required turbines drops tripled in the observed project. This would strongly reduce the cost. But due to low FIT and electricity sale prices and although the FIT state tax of 20% for PV and wind power plants was canceled by the Bulgarian constitutional court, this still would not be enough to get over the break-even.

A wind farm of 824 turbines is not realistic for Bulgaria but the here called small-scale wind farm with 62 turbines could be established. Especially having in mind that Bulgarian largest wind farm “Saint Nicola” mentioned above utilizes 52 of the same Vestas V90-3.0 MW turbines and is also located on the Black Sea coast like the city of Burgas. However, the all-embracing factor is that this plant was commissioned in 2010 having favorable financial conditions.

As mentioned in chapter 4.2 since 2014 there is no one new MW of installed wind power capacity in Bulgaria caused by the already named resolution of the Bulgarian Energy and Water Regulatory Commission that dramatically down cut the FIT and the price of electricity generated by PV and wind.

Comparing all three technologies for transport fuel production in the region of Burgas that have been observed in this work and having in mind the current legal and market price situation, investments cannot be recommended for anyone of the observed plants for now.

In spite of the achieved negative results or exactly therefore, the author would like to shortly present one more TU Wien innovation that would significantly reduce the investment cost of new wind farm projects. The group of prof. Johann Kollegger from the Institute of Structural Engineering has developed a new tower construction method for reinforced concrete tower structures that combines the advantages of precast element construction and climbing formwork (Figure 57). Important features are the usage of half-precast elements providing continuous reinforcement, an easy transport to the building site and a fast building progress. A prototype, which corresponds to the upper part of the concrete section of a hybrid tower for a wind turbine with a hub height of 140 m, was erected in Low Austria. It delivered a positive evaluation of this construction method with large segment heights up to 13 m. Like the other TU Wien innovations brought in this work, also this one was presented at the Hanover trade fair 2016. Prof. Johann Kollegger is optimistic: "*The new construction method is simple and fast. The double-walled elements can be transported without any issues. Taking into account all of our experience to date, our* *new method is expected to be economical and capable of establishing itself compared with the previous construction methods. We believe that our patented process offers benefits for very high wind power stations in particular*." [30]

This new technology would efficiently low the investment cost of every new wind farm project.

Figure 57. Prototype erection by using the innovative construction method [30]

5 SUMMARISED COMPARISON AND DISCUSSION OF THE RESULTS FOR THE SELECTED technologies AND energy carriers

Since the large-scale power plants are not realistic for Bulgarian conditions, the data from the small-scale plants were taken for the summarized comparison of the three reviewed technologies.

Table 9. Energ., economic & ecol. comparison of BD, PV and wind power technol. [OC]

Parameter	Technology			Unit
	Biodiesel	**PV**	**Wind**	
Installed capacity	19,56	36,09	186	MW
FLH	7884	1675	2078	h
Annual production	154,2	45,35	45,35	GWh/y
Depreciation	10	25	20	y
Fuel energy consumption	46	15,5	15,5	kWh/100km
Annual mileage with produced energy carrier	303,33	303,33	303,33	Mkm/y
Total investment	8	39,7	186	MEUR
Investment per MW of installed capacity	0,409	1,1	1,0	MEUR/MW
Investment per km	0,026	0,131	0,613	EUR/km
CO2-eq per total annual mileage [59]	23091	1383,4	276,7	t
Less CO2-eq compared to fossil diesel [59]	47,4	96,9	99,4	%
Net Present Value	**-1,42**	**-34,99**	**-213,31**	MEUR

All three plants were planned for providing an equivalent of transport energy required for covering of the same distance driven by diesel and electrical vehicles. The calculated total mileage of 303,33 Mkm (Table 9) means that the annual fuel demand of over 25.200[17] cars (ca. 17% of the car fleet[18] in Burgas) can be covered with the energy produced by each one of these environmentally friendly technologies.

Unfortunately, as can be obtained from the Table 9 the NPV of all three projects show negative values for the region of Burgas. The biodiesel technology requires the lowest investment per driven kilometer. At the same time the sensitivity analysis showed here

---

[17] An average annual driven distance of 12.000 km per car was assumed

[18] http://www.nsi.bg/en/content/628/basic-page/urban-audit-city-burgas

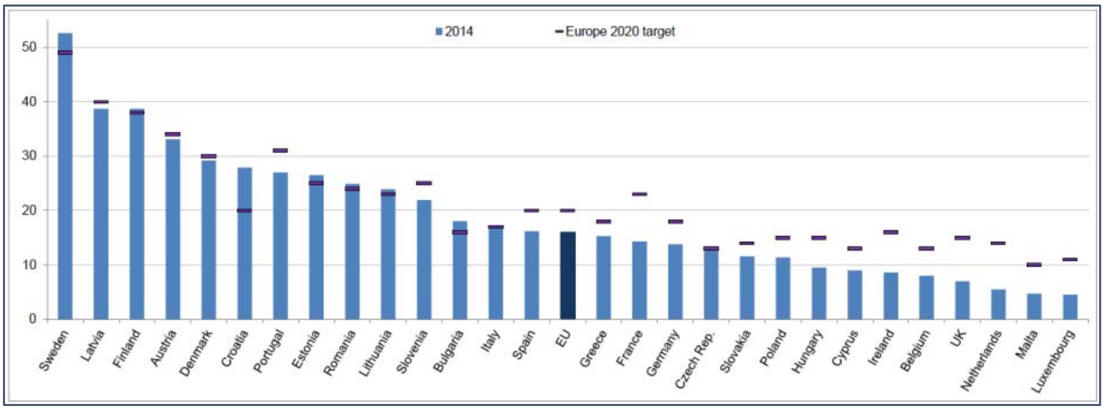
that by only 3% reduction of the feedstock price or by only 2% increasing of the BD price, this investment would make break-even. Due to the very high initial investments of the PV and wind power projects and their in ranges higher negative NPV´s, BD is the only technology where an investment risk could be taken into account by appropriate improvement of above mentioned parameters. So what could be done in order to save at least the small-scale BD plant project despite the negative NPV? Firstly, trying to get raw material to a better price may be from non EU countries. For example there are companies in Belarus (Smorgon, Slutsk), Russia (Barnaul) and Moldova (Chisinau) offering rapeseed oil to a current price of 550 €/t. Of course there will be supplementary costs for transport, customs duty and storage, but with appropriate long term contracts it could be rentable – here is further precisely research needed. Secondly, increasing the percentage of the UCO in the multi feedstock technology or even switching completely to UCO with appropriate contract with the Bulgarian Waste Oil Net company already mentioned above, but also with local restaurants, catering and fast food chains. Especially during the tourist season in the summer months in the region of Burgas there is a big UCO overproduction that could be used to obtain the oil to an even better price.

Comparing the biodiesel situation in Bulgaria four years ago and now one can see a negative development of this industry. While 2012 there still was an optimistic feeling and profitable production, nowadays, caused by changed market prices and not supporting government decisions (possibly due to the still powerful “fossil fuel” lobby), the BD plants go bankruptcy and according to the Bulgarian BD forum only production for self-consumption remains rentable. For the moment, this could be seen as inconsistent with the European directive on the promotion of the use of energy from RES 2009/28/EC, setting until 2020 a 10% part of energy used for transport to be gained from RES.

Producing of transport fuel by electricity generation through PV and wind power plants is even much more ecologically friendly as the BD technology (see CO2-eq [59] in Table 9). But without FIT for PV plants above 30 kWp in Bulgaria since 2015, the electricity sale price has to be more as triple as higher in order to operate just above the break-even. This higher electricity sales price level was fact 3 years ago, but due to the 2014 resolution of the Bulgarian Energy and Water Regulatory Commission is no more available. Therefore, every investment into such PV plants in Bulgaria is now highly not recommendable.

Unfortunately, also the situation of the wind power utilization is not looking well. The big amount of required turbines causes huge investment cost. By increasing the wind speed with 3 m/s the load factor gets higher and the number of required turbines drops tripled in the observed project. This and the TU Wien innovation for economic erecting of WT towers would strongly reduce the cost. But due to low FIT and electricity sale prices and although the FIT state tax of 20% for PV and wind power plants was canceled by the Bulgarian constitutional court, it still would not be enough to get over the break-even. Since 2014 there is no one new MW of installed wind power capacity in Bulgaria caused by the already mentioned resolution of the Bulgarian Energy and Water Regulatory Commission that dramatically down cut the FIT and electricity price generated by PV and wind.

The cancelling of government support for REN plants generally could also be explained by the fact that Bulgaria has already achieved its 2020 target of 16% in the share of renewables in energy consumption (Figure 58) causing former subsidy to be disposed to other sectors of industry.



	2004	2011	2012	2013	2014	2020 target
EU	8.5	13.1	14.3	15.0	16.0	20
Bulgaria	9.4	14.3	16.0	19.0	18.0	16

Figure 58. Share of energy consumption produced from RES in the EU-28, 2014 [18]

(in % of gross final energy consumption)

Comparing all three technologies for transport fuel production in the region of Burgas that have been observed in this work and having in mind the current legal and market price situation, investments cannot be recommended for anyone of the reviewed plants for now.

Only if being very optimistic despite negative results a possible decision for the municipality of Burgas could be an installation of a smaller-scale BD plant for supplying the self-consumption of the “BurgasBus” [60] fleet, which contains of 173 busses (2014) and operates the public and rural transport network of Burgas. This company belongs to the municipality of Burgas, which, as already mentioned in the introduction part of this work, is well known in Bulgaria with its continuously implementation of green technologies and further environmental improvements. The overproduction could be distributed to other transport companies in the municipality and neighborhood regions.

6 CONCLUSIONS to PART I

The development of the transport industry has been showing an exponential progress in the last 100 years. In the European Union the mobility sector consumes already near one third from EU's final energy demand (Figure 59) which makes the transport industry being the largest GHG producer (Figure 60).

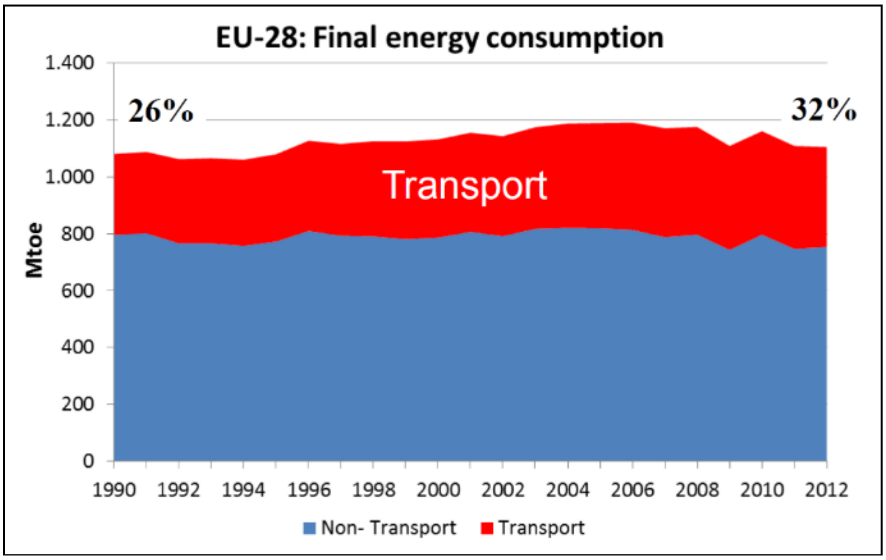


Figure 59. EU-28 final energy consumption [61]

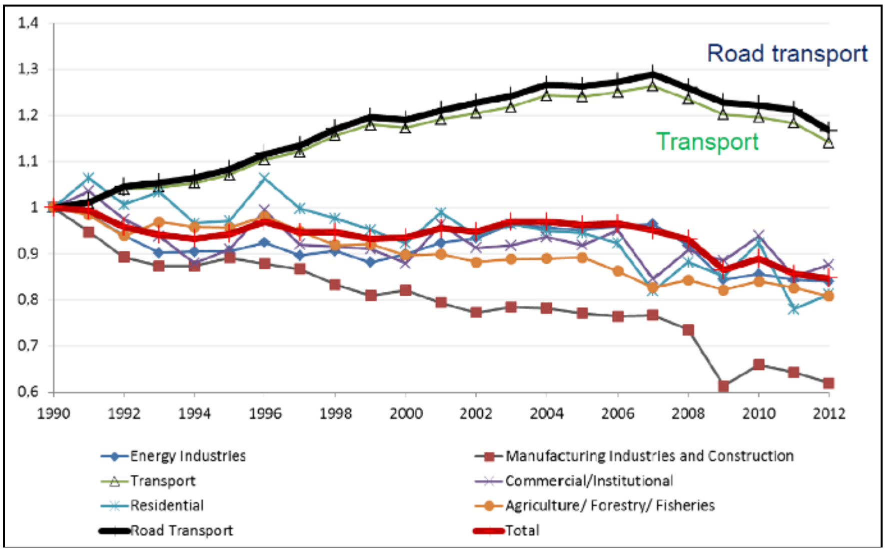


Figure 60. GHG emissions by sector [61]

Fortunately, from the Figure 60 can also be obtained that the idea to make transport more environment friendly and efficient has already reached the car and fuel producers. Since 2007 has been observed a reduction of GHG emissions in transport and all the other sectors have been on this trend for 20 years already. This reduction is obviously caused by implementation of new technologies and bringing on the market of EV, Hybrid and Fuel Cell Vehicles (FCV) but also by making the fossil fuel engines more economic. Increased biofuels utilization also contributes to this encouraging result (Figure 61).

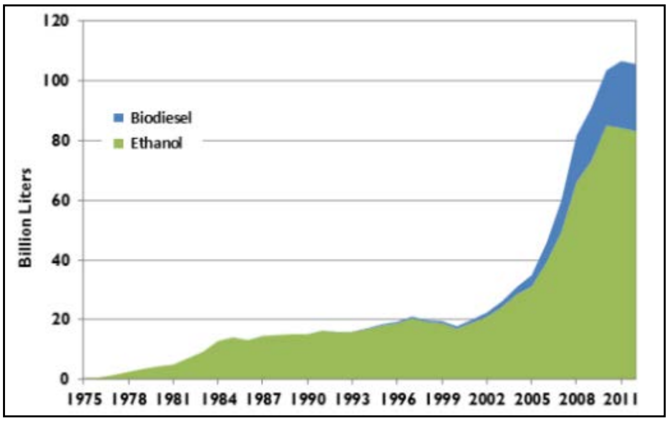


Figure 61. World Ethanol and Biodiesel production [62]

Ecological advantages of above-mentioned new technologies in comparison to vehicles with fossil fuel combustion engines are very well visualized in the ecological assessment given by Amela Ajanovic (Figure 62). In addition, one more important fact can be seen there, namely, the importance of using REN as energy source in transport sector. Since, if the battery electric vehicle (BEV) is charged with electricity generated by combustion of i.e. natural gas (NG) or, hydrogen (H2) in the FCV is not produced by water electrolysis but by reforming of NG, then the CO2 emissions of both motors are almost as much as high as of the internal combustion engines (ICE) driven by fossil fuels.

The outlook for 2050 shown below is really encouraging predicting huge efficiency improvements for all technologies.

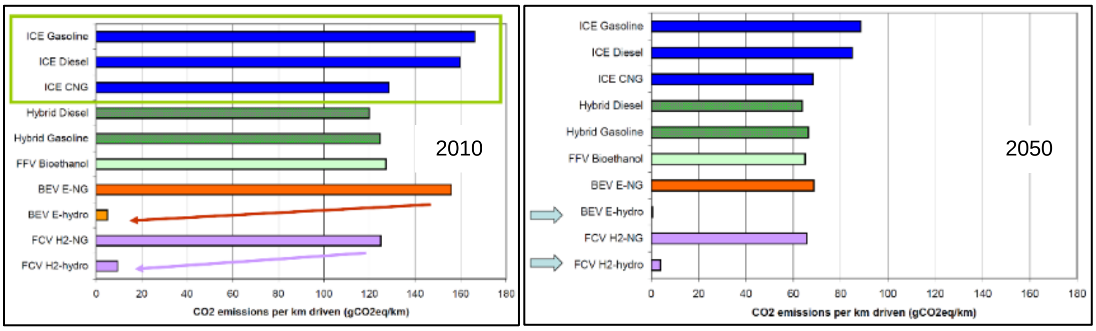


Figure 62. Comparison of vehicles specific CO2 emissions (gCO2eq/km) 2010-2050 [61]

The costs of mobility presented on Figure 63 are also very promising. When now a day the sales prices of the new technology cars are still too high, the forecast for 2050 shows big reduction, so that everyone would be able to afford such a model. And already by now the hybrid technology is on the same cost level like the ICE one.

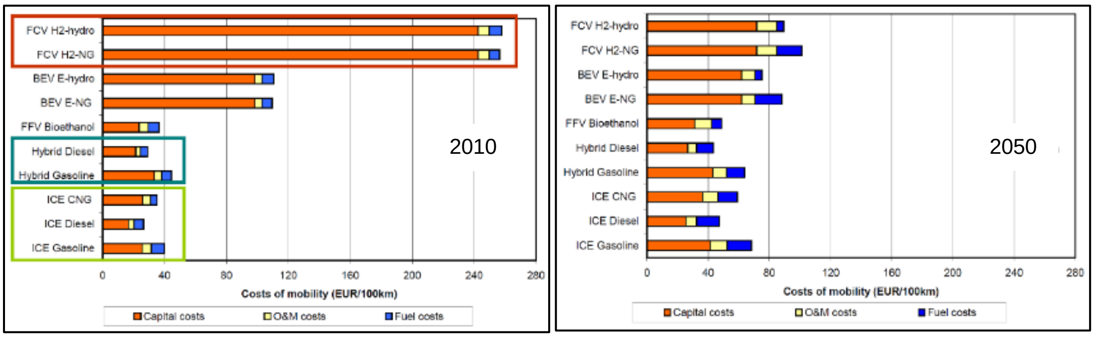


Figure 63. Comparison of total costs of mobility in passenger cars in 2010-2050 [61]

Seeing the encouraging global trend and in spite of the negative results obtained in this work, representing the current BD, PV and wind power plants situation in Bulgaria, the author is optimistic. Up to the end of 2015 in Bulgaria were established 30 charging stations for EV with upward development trend (Figure 64). There are also some incentives for buying EV in Bulgaria such as tax release and free parking (for now in Sofia and Burgas only)[19]. The number of new registered electrical vehicles increases, although very slow and with its less than 0,1% share in the amount of new registered cars, it´s far away from the 22,9% of the leading Norway[20]. At the same time one have to consider the enormous average income and living standard differences between both countries representing the bottom and the top level in Europe.

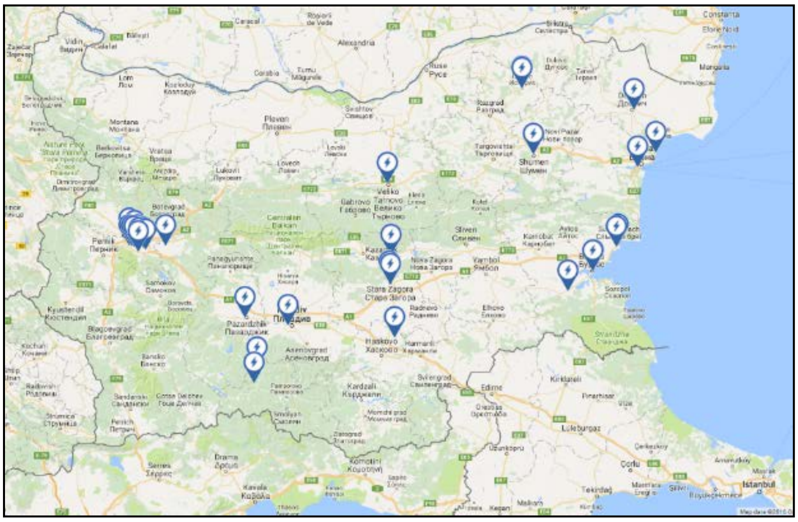


Figure 64. Distribution of charging station for EV in Bulgaria (2015) [63]

---

[19] http://www.elektromobili.bg/stimuli

[20] http://www.emic-bg.org/news/item/1356

Bulgaria has a well-established energy sector. The country is one of the main exporters of electricity in South Eastern Europe and has the perspective to export even more. Due to Bulgaria’s almost unexploited natural resources the hydro, solar, biomass, geothermal and wind energy potential is considered high. The Renewable and Alternative Energy Sources and Biofuels Act (ERSA) was adopted in Bulgaria in 2007. This legal act allowed the development of the RES in Bulgaria.

Bulgaria is utilizing Renewable Energy Sources in three different ways:

- Heating and cooling - solar thermal, biomass, geothermal
- Electricity - wind, small hydro, solar PV, biomass
- Transportation - biomass

Bulgaria is trying to reach their 2020 renewable energy targets through increasing the RES part of the energy needed for:

- Heating and cooling up to 24%,
- Electricity generation by 21%
- Energy demand for transportation by 8% [64].

Biomass

Biomass could still be considered as an unexploited RES, which has a big technical potential of installation. Bulgaria is a country with a large biomass potential, since 60% of land consists of agricultural land, and about 30% is covered by forest. According to the National Long-term Program (2008-2020) for promoting of utilization of biomass, the latter could cover about 9% of the Bulgarian end energy consumption. The national program foresees that the share of energy production from biomass will rise up to 9,7 TW/h in 2020. Furthermore, the biomass energy production is up to 3 times cheaper compared to the common used fossil diesel fuel. Production of energy from biomass could be seen as a business with great potential in Bulgaria if the financial government support would be appropriate [64, 65].

Solar Energy

Its geographical location in South Eastern Europe makes Bulgaria very suitable for solar energy utilization. The solar potential is significant. For most of the country solar radiation is 20% higher than in Central European countries. According to the Bulgarian´s National Renewable Energy Action Plan (NREAP) [65] 300 MW of new solar capacity is expected to be built by 2020. There are large solar PV projects proposed, especially in the south regions of the country, but the government’s preference is clearly to shift the development of PV plants to industrial areas, rooftop and facade wall installations, and smaller capacities by simplifying the licensing procedure for these small-sized projects and offering FIT them only. According to this fact both PV plants observed in this work wouldn´t get any financial support.

Wind Energy

Wind power is currently the third biggest (after biomass and hydro) renewable energy source in Bulgaria. The country has good wind resources especially in the North East, along the Black Sea coast (were also the observed region of Burgas is located) and in the South West part of Bulgaria. 90% of the Bulgarians wind farms are based in the Black Sea coast area of Kavarna such as the already mentioned Bulgarians largest wind farm St. Nikola with installed capacity of 156 MW (chapter 4.3). Until the end of 2015 local and foreign private investors had built up wind farms with a total power of about 700 MW converting the wind energy into electricity. Midterm potential is estimated to be around 3,4 GW, which makes Bulgaria one of the top countries in the region for investments in this sector. By 2020 the government intends to reach around 1,4 GW of installed wind power capacity. Over half of the increase in energy capacity planned by 2020 is expected to be sourced via wind power [64, 65].

Energy Efficiency

Bulgarian energy consumption is higher than the average one in Europe. Therefore, the saving of energy has a big economic potential in this country. For 2-3 years, Bulgaria has been implementing solid energy efficiency measures in the retrofitting of old and construction of new buildings. Replacement of old oil-fired boilers by modern ones, utilizing biomass as a fuel in combined heat and power plants, belongs as well to the energy efficiency approach. Especially the city of Burgas, a municipality of the Bulgarian Black Sea coast chosen in this work, is a good lead in the realization of the above-mentioned measures. A business plan for such an energy efficiency project in Burgas (7.100 MWh energy and 13.500 tons of CO2-emissions saving per year) [67] was elaborated by author and his colleagues Antonietta Di Chio (Italy) and Ulrich Tschiesche (Austria) during their study at the master program “Renewable Energy Systems” in the Vienna University of Technology (2015-2017).

Nevertheless, the voices of the supporters of the development of the traditional energy in Bulgaria have to be taken into account as well. They arguing with lower price for electricity produced from fossil fuels and nuclear energy. The electricity price is a very sensitive topic in Bulgaria, since the electricity bills consume a huge part of the people's incomes, especially in winter. On the other front the supporters of RES argues with environmental friendly technologies, diversification of the energy supply and limitation of the dependence from Russian imports of fossil fuels and nuclear technologies. However, the major trends for development of the energy sector in Bulgaria now are related to a drop in electricity consumption and an increase in natural gas and RES consumption. Bulgaria also faces challenges in terms of the efficiency of energy production, and still has some work to do in order to bring the sector in line with European standards and EU directives. Energy efficient technologies and clear pricing policy have to be introduced in the country.

As many European countries also Bulgaria experienced important development since 2007 in the sector of RES. Bulgaria had generous FIT that led to a huge rise in RES applications. The outcomes of those, unfortunately only initial, support measures were very clear – the level of RES applications in the country increased significantly in terms of projects, power installed and employment generated. But the legal and regulatory changes introduced in Bulgaria in 2012-2014 led to a significant decrease of the support for renewable energy projects. These changes, some of them retroactive, provoked a strong protest from investors that complained about changing rules, lack of transparency and problems for their investment. The investors' interest in the RES sector slowed down significantly. The new Bulgarians REN strategy is more restrictive and limits investments and renewable support to the level only needed to fulfil the obligatory requirements set by the European Union [34].

In conclusion could be said that after observing the current situation due to the costly utilization of the renewable energy sources the main primary energy sources in Bulgaria will, unfortunately, remain to be oil and natural gas.

The author believes that the stagnation of REN support in Bulgaria is only temporary and that the global trend will force the government to recognize again the advantages of the renewables and to apply for financial assistance from the EU to be able to resume the FIT and other early available incentives for energy producing from RES.

The three TU Wien innovations shortly presented in this work will help to save costs for electricity storage, land use and installation and at the same time making the use of REN even more environment-friendly.

Finally yet importantly has to be mentioned here that improvement of the societies' consume behavior to a more rational energy use should be educated from cradle on. Understanding the principals and appreciating the ecological advantages of producing energy from the renewable energy sources will make the Earth being green again.

Idea -> Innovation -> Revolution

7 INTRODUCTION to PART II

The objective of this part is to present a new energy technology for electricity generation and production of hydrogen by utilizing of a poisonous substance in the waters of the Black Sea as an energy carrier. The positive side effect of this innovative energy converting method is cleaning of the seawater from the hazardous matter and establishing of a safety ecological equilibrium in the basin.

With this part of the master thesis, the author aims to popularize the inventions of the Bulgarian scientists from the Institute of Chemical Engineering in Sofia, led by prof. Beschkov, as well as the progress of their innovative work.

In Part I of the thesis were calculated and described various power plant projects for the city of Burgas, a municipality on the Bulgarian Black Sea coast. These projects are based on renewable energy sources such as wind, solar and biomass. Unfortunately, negative Net Present Values were obtained for all these REN power plants.

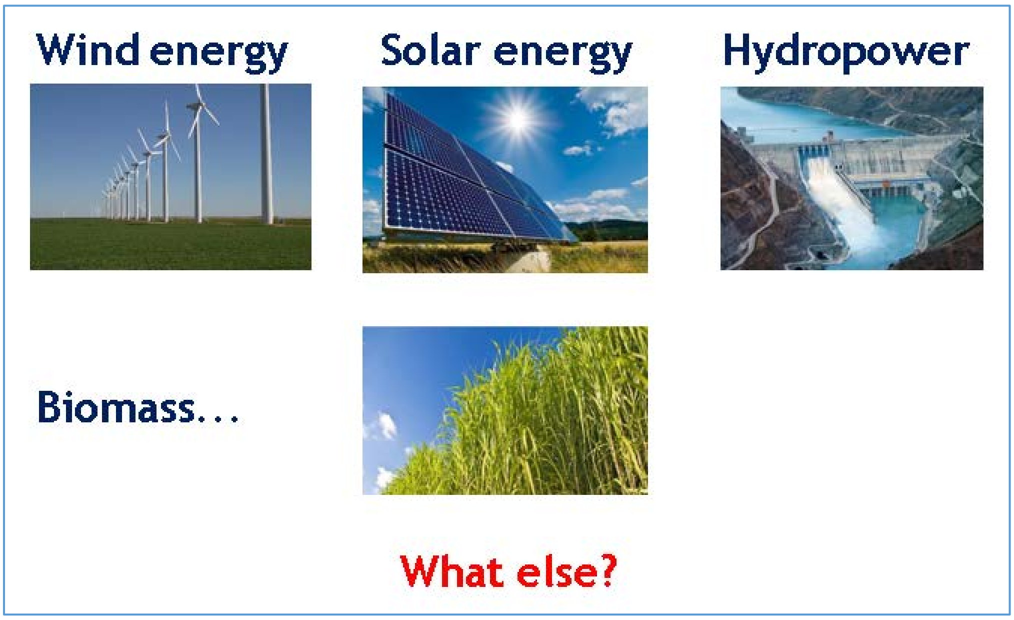


Figure 65. Energy from renewable energy sources. What else? [89]

What else? Could the enormous and steadly growing amount of hydrogen sulphide in the Black Sea waters be also considerd as a renewable energy source and power generation out of it be feasible, efficient and profitable?

The technology giving positive answers to these questions will be presented here.

7.1 Black Sea – a reservoir of hydrogen sulphide

The Bulgarian city of Burgas, described in the projects at the first part of this thesis, is located on the west coast of the Black Sea (Figure 66). The Black Sea is an inland elliptical basin located between South-East Europe, Eastern Europe and Western Asia with an area of about 436.400 km^2 (without the Sea of Azov). Bulgaria, Romania, Ukraine, Russia, Georgia and Turkey are the six countries having shore strips on the Black Sea coast. It is connected to the Eastern Mediterranean via the Bosporus and the Dardanelles. The average depth of the Black Sea is 1.253 m with a deepest point at 2.212 m. The basin is 1.175 km long and has a total volume of 547.000 km^3 [68]. The Black Sea is unique because 90% of the seawater is anaerobic. This anaerobic seawater contains hydrogen sulphide (H2S), produced by sulphur reducing bacteria (SRB) at the process of their anaerobic bacterial respiratory.

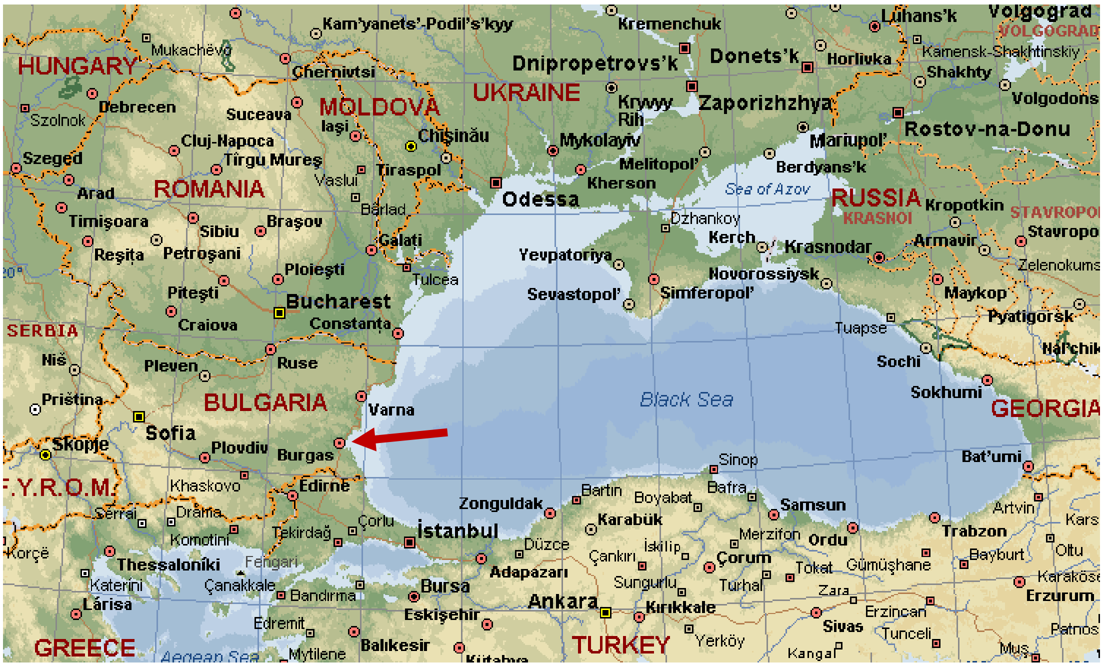
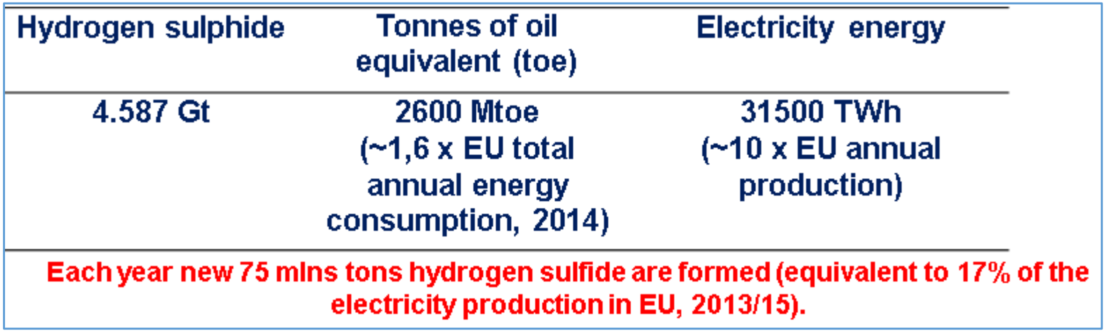


Figure 66. Black Sea [69]

Hydrogen sulphide is common in some geothermal springs and closed deep water basins. Its availability in geothermal springs is due to volcanic gases and its presence in closed deep water reservoirs is caused by the anaerobic sulphate reducing bacteria decomposition of sulphur-containing organic matter. Deep Black Sea waters contain immense amount of H2S (as hydrosulphide and sulphide ions) estimated as 4,6 billion tons. The Black Sea is the largest water basin containing hydrogen sulphide [70]. The enormous amount of H2S, its yearly new formations and energy equivalents are presented in the Table 10 below:

Table 10. Amounts and energy equivalents of H2S in the Black Sea [89]



Hydrogen sulphide	Tonnes of oil equivalent (toe)	Electricity energy
4.587 Gt	2600 Mtoe (~1,6 x EU total annual energy consumption, 2014)	31500 TWh (~10 x EU annual production)

Each year new 75 mlns tons hydrogen sulfide are formed (equivalent to 17% of the electricity production in EU, 2013/15).

Alone the 75 million tons of hydrogen sulphide, which a newly formed each year, equivalent to 43 billion m³ of natural gas. This amount is tenfold larger than the annual gas consumption of Bulgaria (with a population of 7,2 million people) [89].

The layer containing H2S begins at a depth of about 200 meters below the surface. The thin upper layer of marine water (up to 150 m) supports the unique Black Sea ecosystem [70].

The two Russian scientists Andrusov and Zelinskij from the University of Novorossiysk identified the existence of hydrogen sulphide in the waters of Black Sea for the first time in 1890-91. On our planet, there are three main sources for the natural formation of hydrogen sulphide. The first origin is the sulphate reduction at the process of anaerobic disintegration of organic materials. The second source is the rotting of organic matter containing sulphur. And thirds, H2S comes out of the earth shell cracks through geothermal water springs. In the Black Sea on these natural ways are produced about 75 million tons of H2S per year. In the upper water layers, its concentration is regulated by the natural oxidation [71, 89].

Organic and industrial wastes flowing into the Black Sea by the big European rivers such as Danube, Dnepr and Dnestr are the main source for increasing the volume of hydrogen sulphide year by year and affecting the sea life there. Due to human activity in the past few centuries, the quantity of hydrogen sulphide is increasing dramatically. Because of the extremely toxicity of H2S the sea is practically dead at depths below 200 meters with the exception of the above mentioned sulphur reducing bacteria.

The closed nature of the Black Sea basin, its tectonic features and the anaerobic decomposition of the sulphur-containing organic materials lead to a constantly accumulation of hydrogen sulphide in the anaerobic zone of the sea.

The anoxic conditions have been presented in the deepest parts of the Black Sea for nearly 7.300 years. About 9.000 years ago following the rise of the world sea level, saline Mediterranean water streamed via Bosphorus into the Black Sea, which at those times was an aerated fresh water lake. The consequence of this ecological incident was the formation of two water layers in the Black Sea basin - fresh water above the heavier salinity water layer from the Mediterranean Sea with limiting supply of dissolved oxygen. The salty water, rich on organic components, leads to massive vegetation of planktonic biomass. The main source of hydrogen sulphide is the decomposition processes of the organic matter, which slides to the bottom in the form of organogenic mineral sludges (sapropelles). They are the product of dead planktonic biomass. There is an excess of an enormous amount of organic matter that creates favorable conditions for the development of bacterial sulphatreduction shown on Figure 67.

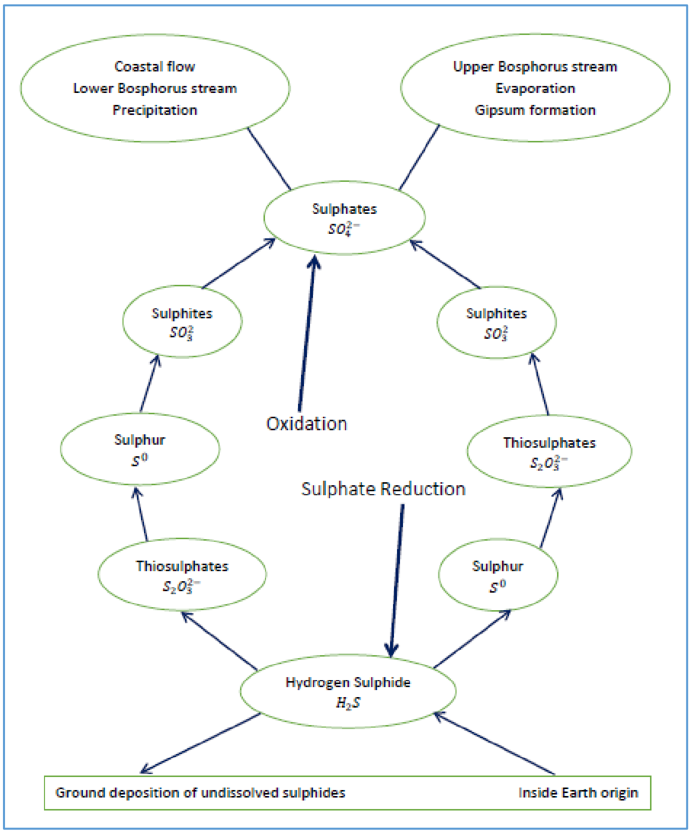


Figure 67. Processes of oxidation and reduction of H2S in the Black Sea [72]

The geochemical conditions of the freshwater lake did not allow the formation of free H2S in it at the period of its fresh water existence. Initially, after the flood, H2S covered the whole water mass from the bottom to the surface of the sea. Gradually, with stabilization of the hydrodynamic and hydrochemical conditions began to form the so-called oxygen or biotic zone. Indicatively, the hydrogen sulphide zone starts from depths of 130-140 m. From the depths of 130-140 m to 180-200 m, there is the so-called redox[21] layer - a zone of coexistence of oxygen and hydrogen sulphide. Below it, to the maximum depths there is the abiotic hydrogen sulphide zone, so that 90% of the whole Black Sea water mass is uninhabitable. H2S concentration increases regularly until 1.000 m depth. After that the increase slows down, and at 1500 m, the concentration of hydrogen sulphide remains nearly constant at 10 mg/l. Another important supplier of H2S, whose role is underestimated, are the geological sources - mud volcanoes (Figure 67) as well as destructed gashydrates deposits that contain solids of hydrogen sulphide [72].

"The Black Sea is a natural geobiotechnological reactor, which is a potential source of energy and other natural resources. The sapropel, diatomic and cocolitic muds, hydrogen sulphide, gas hydrates, carbon sulphide gases, natural gases and fresh water are the most promising easy alternative power resources. Hydrogen sulphide in the Black sea is considered not only as major characteristic, but also as a possible energy source" [72]

In the seawater, H2S is disseminated not only in the dissolved gas phase but also as sulphides and hydrosulphides. The annual production of hydrogen sulphide in the Black Sea basin amounts to 75 million tons. Due to the geographic (closed basin), biologic (activities of the SRB) and tectonic (fractures and mud volcanoes, as well as the destroyed gas hydrate deposits) characteristics, Black Sea is an enormous natural reservoir for H2S. With the innovative waste-less electricity producing method for using the oxidation energy of hydrogen sulphide, presented in this work, an unlimited and renewable energy source can be utilized by simultaneously cleaning the seawater from the poisonous gas and establishing a safety ecological equilibrium in the waters of the Black Sea.

7.2 Natural equilibrium of H2S in the Black Sea

The equilibrium concentration of hydrogen sulphide in the Black Sea is about 10 ppm at the depth of 1.000 m. The daily production of H2S by SRB is about 10.000 tons

---

[21] Redox (Reduction and Oxidation) are terms from the electrochemistry. "*Reduction refers to a process in which electrons are added to a species, means electrons are consumed by the reaction. Oxidation refers to a process in which electrons are removed from a species, means electrons are liberated by the reaction"* [81].

and the whole volume of H2S is estimated to be around 4,6 billion tons (constantly rising). The H2S mixture in the seawater is considered as a non-ideal (gas-liquid) solution [73].

The survey of different literature sources for distribution of H2S and oxygen in the Black Sea shown on the Figure 68 describes different concentrations of hydrogen sulphide at different sea depths varied from 7 to 14 ppm.

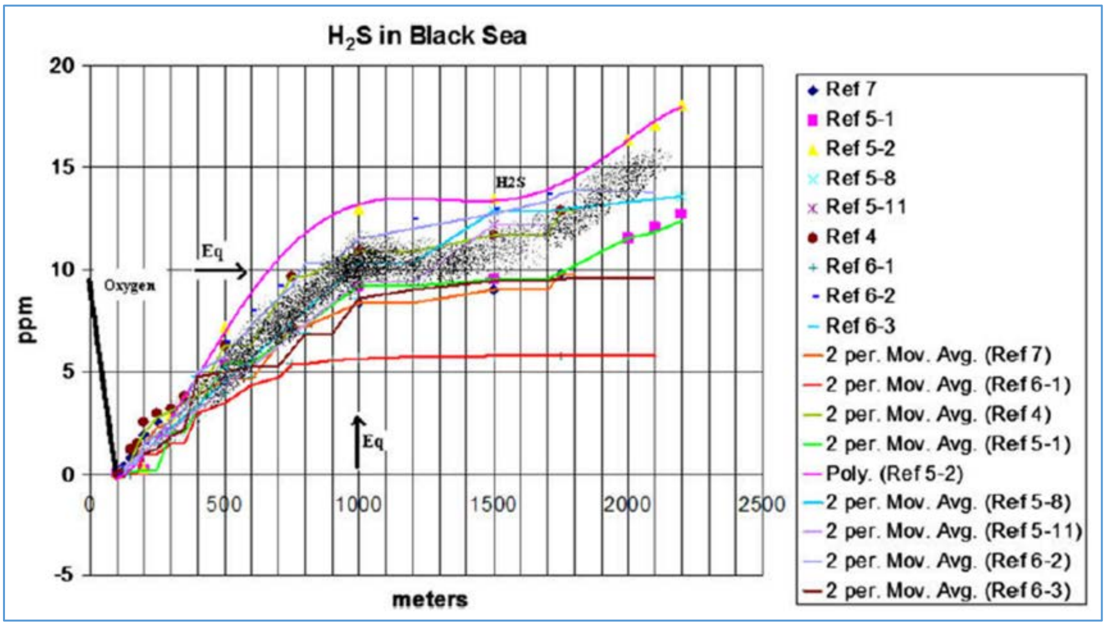


Figure 68. Concentration of H2S and O2 in Black Sea water from different authors [73]

As can be obtained from the Figure 68 the H2S concentration at 2.200 m at the bottom of the sea has a value of about 14 ppm (formation of hydrogen sulphide from sulphur and sulphate ions (SO_4^{--}) by the anaerobic sulphur reducing bacteria). At the surface of the sea down to the 100 m depths, the H2S concentration is zero due to the biological cycle of the sulphur oxidizing bacteria (SOB). Due to its activity, the concentration of oxygen (O2) at the same depths shows an inverse behaviour. It has values of about 8-9 ppm at the Black Sea surface and decrease down to zero at depths of about 100 m. It exists a natural equilibrium between the SOB and SRB bacteria at the surface and bottom of the Black Sea. In addition, about 25% of hydrogen sulphide are removed from the Black Sea by the photosynthesis bacteria (purple bacteria) which convert H2S to elemental sulphur and hydrogen gas to water [73]. These reactions are illustrated in Figure 69 below:

$$SO_4^{--} \xrightarrow[\text{}]{\substack{\text{anaerobic bacteria}\\ \text{sulfur reducing bacteria}}} H_2S + S^{--} \quad (SRB)$$

$$H_2S \xrightarrow{\substack{\text{photosynthesis}\\ \text{(purple bacteria)}}} S + H_2$$

$$H_2S \xrightarrow{\substack{\text{aerobic bacteria}\\ \text{thiobacillus}}} SO_4^{--} \quad (SOB)$$

Figure 69. Biologic. reactions for formation and consumption of H2S at diff. depths [73]

All these reactions will lead to certain concentrations of hydrogen sulphide at the equilibrium zone at certain depths of the Black Sea water. The solubility of H2S in the seawater is high and depends on temperature, pH, pressure, salinity as well as on the nature of the hydrogen sulphide and water molecules. It´s expressed with the following dissociation constants presented in Figure 70:

$$H_2S \leftrightarrow H^+ + HS^- : K_1$$

$$HS \leftrightarrow H^+ + S^{--} : K_2$$

$$H_2O \leftrightarrow H^+ + OH : K_w$$

Figure 70. Dissociation constants for H2S and H2O in the Black Sea [73]

According to the Le Chatelier's principle[22] various researchers came to the conclusion that with the depth of the sea the concentration gradient of hydrogen sulphide reaches a plateau region, so called equilibrium zone. It´s located in the depths between 800 - 1.200 m, where the temperature is 8°C, salinity is 20.000 ppm and H2S concentration has a value of 10 ppm demonstrated in the next Figure 71. It illustrates the bioactivities of all three bacteria (SOB, the photosynthesis bacteria and SRB) at different depths and explain the dissociation constants of hydrogen sulphide with its HS^- and S^{--} ions at the different pH, temperature and salinity regions of the Black Sea water. The concentrations of H2S and oxygen as a function of depth can also be obtained from this picture [73].

---

[22] Le Chatelier's principle can be summarized as "*If a chemical system at equilibrium experiences a change in concentration, temperature, or total pressure, the equilibrium will shift in order to minimize that change"* [73]

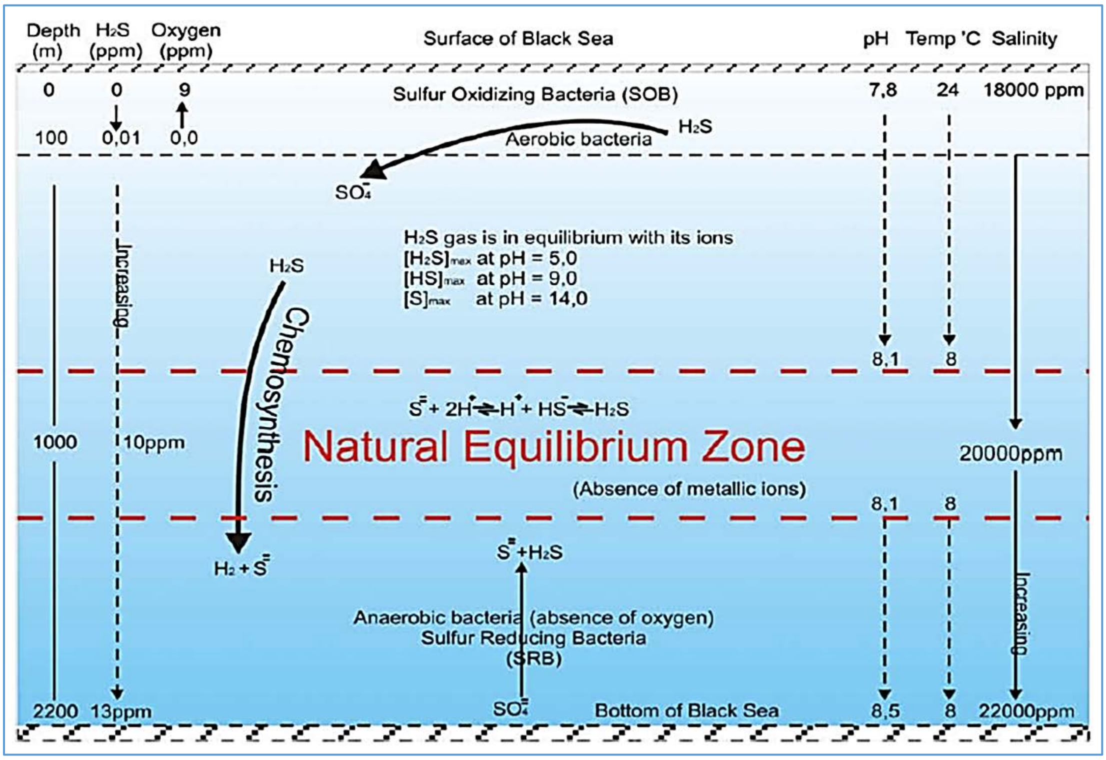


Figure 71. Natural equilibrium of Black Sea [73]

8 HYDROGEN SULPHIDE as RENEWABLE ENERGY SOURCE

Hydrogen sulphide is a colorless, very poisonous and corrosive gas that can be recognized by its typical smell already when there is only one hundred-thousandth part of it at the air. It´s dissolvable in water in a ratio of 3 volumes of H_2S to 1 volume of H_2O. In a volume of about 0,1% in the air H_2S causes heavy poisonings [74].

Due to the very high toxicity of H_2S there are no life forms (except of some bacteria) in the Black Sea waters in depths below 150-200 m. It means that a possible utilization of hydrogen sulphide as a new energy source will simultaneously have a huge positive ecological effect on the Black Sea environment.

The idea of utilizing the H_2S from the Black Sea as a power-producing source was born at the end of 1960's when new data about its formation and distribution were available. The interest towards utilization of hydrogen sulphide increased rapidly in relation with deteriorated ecological situation in the Black Sea and shortage of energy resources [74].

Hydrogen sulphide ignites at 300º C in the air and is compared even with such high caloric power-producing source as methane. Both reactions of combustion are shown below:

$$2H_2S + 3O_2 \Rightarrow 2SO_2 + 2H_2O + 248\ \text{Kcal} \qquad (13)$$

i.e. from 1 m³ gas H_2S is obtained 5.535 Kcal heat [74]

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O + 190\ \text{Kcal} \qquad (14)$$

i.e. from 1m³ methane is obtained 8.500 Kcal heat [74]

However, the quite low concentration of gaseous H_2S in the seawater connected with serious production cost for its extraction and concentration as well as the environment harmful sulphur dioxide emissions make this H_2S utilization method not reasonable.

Also other technologies were investigated in the last decades for utilizing of hydrogen sulphide such as decomposition to the harmless products hydrogen and elemental sulphur by electrolysis, photolysis, thermolysis and plasma methods. However, in all of these cases the energy consumption is comparable or even higher than the energy that could be yielded from the produced hydrogen. In addition, the accumulation of huge amounts of sulphur as a side-product is inconvenient because of the necessity of its placement on an appropriate market [77].

Another important fact that plays a crucial role for development of a H2S utilizing technology is that, as already shown in Figure 71 in the Black Sea waters hydrogen sulphide exists in different forms, namely undissociated H2S° molecules and sulphide (HS^{-}), polysulphide (S_n^{2-}) and sulphide (S^{2-}) anions. The distribution ratio of these forms is determined by the pH of the water (Figure 72).

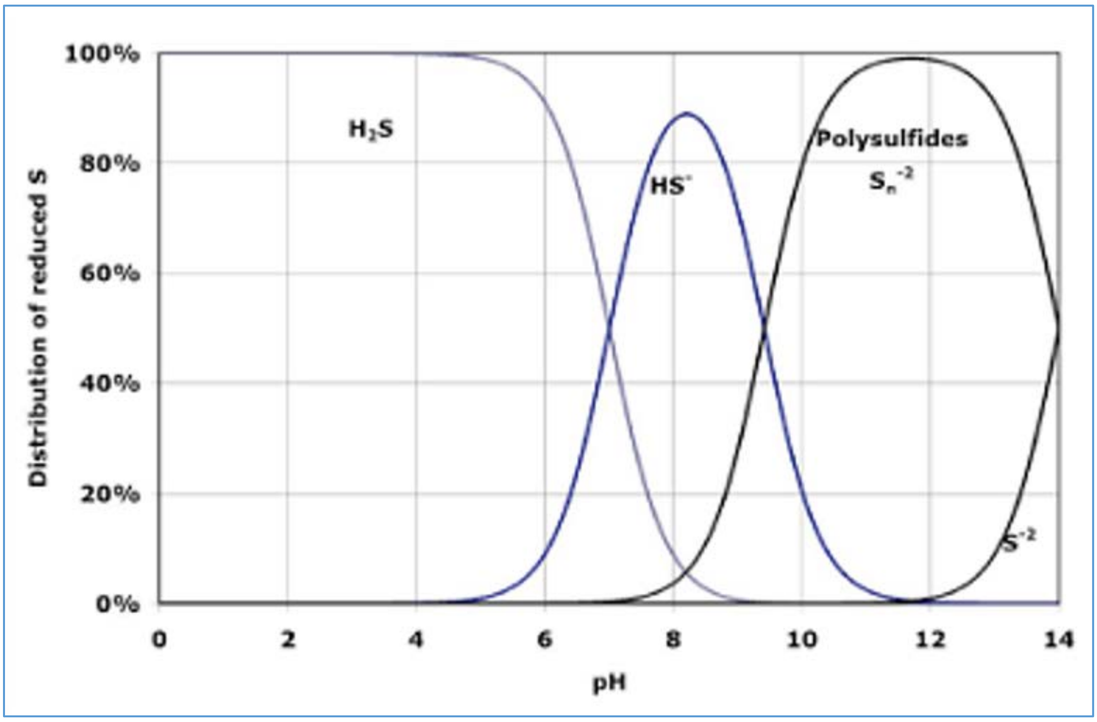


Figure 72. Distribution of different sulphide forms of H2S in dependence of pH [75]

According to the calculated data at pH>10 the content of S^{2-} ions can be neglected. At pH=7 the content of H2S° molecules and HS^{-} ions is approximately the same. And at pH=4 hydrogen sulphide is almost completely in the form of undissociated H2S° molecules (99.8%). In the Black Sea water with pH values about 8 (Figure 71) in the form of H2S° can be found only about 15% of all bivalent sulphur. The rest of it is chemically bonded in the heavy metal sulphide form, so the possibility of H2S° transfer to the gas phase is difficult.

From the above mentioned follows that the extraction of hydrogen sulphide from the seawater is hampered by the following significant circumstances:

- low concentration of H2S (hundreds fold lower than in its saturated solution)
- the concentration of the undissociated form of H2S is not more than 15%; the prevailing form of up to 85% is the dissociated one, i.e. ionic and chemically bound. It means that the H2S in the Black Sea water is a mixture of 85% sulphides and only 15% pure H2S gas [74, 76].

This explains why for decades, despite the many attempts to utilize the hydrogen sulphide from the Black Sea waters, there have not been developed practically realizable technologies for extraction of H2S gaseous form from the seawater yet and why studies in the last years have been focused on the utilization of the prevailing ionic form of hydrogen sulphide in the Black Sea.

In the last years, a number of scientists have been investigating possibilities for the use of sulphides as an alternative fuel in fuel cells such as Dutta et al. (2008), Zhai et al. (2012), Kim & Han (2014), Martinov et al. (2013-2017), Razkazova-Velkova et al (2013-2015), Beschkov et al. (2012-2017). There are also some researches for utilizing the sulphides as an energy source in microbiological fuel cells (Reimers et al. (2006), Lee et al. (2012), Cai & Zheng, (2013), Vanitha et al. (2016)). Through oxidation of sulphides into sulphate ions in the new developed sulphide driven fuel cells (SDFC) is gained more energy than in the common conversion of sulphides into elemental sulphur. The sulphates are environmentally harmless in a wide range of concentrations and can be released into the water, as they are anyway present in the natural water basins [78]. Moreover, they will be used by the SRB in Black Sea waters for their anaerobic bacterial respiration. On this way new amounts of sulphides will be produced, which again can be utilized in the sulphide driven fuel cells (SDFC). By closing this bio-electro-chemical natural cycle the humanity obtain a new sustainable and renewable energy source and simultaneously maintain the ecological balance in the natural waters.

Developing of such an effective electricity production methods, like the one presented in this work, by utilizing in fuel cells the oxidation energy, contained in the enormous and constantly growing amounts of H2S in the Black Sea, would provide not only Burgas and Bulgaria, but all the countries around the sea and other water basins containing H2S, with a new sustainable and renewable energy source.

9 FUEL CELL

9.1 Principle

Fuel cells (FC) are based on the concept of electric power generation by using the electrochemical redox reaction between the fuel (H2 is the most commonly used elemental due to its high chemical reactivity) and the oxidizer (O2) in the presence of catalysts. In the FC the energy of the fuel is directly converted (without combustion) into a DC electricity. The only by-products are H2O and heat. In comparison with the indirect energy conversion, which goes via heat first, the electricity generation in the fuel cell is not limited by the Carnot factor, thus has a much higher efficiency. The functional concept of a FC is presented on the Figure 73:

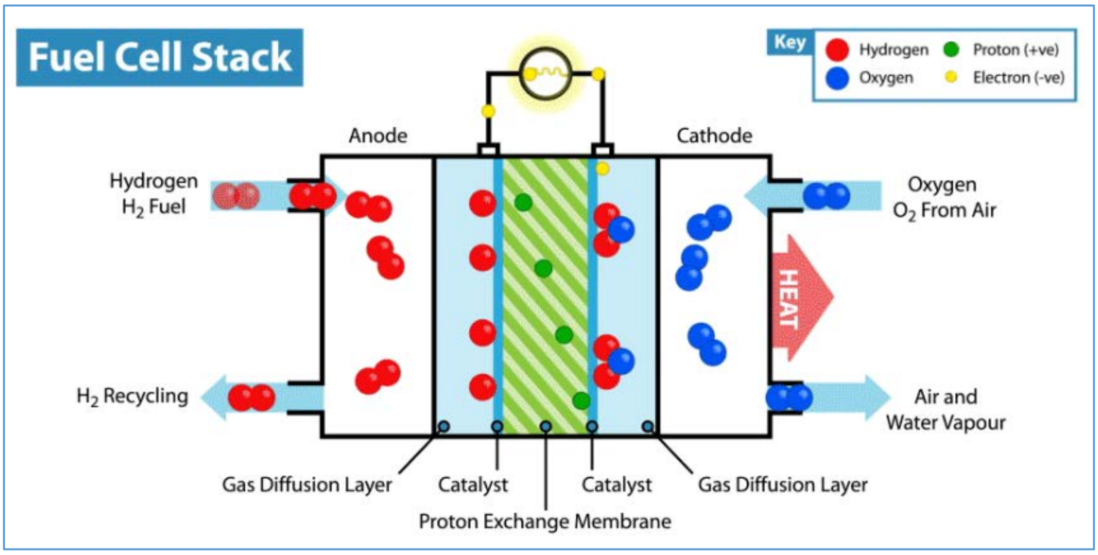


Figure 73. Fuel Cell Stack [79]

The fuel supply carries out on the anode side of the FC. In cases of using hydrogen or methanol occurs a direct fuel oxidation[23] and by using of hydrocarbon fuels - an indirect oxidation via a reforming process. On the cathode side, a reduction[24] of oxygen from air (in most fuel cells) takes place. Streams of fuel and oxidizer pass through porous metal electrodes (plates), which are separated by an electrolyte. Outside the electrolyte, the electrodes are electrically connected. The anode (fuel electrode) converts hydrogen molecules into ions and electrons. The ions migrate into the electrolyte. It consists of a solid membrane or matrix having ion-conducting

---

[23] Oxidation – removing of electrons from a species. In a FC the process is carried out on the anode side [81]

[24] Reduction – adding of electrons to a species. In a FC the process is carried out on the cathode side [81]

characteristics. The oxidizer plate (cathode) separates oxygen molecules into oxygen atoms. They also move into the electrolyte where they recombine with the hydrogen ions to create water and heat. Electricity can be captured from the circuit and put to useful work. Catalysts increase the process speed and don´t participate in the reaction itself. Fuel cells typically generate a voltage of around 0,7 – 0,8 V per cell and a power output of a few tens or hundreds of watts with an efficiency of about 60 - 70 %. More series connected FC´s build the so-called Fuel Cell Stack. On this way, it is possible to define the desired power output of the whole module [80].

9.2 Electrical characteristics

The performance of a fuel cell can be summarized with its main electrical characteristics, namely the current-voltage and power density curves (example presented on Figure 74). The current-voltage (i–V) curve shows the voltage output of the FC for a given current output. Since the larger a fuel cell the more electricity can it generate and in order to be able to compare FC´s with each other, i–V curves are normalized by the area of the fuel cells (A/cm^2).

An ideal FC would generate any amount of current (as long as it is supplied with sufficient fuel) at a constant thermodynamically determined voltage. However, a real fuel cell has a lower voltage output than the ideal one. Furthermore, the stronger the load of a real FC (more current drawn out of it), the lower is its voltage output, hence, lower the total power that can be obtained. The power (P) delivered by a fuel cell is the product of its current and voltage values (Formula 6):

$$\mathbf{P = i*V} \qquad (6)$$

The power density curve is produced by multiplying the voltage at each point on the *i–V* curve by the corresponding current density (**Figure 74**). Fuel cells are designed to operate at or below the power density maximum. [81].

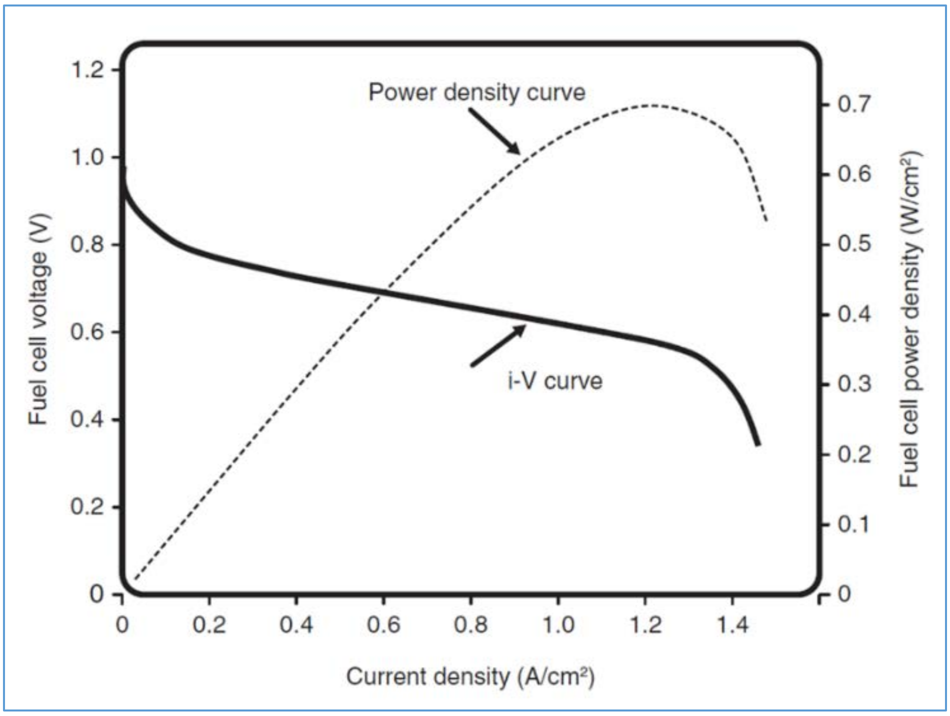


Figure 74. Combined FC current-voltage (i-V) and power density curves [81]

One further important characteristic of a fuel cell are their losses, which determinate the efficiency of the FC. In real conditions due to the irreversible losses, the voltage output level is less than the ideal (thermodynamic) fuel cell voltage (Figure 75). The losses go up with the increase of the current load of the cell. As shown in Figure 75 three main types of losses determine the form of the FC´s i-V curve:

- Activation losses (These are the losses due to electrochemical reaction. They affect the initial part of the curve)
- Ohmic losses (are the ones caused by ionic and electronic conduction. These losses define the curve shape in its middle part) and
- Concentration losses (are the losses occurred due to mass transport and signifying the last section of the i-V characteristic)

With other words, the real voltage output of a fuel cell can be expressed by the following formula where all the voltage drops caused by the losses are subtracted from the ideal (thermodynamically obtained) voltage:

$$\mathbf{V = E_{thermo} - \eta_{act} - \eta_{ohmis} - \eta_{conc}} \tag{7}$$

where:

V is the real output voltage of the fuel cell

E_{thermo} represents the ideal (thermodynamic) fuel cell voltage output

η_{act} gives a description of the voltage drop due to activation losses (reaction kinetics)

η_{ohmis} is the voltage drop due to ohmic losses (from ionic and electronic conduction)

η_{conc} shows the voltage drop due to concentration losses (mass transport)

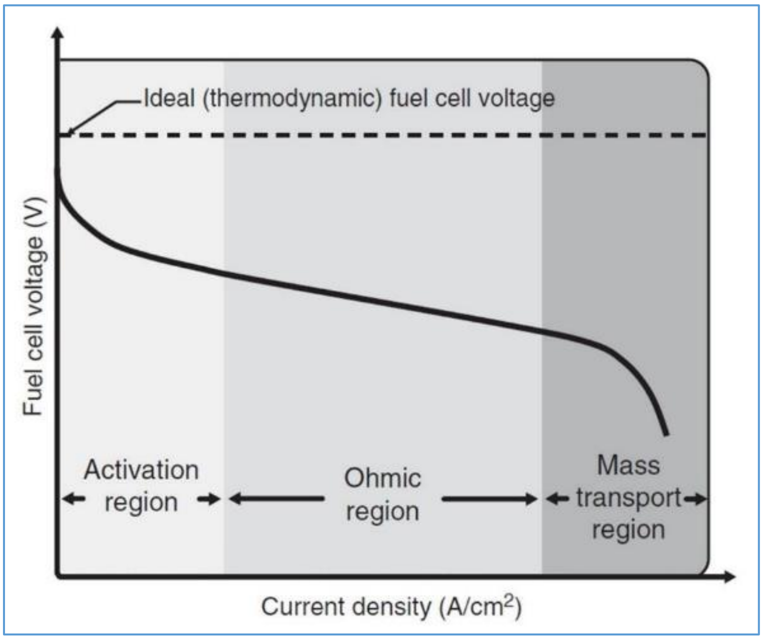
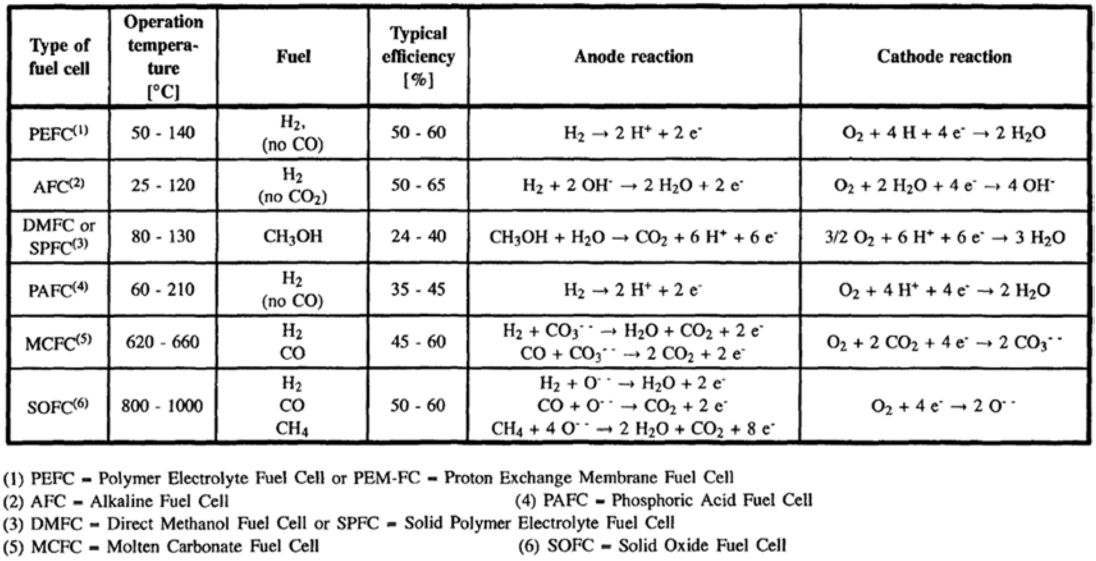


Figure 75. FC *i–V* curve in contrast to the ideal, thermodynamic. predicted voltage [81]

9.3 Fuel cell types

There exist various fuel cell types classified usually in relation to the used electrolyte. In Table 11 are listed FC types with their operating temperatures, fuel variety, efficiency levels and anode-cathode electrochemical reactions.

Table 11. Fuel cell types [80]



Type of fuel cell	Operation tempera-ture [°C]	Fuel	Typical efficiency [%]	Anode reaction	Cathode reaction
PEFC(1)	50 - 140	H_2, (no CO)	50 - 60	$H_2 \rightarrow 2\ H^+ + 2\ e^-$	$O_2 + 4\ H + 4\ e^- \rightarrow 2\ H_2O$
AFC(2)	25 - 120	H_2 (no CO_2)	50 - 65	$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$	$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$
DMFC or SPFC(3)	80 - 130	CH_3OH	24 - 40	$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$	$3/2\ O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$
PAFC(4)	60 - 210	H_2 (no CO)	35 - 45	$H_2 \rightarrow 2\ H^+ + 2\ e^-$	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$
MCFC(5)	620 - 660	H_2 CO	45 - 60	$H_2 + CO_3^{--} \rightarrow H_2O + CO_2 + 2\ e^-$ $CO + CO_3^{--} \rightarrow 2\ CO_2 + 2\ e^-$	$O_2 + 2\ CO_2 + 4\ e^- \rightarrow 2\ CO_3^{--}$
SOFC(6)	800 - 1000	H_2 CO CH_4	50 - 60	$H_2 + O^{--} \rightarrow H_2O + 2\ e^-$ $CO + O^{--} \rightarrow CO_2 + 2\ e^-$ $CH_4 + 4\ O^{--} \rightarrow 2\ H_2O + CO_2 + 8\ e^-$	$O_2 + 4\ e^- \rightarrow 2\ O^{--}$

(1) PEFC – Polymer Electrolyte Fuel Cell or PEM-FC – Proton Exchange Membrane Fuel Cell
(2) AFC – Alkaline Fuel Cell
(4) PAFC – Phosphoric Acid Fuel Cell
(3) DMFC – Direct Methanol Fuel Cell or SPFC – Solid Polymer Electrolyte Fuel Cell
(5) MCFC – Molten Carbonate Fuel Cell
(6) SOFC – Solid Oxide Fuel Cell

The polymer electrolyte (PEFC) and alkaline (AFC) fuel cell designs are efficient, compact and robust low-temperature methods for electricity producing. These FC models have the highest power density, good load change behavior and good efficiency at partial load, therefore ideally suitable for mobile applications. The direct methanol fuel cell (DMFC) operates on liquid or gaseous methanol combined with a reforming process. This model offers a good storage capability in mobile systems. The next type - phosphoric acid fuel cells (PAFC) have gained the most practical experience. Due to its higher operating temperature the CO poisoning problem is minimized and it provides a good quality steam of approx. 200° C that can be used in combined heat and power (CHP) mode. The molten carbonate fuel cell (MCFC) can operate with H2, methanol, methane or coal gas with external or internal (partial or full) reformation. Drawbacks of this FC are its low current and power densities. The solid oxide fuel cell (SOFC) converts gaseous hydrocarbons as a fuel either directly or after internal reforming with a very low emission level. Its very high operating temperature allows fast chemical reactions, what on the other hand side leads to stringent requirements for materials and construction.

Fuel cells are also appropriate for stationary applications such as large-scale central power generation, distributed generation and cogeneration. Through waste heat recovery in a cogeneration system the FC efficiency can be increased up to 80% [80].

9.4 Advantages and disadvantages of fuel cells

9.4.1 Advantages

Fuel cells as energy converter combine many of the advantages of combustion engines and batteries such as:

- high efficiency due to direct conversion of chemical energy into electricity
- FC generate in times more energy per unit weight than engines and storage batteries
- Fuel cells contain no moving parts, means they are silent, reliable and long-live systems required little maintenance
- obtain fast start-up and load response
- cleanness - no harmful gas emissions such as NO*x* and SO*x*
- easy independent scaling between power (defined by the size of the FC) and capacity (defined by its fuel tank volume). Well scaled from 1 W up to MW power plant ranges
- FC are faster rechargeable (refuelled) than batteries [81].

9.4.2 Disadvantages

Depending on the type of the FC apply various special restrictions. For instance in low-temperature fuel cells have to be used noble metal electrodes in order to increase the reactivity. Whereas in high-temperature FC expensive noble metal catalysts are not used since the thermal activation is insensible to pollutants. To avoid dilution of the electrolyte, the product water has to be removed by evaporation or vaporization, what is anyway the case in high-temperature fuel cells [80].

The alternative fuels such as gasoline, methanol or formic acid usually require reforming before using. This obstacle makes the use of additional equipment necessary and reduces the performance of the fuel cells.

As main disadvantage of the FC still can be considered their relatively high costs.

The power density limitation of the fuel cells is another relevant hurdle for their implementation. The power density shows how much power the system can generate per unit volume (volumetric) or per unit mass (gravimetric). And although significantly improved in the last years, fuel cells still show lower volumetric power density performance compared to the combustion engines and batteries (on a gravimetric basis FC perform closer to the other both energy converter types) [81].

9.5 New approaches in fuel cell design

9.5.1 Fuel cell for aqueous sulphide

With the goal of cleaning the waste gases and waters from the environment harmful sulphides in the past decades various not electro- but physico-chemical methods such as chemical oxidation and conversion by using of catalysts were used for oxidizing sulphides to harmless products such as elemental sulphur or sulphate. The disadvantage of these methods - the significant amount of energy and chemical needed, forced the scientists to research on development of more energy efficient and environment friendly technologies. The electrochemical oxidation is such a one. The methods based on it have several advantages such as higher energy converting efficiency, environmental compatibility, ability for automation, versatility and cost effectivity [84].

In chapter 8 were already presented the three different forms of aqueous hydrogen sulphide, namely the undissociated H2S° molecules and the sulphide (HS^{-}) and polysulphide (S^{2-}) anions. The distribution ratio of these sulphide forms is determined by the pH of the water. Their electrochemically oxidation in the anode compartment of a fuel cell lead to a flux of released electrons, hence, generation of electricity. By-products such as elemental sulphur, polysulphides, sulphites, sulphates, dithionate and thiosulphate may be produced in dependence on the test conditions of various experiments [84].

Dutta et al., 2008, achieved positive experimental results on removal of aqueous sulphide through electrochemical oxidation and generation of electricity in a FC at ambient temperature, pressure and neutral pH. However, the main disadvantage here is the accumulation of elemental sulphur in the anode compartment, which decreases the electrochemical activity over time, quasi lowers the performance of the fuel cell. Therefore further researches were needed for deployment of methods for reactivation of the anode and recovering of the sulphur built on its surface.

9.5.2 Microbial Fuel Cell

In recent years, one of the most famous research area in the fuel cell technologies belongs to the microbial fuel cells (MFC). These FCs are bio-electro-chemical systems that use the respiratory process of electrogenic bacteria (i.e. *Lysinibacillus macrolides*) for electricity generation. The electrons released during the breakdown of organic matter by anaerobic bacteria are transferred to the anode section of the MFC and the H2 molecules flow to the cathode and convert into water. For fuel, the MFCs can use renewable organic substrates such as food processing water or various wastewaters.

A cost effective MFC green technology was suggested in a new system design (Vanita et al. 2016) with low liquid by utilizing pencil graphite lead as electrode material and salt bridge as proton exchange membrane. With lab-scale models, the researches proved that *Lysinibacillus macrolides* bacteria can operate in anaerobic conditions as electrochemical substance and utilized the flow of rendered electrons in built lab scale microbial fuel cells (Figure 76) [82].

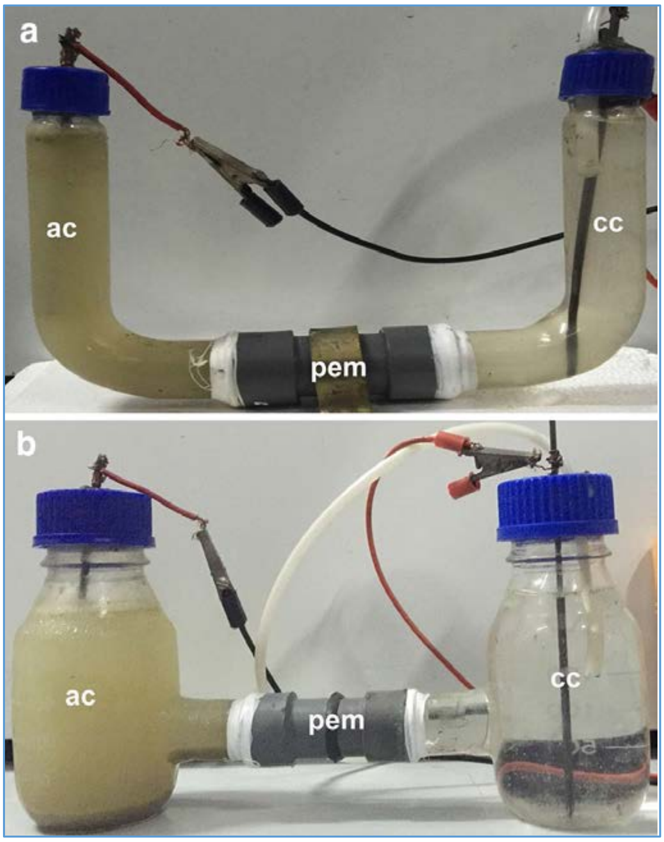


Figure 76. Lab scale microbial fuel cell models: a. UT-MFC and b. HT-MFC [82]

- ac - anode chamber
- cc - cathode chamber
- pem - proton exchange membrane (a salt bridge, built by using KCl and agar)

The newly designed UT-MFC (U shape, Figure 76a) showed higher electron production respectively an voltage output of about 377 ± 18,85 mV when compared to only 237 ± 11,85 mV from the HT-MFC (H shape, Figure 76b). The increased internal resistance of the HT model caused by the bigger liquid volume could explain this. Microbial fuel cells are recognized to be eco-friendly generators of green energy using wastewaters as a fuel [82].

"*Microbial fuel cells are tangible proof that bacteria use organic substrates to produce reducing power and to transfer electrons through exogenous materials to oxidants in the environment*" (Reimers at al. 2006).

9.5.3 Benthic Microbial Fuel Cell

Benthic microbial fuel cells (BMFC) are in seafloor environments operating MFC that generate electrical power by biogeochemical reactions of converting the chemical energy stored in organic carbons into electricity. BMFC´s functionality is based on the natural redox (see footnotes 21, 23 and 24) processes carried out in aqueous sediments.

The electrodes, as mentioned in previous chapter, are made of a noncorrosive material (e.g. graphite). The anode is imbedded into the anoxic sediment and the cathode is positioned in an overlying oxic water (Figure 77). An external circuit connects electrically the both electrodes. The fuel cell function is based on the biological activity of the sediment surface layer that acts as a native membrane and divides the natural reductants from the oxidants simultaneously enabling the internal ion flow between the anode and the cathode. The electron flow occurs via the load at the external electrical connection between the electrodes [83].

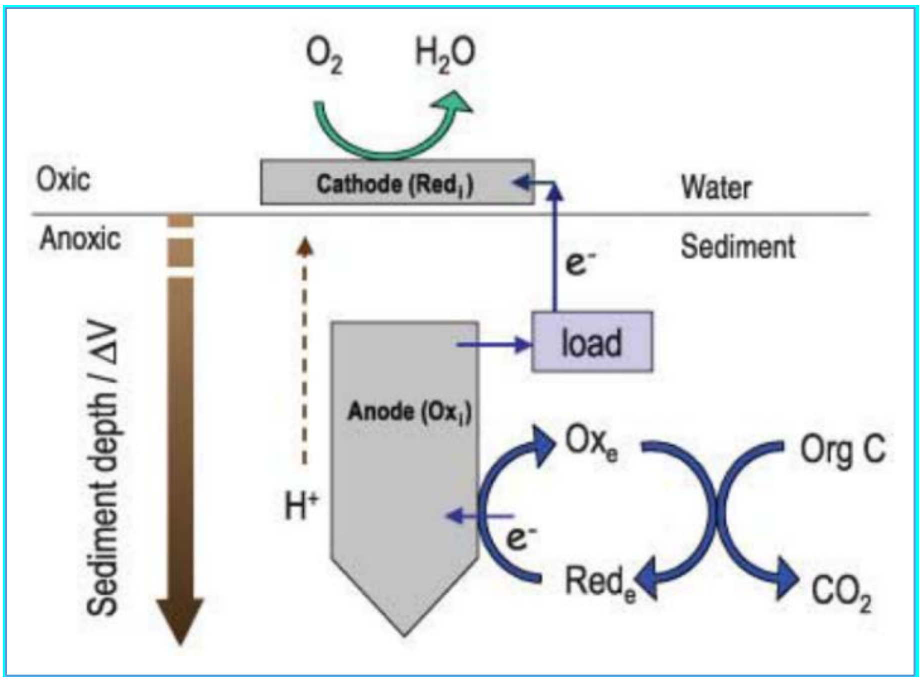


Figure 77. Shematic diagram of a benthic microbial fuel cell (BMFC) [83]

The presence of hydrogen sulphide in the benthic sediments respectively its oxidation even increases the obtained power density of the BMFC initially. However, the disadvantage of a long-term operation is the deposition of elemental sulphur on the anode electrode causing its deactivation and limitation of mass transport, hence a significant decrease in the power density (see also chapter 9.5.1).

Under deployment is the overcoming of the above-mentioned disadvantage and potential application of BMFCs as energy sources for autonomous sensors and communication appliances operated in fresh and salt waters [83].

9.5.4 Direct Alkaline Sulphide Fuel Cell

As described in the above chapters the main disadvantage of presented sulphide fuel cells is the sulphur deposition on anode. A team of Korean researches (Kwiyong Kim and Jong-In Han, 2014) suggested a new approach, namely using of alkaline sulphide as a fuel in the so-called direct alkaline sulphide fuel cell (DASFC). In this technology electricity is produced through oxidizing of sulphide not to sulphur, like in previous methods, but down to sulphur oxyanions such as thiosulphate ($S_2O_3^{2-}$), sulfite (SO_3^{-}) or sulphate (SO_4^{2-}). On this way, more energy stored chemically in H2S can be retrieved and converted into electricity with the additional advantage of absence of sulphur deposition on the anode electrode. Another plus in contrast to the widely spread hydrogen and methanol FCs, which use noble catalysts for their oxidation process, is that the alkaline sulphide as a fuel features high electrochemical activities so that there is no implicitly need of catalyst. However, for achieving of even better electrical characteristics of the fuel cell, the already very good activity of alkaline sulphide can be further increased by using of electrocatalysts such as Pt/C[25] (Figure 78) [85].

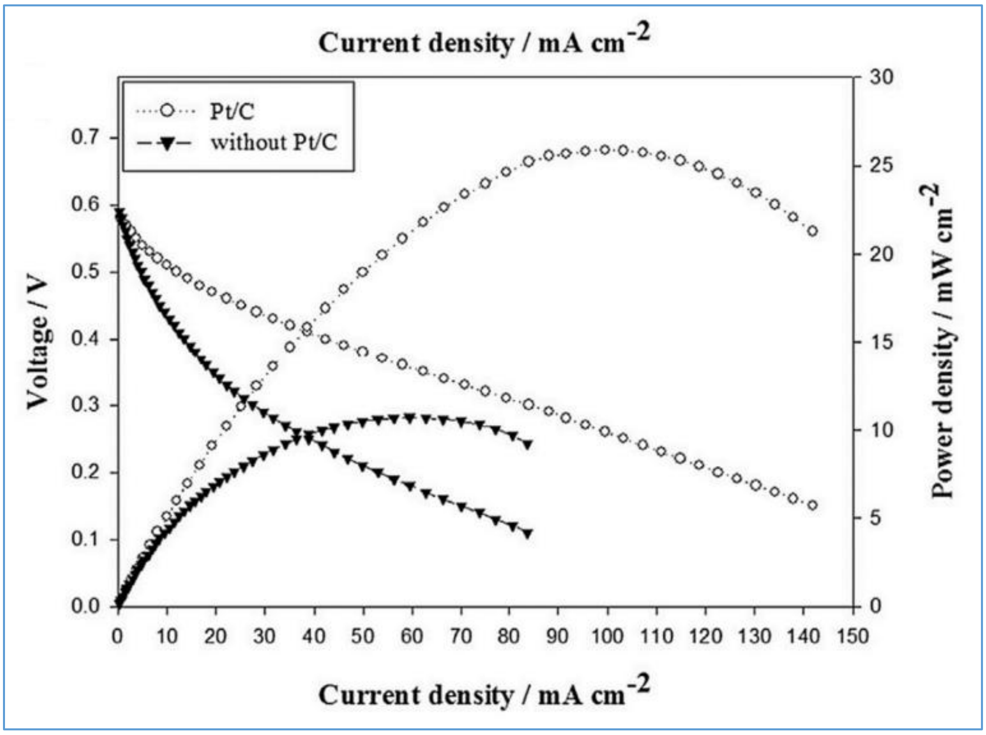


Figure 78. Effect of presence of Pt/C catalyst on the performance of DASFC [85]

---

[25] *"Platinum on carbon, often referred to as Pt/C, is a form of platinum used as a catalyst. The metal is supported on activated carbon in order to maximize its surface area and activity"* [86].

Increasing of temperature, sodium hydroxide (NaOH) and sulphide concentrations also lead to better electrical performance of the DASFC [85].

The main disadvantage here is that direct alkaline sulphide fuel cell operates with relatively high concentration (up to 3 M (mole)) of the strong alkaline solution of NaOH for producing of the alkaline sodium sulphide (Na2S) through reaction with H2S. This circumstance does not allow an application of DASFC in the Black Sea due to the environment protection and further reasons explained in the next chapter.

10 SDFC – ELECTRICITY GENERATION from H2S in the BLACK SEA

Invention of a new environment friendly technology for electricity generation by utilizing of hydrogen sulphide in the Black Sea as a fuel and at the same time rescue its waters from this poisonous substance and improvement of the ecological situation in the basin has been the main goal of the Bulgarian team of scientists led by prof. Venko Beschkov from the Institute of Chemical Engineering in Sofia. Their research work was supported by the project "Hydrogen production from Black Sea water by the sulphide-driven fuel cell HYSULFCEL" (http://www.bs-era.net), 7th FP[26] of the European Union, Pilot Joint Call 2010/2011 of the Ministry of Education, Youth and Science, Republic of Bulgaria.

"Chemical and microbial fuel cells represent a new and modern approach to the removal and disposal of pollutants produced naturally or due to human activity and generate energy at the same time (Zhai et al. (2012), Cai & Zheng (2013), Demirbas (2009), Beschkov et al. (2015))" [78].

Solid oxide fuel cells (SOFC) were one of the first attempts for using of H2S as a fuel (Pujare et al., 1987 and Jian-Jun et al., 2004). Their disadvantage, however, is the very high operating temperature (750°-900° C) and producing of sulphur as final product.

In the previous chapter were observed some new approaches in the FC technologies for utilizing of sulphides as an energy carrier for generation of electricity. The possibilities for using of modern microbial fuel cells are not applicable in the Black Sea due to the sulphite´s high toxicity for most bacterial species [87]. On the other side the above presented BMFC and DASFC show the obstacle of elemental sulphur deposition on the anode electrode causing its deactivation and limitation of mass transport, hence a significant decrease in the power density.

Furthermore, the DASFC operates with relatively high concentration (up to 3 M) of the strong alkaline solution of NaOH for producing of the alkaline sodium sulphide (Na2S) through reaction with H2S. This leads to higher pH in the range above 12. At different pH levels, also the processes conducting on the electrodes of the FC are different with diverse output materials and electrical characteristics (the higher pH the better performance of the sulphide FC). But the pH of the Black Sea possess values

---

[26] https://en.wikipedia.org/wiki/Framework_Programmes_for_Research_and_Technological_Development

between 7 and 8,5 (chapter 8). This equates to a lower H2S concentration up to 22 mg/l, which corresponds to mM (1.000 times less than in the DASFC technology). The DASFC operates on land with H2S gained from waste materials. This allows using of many treatment technologies, what is not possible to be done inside the sea. The sulphide driven fuel cell (SDFC) of prof. Beschkov is foreseen for operation in and with the Black Sea waters. These circumstances engage in using of hazardless materials in order to guarantee the environmental protection of the see [88].

After all listed disadvantages the goal of the Bulgarian team was to invent an energy efficient, sustainable, environment friendly and in the Black Sea waters applicable fuel cell technology enabling an operation under ambient conditions and closing of the fuel-final product circle, hence, make it renewable. The idea was to generate electricity from the H2S by electrochemical conversion of toxic sulphides down to harmless sulphates. Thus, on the one hand side gaining more energy and avoiding sulphur accumulation, and on the other, make the process renewable by releasing the sulphates into the sea, where they get converted back into hydrogen sulphide through the anaerobic respiratory of the sulphur reducing bacteria (chapter 7).

The initial project of the Bulgarian researchers in 2011 was to utilize the H2S from the Black Sea as a raw material for hydrogen production by electrolysis. However, the energy input (187-223 MJ/kg) was higher than the energy yield from the produced H2 (144,2 MJ/kg) [8]. So the further experimental works have been targeted into optimization of the already existed H2S oxidizing fuel cell technology. The goal was to overcome the well-known disadvantages such as sulphur accumulation and low enthalpy of sulphide-to-sulphur conversion (263 kJ/mole). Within the last 4 years has been developed the new sulphide driven fuel cell with increased efficiency, which generates electricity by using H2S-containing seawater as a fuel and transforming the sulphide forms in it into sulphate ones. Thus, yielding more energy by increasing the enthalpy to 788 kJ/mole and resolving the sulphur accumulation problem. The final product - the harmless sulphates, do not poison the catalysts used in the process and even more get entered back into the sea closing on this way the natural microbial cycle, hence, making the process renewable [90, 93].

In order to demonstrate the difference between the old (sulphide to sulphur oxidation) and the new (sulphide to sulphate oxidation) FC operating principals, their electrochemical electrode reactions are shown below [91, 93]:

FC with sulphide ***to sulphur*** oxidation:

Anode:

$$2S^{2-}\ \mathbf{-\,4e^-} = \mathbf{2S} \tag{15}$$

Cathode:

$$O_2 + 4H^+ \mathbf{+\,4e^-} = 2H_2O \tag{16}$$

Net reaction:

$$O_2 + 4H^+ + 2S^{2-} = \mathbf{2S} + 2H_2O \tag{17}$$

SDFC based on sulphide ***to sulphate*** oxidation (with ***proton*** exchange membrane):

Anode:

$$S^{2-} + 4H_2O \mathbf{-\,8e^-} = \mathbf{SO_4^{2-}} + 8H^+ \tag{18}$$

Cathode:

$$2O_2 + 8H^+ \mathbf{+\,8e^-} = 4H_2O \tag{19}$$

Net reaction:

$$S^{2-} + 2O_2 = \mathbf{SO_4^{2-}} \tag{20}$$

or

SDFC based on sulphide ***to sulphate*** oxidation (with ***anion*** exchange membrane):

Anode:

$$S^{2-} + 6OH^- = SO_3^{2-} + 3H_2O \mathbf{+\,6e^-} \tag{21}$$

$$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O \mathbf{+\,2e^-} \tag{22}$$

Anode total:

$$S^{2-} + 8OH^- = SO_4^{2-} + 4H_2O \mathbf{+\,8e^-} \tag{23}$$

Cathode:

$$2O_2 + 8H^+ \mathbf{+\,8e^-} = 4H_2O \tag{24}$$

Net reaction:

$$S^{2-} + 2O_2 = \mathbf{SO_4^{2-}} \tag{25}$$

As can be seen from the above equations the conversion of the sulphide to sulphate ions instead to elemental sulphur is not only environmentally but also energetically much better, because of the transfer of eight instead of only two electrons (per sulphide anion), thus four times more energy can be obtained [92].

Sulphide to sulphate oxidation in a fuel cell may occur through a proton exchange membrane permeable for hydrogen protons (Figure 79a, Equations 18-20) or through an anion exchange membrane (Figure 79b, Equations 21-25) permeable for hydroxyl anions. In the latter, the oxidation process passes through intermediate reactions such as sulphide to sulphite (Equation 21) and sulphite to sulphate (Equation 22) [93]. The principal sketch of both SDFC types is shown on Figure 79 below. The fuel cell consists of two compartments. The one containing the anode electrode is called sulphide reactor (SR) and the other compartment, containing the cathode electrode is the oxygen reactor (OR). The two compartments are connected through an ion permeable membrane.

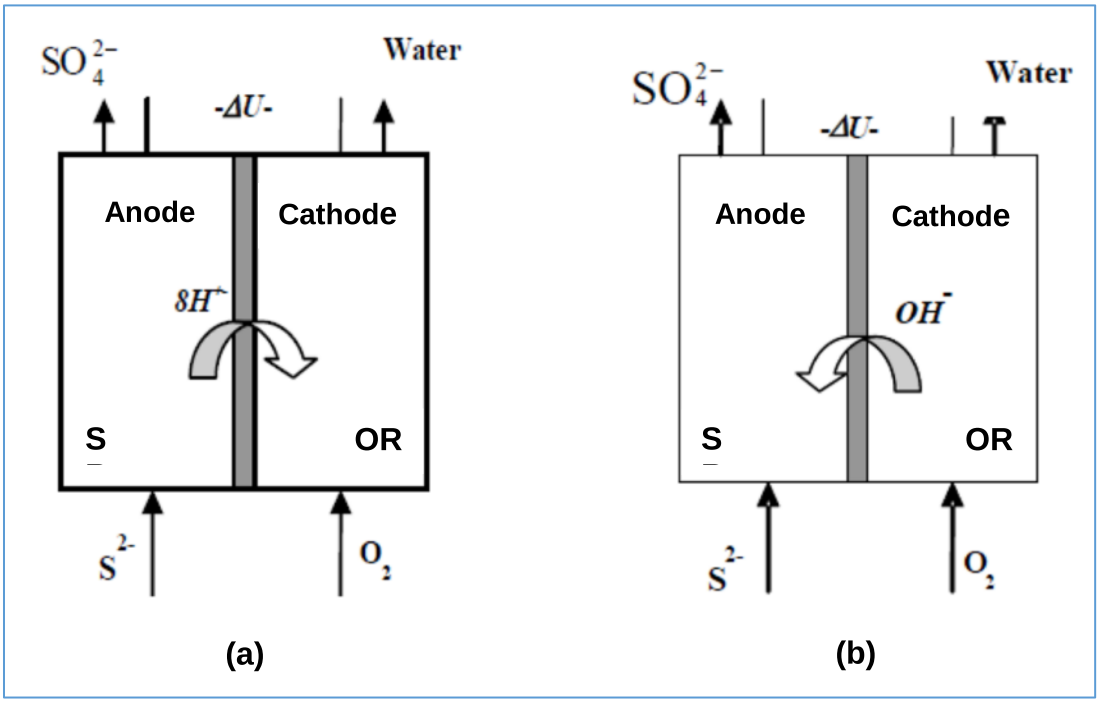


Figure 79. SDFC with hydrogen proton (a) and hydroxyl anion exchange (b) [23]

In the Black Sea out of environment protection reasons, marine water will be used as electrolyte solution. The availability of calcium and magnesium cations there would block the proton exchange membrane. This led to the decision of using the anion exchange prototype in further research activities [93]. Other ecological restrictions and such, based on sulphide high corrosiveness that had to be obeyed in further development works were as follow [75]:

- Not using of chemical oxidizers for the cathode compartment (e.g. cyanoferrate, bichromate etc.) instead of oxygen
- Not using of other supporting electrolytes but marine water
- Not using of any sulphur-containing compounds but HS^- or S^{2-}
- Not using of metal parts in the fuel cell (incl. electrodes)

Other observed specific characteristic was that spontaneous electrode reactions didn´t fit the required ones and that´s why selective catalysts were required for supporting the oxidation process. Cobalt spinel and zirconia embedded into activated carbon, carbon felt, activated carbon solely and graphite were studied; five different ion-exchange membrane were tested [75].

10.1 Design of SDFC

The leading intention at the construction process was to improve the energy efficiency of the FC. The milestones in the minimizing of the internal losses (in order to ensure a higher electromotive force) were choosing of proper electrodes, catalysts and optimal design. The experimental works were carried out with different prototypes. Various sizes, materials and positions of sulphide and oxygen compartments, their electrodes as well as the electrical connections between SR and OR sections were investigated. As oxidant were used air or pure oxygen (economically and environmentally the most appropriate oxidizer) blown into the cathode space. The initial experiments were carried out with constructions equipped with various salt bridges as connection between anode and cathode sections (Figure 80a). On later stage was established that the ion exchange membrane constructions (Figure 80b) provides better electrical characteristics. The membrane Celgard 3510 was selected due to its best performance [90, 92-98].

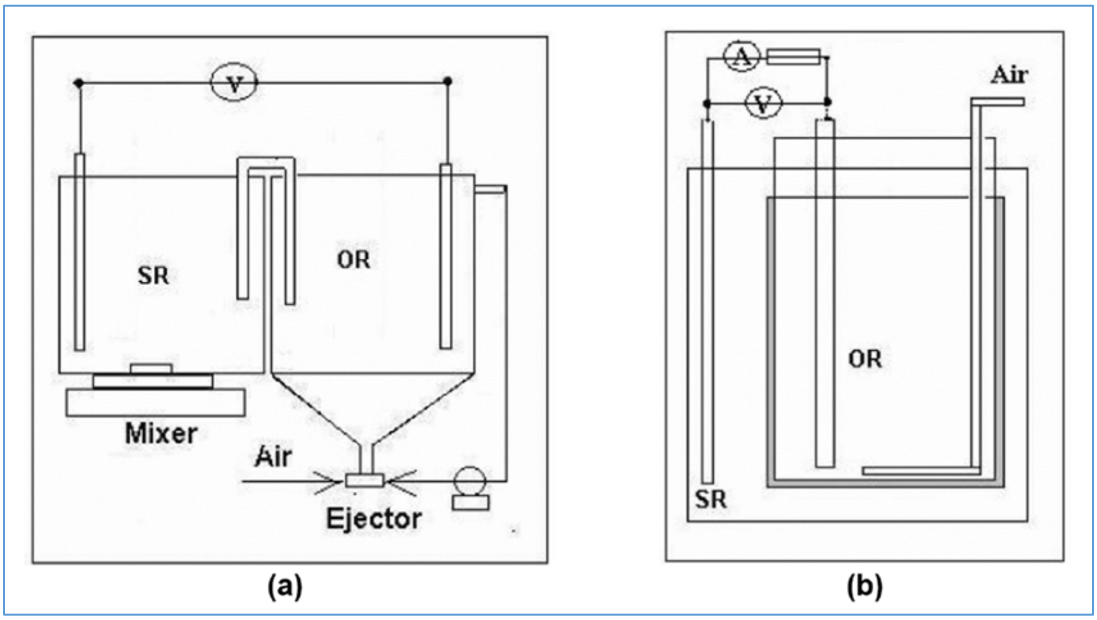


Figure 80. FC constructions with salt bridge (a) and ion permeable membrane (b) [94]

During the years 2011-2014 the design has been optimized and finaly reached to an operating pilot-scale industrial model tested in real conditions in the Black Sea waters. The intended application of the SDFC is deploying of the generated electricity for sea water electrolysis to produce hydrogen. It could be stored e.g. in form of metal hydrates. The oxygen is planned to be used directly in the oxidation reactor of the fuel cell. The design of the fuel cell has undergone various stages of optimization described in detail in scientific publications (Martinov et al. 2013, Razkazova-Velkova et al. 2013) and resulted in an well-functioning lab-scale model (Razkazova et al. 2014). But the energy obtained from a single fuel cell was not enough for the process of electrolysis. Therefore was designed and assembled a semi-scale industrial installation built of two in a stack[27] connected FCs (Figure 81).

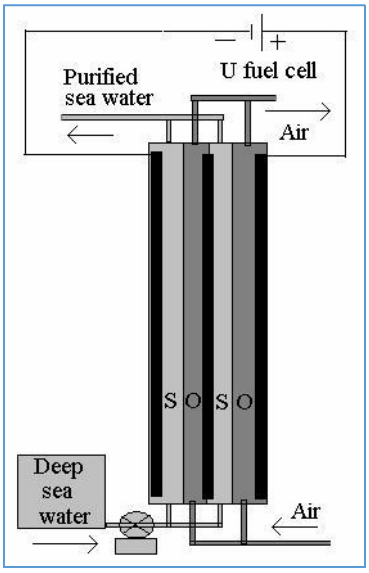


Figure 81. Semi-scale industrial installation of SDFC [97]

A peristaltic pump provides the supply of the sulphide reactors with H2S-containing deep layer´s seawater and its mixing. The aeration of the oxygen compartments is solved by a direct air supply. The volume of each oxygen compartment is completely filled with upper layer´s seawater (no H2S in it) and with granulated active coal. This ensures shattering of the airflow into very small sized air bubbles, thus, better oxygen dissolution and at the same time increasing of the active cathode surface and reducing of the cathode-anode distance.

It was clear that also with a two-cell stack the required energy levels could not be achieved. However, the idea was to test the combination of the individual cells and

---

[27] See page 33

the corresponding electrical characteristics of the stack. The obtained results led to the conclusion that 5-6 fuel cells connected in the proposed way and operating with increased sulphide concentrations would achieve the voltage and power levels necessary for electrolysis performing, i.e. the production of hydrogen is feasible [97]

10.2 Electrodes in the SDFC

For optimization of the electrochemical characteristics of the sulphide driven fuel cell different types, designs and sizes of the electrodes were tested. Best results were achieved with electrodes containing cobalt (Co) in an activated carbon matrix in the anode (sulphide) compartment and pure activated carbon in the cathode (oxygen) section [95]. The FC electrodes have to satisfy several conditions:

- to be mechanically strong and chemically resistant
- catalysts deposition on the electrodes must not be possible (in order to keep the contact surface active during long-term operation)
- the electrodes material must not poison the catalyst (in order to keep it chemically active during long-term operation)

Various types of electrodes were tested, amongst others such as:

- Graphite rods
- Electrode over Nickel (Ni) foam (it contains activated carbon, graphite and cobalt catalyst)
- Graphite rods with on the surface deposited activated carbon
- Pyrolized and activated carbon padding

Comparisons of the electrical power and oxidation rates values obtained with SDFCs by using the above-mentioned types of electrodes are presented on the Figure 82 and Figure 83:

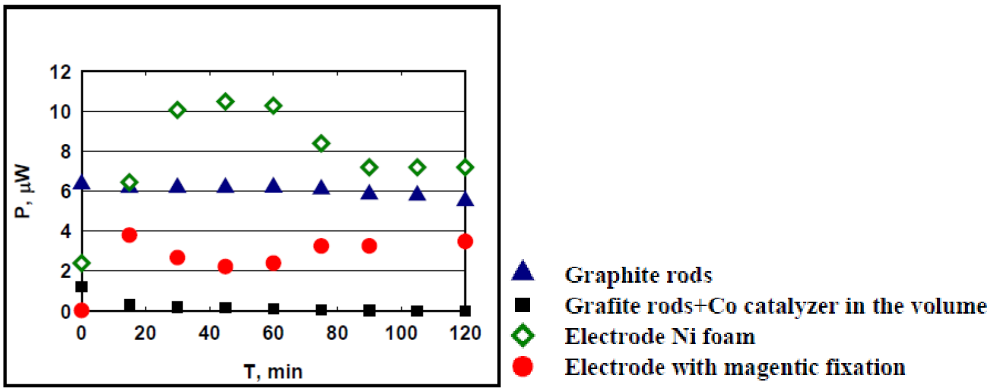


Figure 82. Electrical power obtained from SDFC with different electrodes [92]

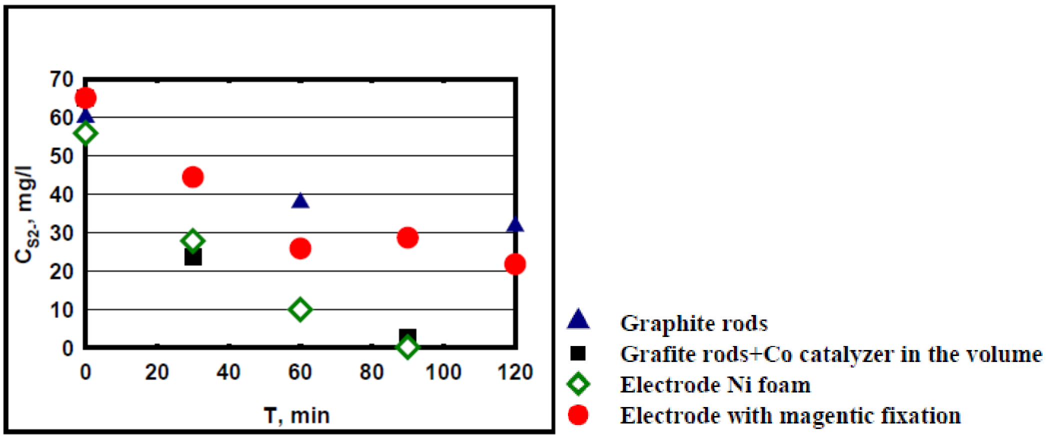


Figure 83. Oxidation rate with different electrodes [92]

The higher the power and the faster the oxidation process, the better is the performance of the fuel cell. From both electrochemical diagrams above is visible that the best results were obtained with the Ni foam electrodes. However, it was observed that after some period the working solution in the fuel cell destroys the Ni foam, so this type of electrode cannot be used.

It was detected that the surface of the electrodes significantly influences the generated electrical power of the fuel cell. The experiments were made by depositing of activated carbon over the electrodes and by its pouring into the FC compartments. This led to an improvement of all electrical parameters and the obtained power increased over 3,6 times from 2,2 µW to 8 µW compared to pure graphite electrodes (Table 12).

Table 12. Electric parameters with two types of graphite electrodes [92]

Type of Electrode	U, mV	I, mA	P, µW	U, mV (open circuit)
Graphite +AC	42	0.19	8	320
Graphite	22	0.1	2.2	200

A comparison of SDFC performance with activated carbon added into the sulphide (anode) reactor only to such with adding in both reactors is presented in Table 13.

Table 13. Electric parameters with AC in one (SR) or both (SR & OR) compartments [92]

Type of Electrode	U, mV	I, mA	P, µW	U, mV (open curcuit)
AC in the SR	31.8	0.15	4.8	180
AC in both reactors	74.5	0.34	25. 3	440

As can be seen when activated carbon is poured into the oxygen (cathode) reactor as well, the obtained power increases even over 5 times. So it was decided to continue the experiments with the better-performed variants.

Another substantial possibility to improve the FC performance is the deposition of a catalyst on the electrodes. This increases the sulphide oxidation rate as well as the power of the fuel cell. In order to prove it experimentally, electrodes of pyrolized and activated carbon padding with and without Co catalyst were prepared. The different levels of achieved power are presented on the next Figure 84:

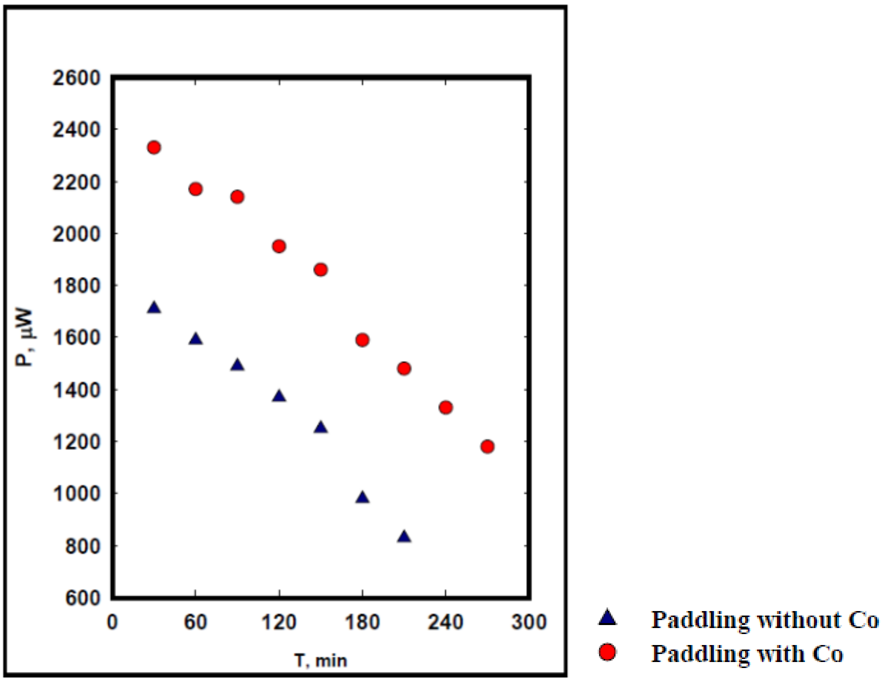


Figure 84. FC power with electrodes with and without deposited catalysts [92]

The padding electrode enriched with catalyst showed better performance. Unfortunately, after few hours of operation, the catalyst was extracted from the paddling and was no more active.

The main perspectives for more efficient SDFC were to create electrodes with bigger specific surface and with tightly incorporated catalyst in them. Best results were achieved with electrodes containing cobalt (Co) in an activated carbon matrix in the anode (sulphide) compartment and pure activated carbon in the cathode (oxygen) section. The energy efficiency of the fuel cell was improved by optimizing the material, design, number and position of the electrodes [92, 95-98].

10.3 Using of catalysts

The efficiency of the SDFC depends on the conversion rate of sulphide into sulphate in the anode (oxidation) section of the fuel cell per unit time. Thus, the accelerating of the process by using of appropriate catalysts is very important [91].

Different catalysts such as activated carbon, zinc sulphide, cobalt sulphide and some other cobalt- and manganese-containing compounds were tested. The experiments were carried out with various initial sulphide ions concentrations in the range 25-125 mg/dm^{-3}. At the entire range was observed that by using of catalysts over 90% of the sulphide ions were oxidized in about 3 hours whereas without catalysts the process ran much slower and reached only 40% oxidation in the same period. The best results were established with spinel-type[28] cobalt and manganese oxides incorporated in a matrix of activated carbon [70, 100]. From the next Figure 85 can be obtained the significant acceleration of the oxidation process by using of catalysts. They increase the velocity not of the main reaction only, but have the same impact on the secondary reactions as well. On this way, the catalysts prevent accumulation of intermediates and the delay of the main oxidation reaction. The retention section in the oxidation rate in the case of catalyst absence is due to exactly such accumulations and competitive reactions.

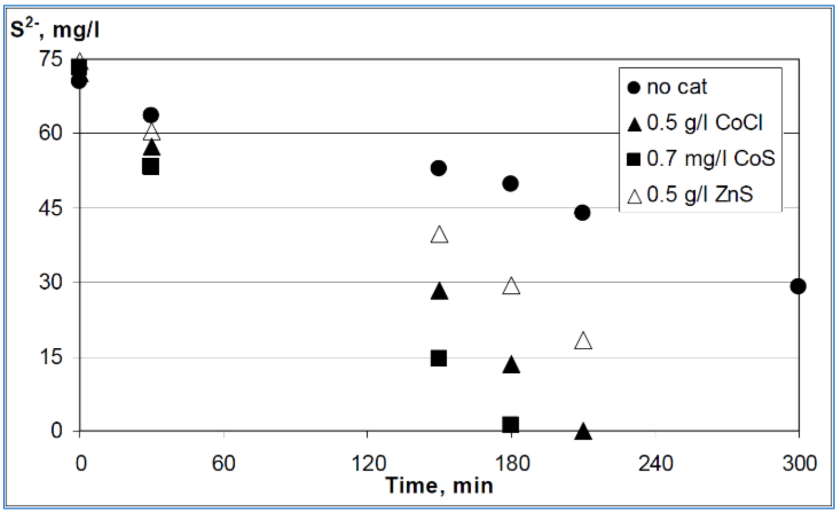


Figure 85. Influence of the different type of catalysts on the oxidation rate [100]

On the Figure 85 is well visible the constant oxidation rate by using of catalysts as well as the better performance of the cobalt-containing catalysts.

---

[28] Spinels are any of a class of minerals which crystallize in the cubic (isometric) crystal system [101]

It was also experimentally proved that the increasing of the amount of the used catalysts leads to a negligible impact on the oxidation rate (Figure 86). It rose with 5% only by adding of 40% more catalyst.

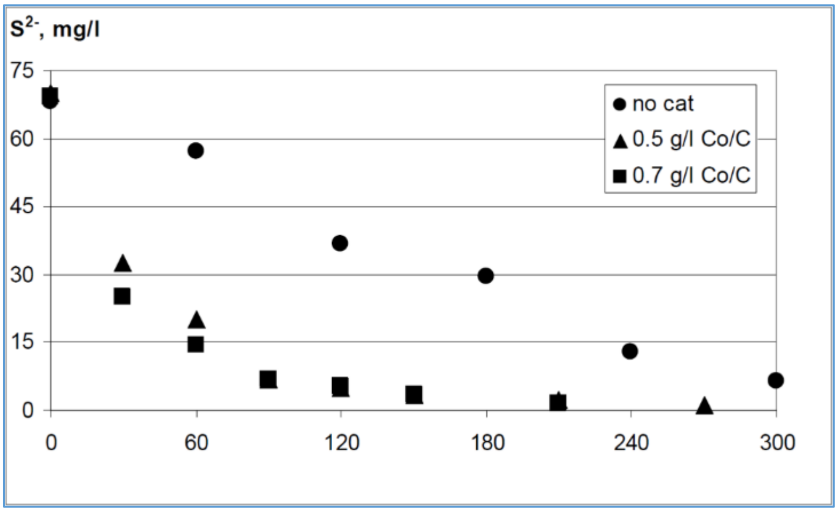


Figure 86. Influence of the quantity of the added catalyst [100]

In addition, experiments with fixed catalyst were carried out. The goal was gaining of applicable experience for integrating of catalysts into electrodes in order to use the latter in a continuously way. The better performance of the fixed catalyst is obtainable from the comparison made in the Figure 87. About 80% of the sulphide ions are oxidized in the first 60 minutes in the case of the not fixed type, whereas, despite the considerably decreased interfacial surface, with the fixed catalysts a rate of about 95% is achieved at the same time. This fact led to the conclusion that the used catalysts can be successfully incorporated into the next produced electrodes [70, 100].

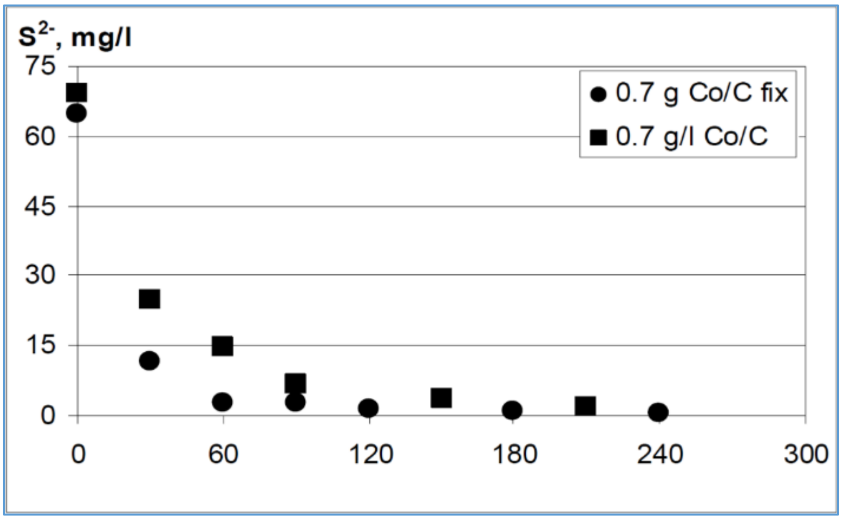


Figure 87. Comparison between fixed and added into the reactor catalyst [100]

Later on, the catalyst experiments were continued with various metal oxides integrated into a matrix of activated carbon (prepared in accordance with Ljutzkanov BG Patent, 2002). Additional advantage of the activated carbon is that it also acts as a catalyst (Dermendzhieva et al., 2013). The tests had shown that the adding of this type of catalysts into the reactor effects in about 50-90 % acceleration of the oxidation process in the first hour (Figure 88). Zirconium oxide (ZrO2) was selected for further experiments due to its 40% better performance compared to the other metal oxides [92].

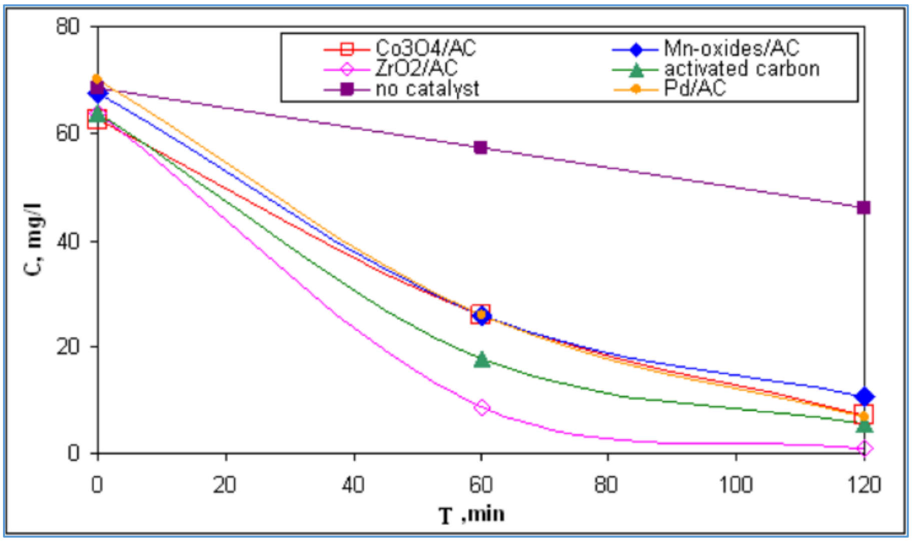


Figure 88. Influence of the type of catalyst on the oxidation rate [92]

The efficiency of the SDFC was experimentally improved by selecting of catalysts with the best-achieved acceleration of the oxidation rate. Additionally, it was decided to use fix catalysts incorporated into the electrodes.

10.4 Influence of fuel´s (H2S) temperature and concentration

10.4.1 Influence of temperature on the oxidation of sulphides

Experimentally was investigated the impact of temperature levels on the oxidation rate of hydrogen sulphide and on the obtained electromotive force[29] (emf) at the same concentration of sulphide ions in the simulated solution of seawater. Tests with two temperature values of the fuel solution, namely 20° C and 8° C (the latter represents the real conditions in the 1.000 m depth of the Black Sea waters (see Figure 71)) were

---

[29] Electromotive force, also called emf, is the voltage developed by any source of electrical energy such as a battery or dynamo. It is generally defined as the electrical potential for a source in a circuit. A device that converts other forms of energy to electrical energy supplies an emf to a circuit [102].

carried out. The impact on the oxidation rate of sulphide ions is presented on the Figure 89. As can be observed the quantity of sulphides at 20° C warm solution reduced faster (thus, the oxidation rate is higher) than at the lower temperature of 8° C.

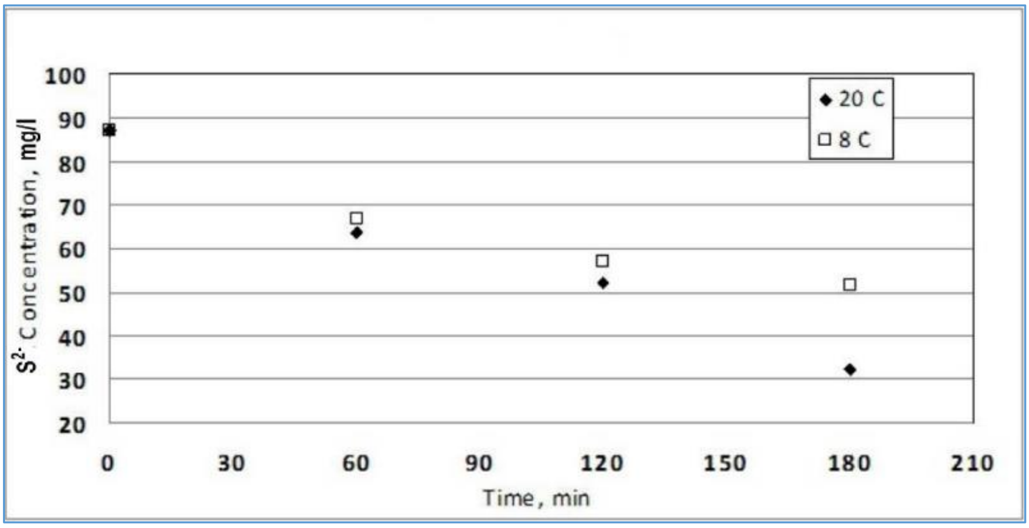


Figure 89. Influence of temperature on the oxidation rate [98]

The next Figure 90 shows similar results at the case of electromotive force comparison at both temperature levels. Namely, the higher temperature led to higher reaction rates and respectively to higher voltage outputs.

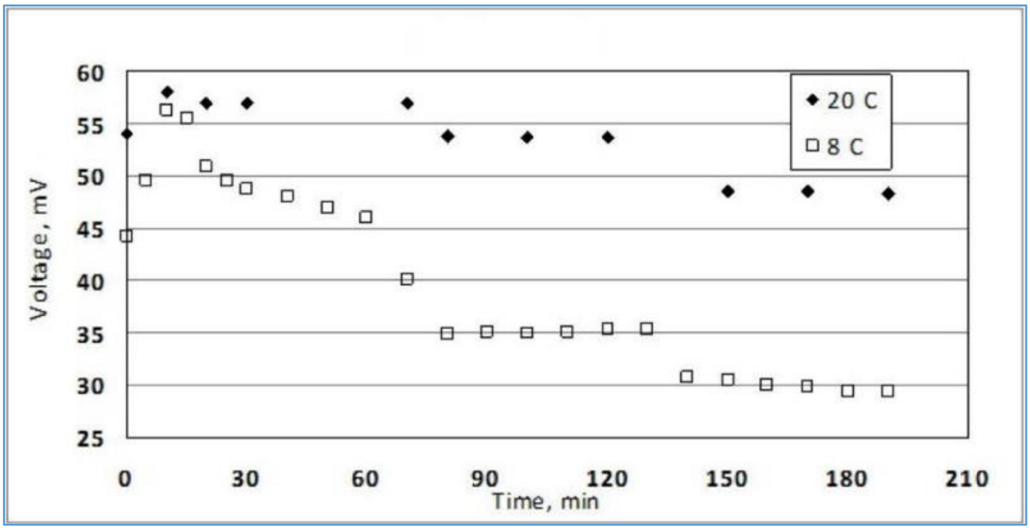


Figure 90. Effect of temperature on the resulting electromotive voltage [98]

At both temperatures were observed initial rises in the voltage. This is explained by the accumulation of ions around the electrodes at the first minutes. In the next section (15-60 min) were recorded comparatively steady voltage levels at 20° C, whereas at 8° C a steeper drop was observed. The latter is explained by the slower interflow of the by-products in the reaction. Then also at this temperature, the voltage output remained relatively constant. The drops after the first and the second hour of the tests occurred due to taking out of samples. This reduced the volume of the fuel solution in the cell reactor [98].

Although at higher temperature (20° C) experiments, the SDFC achieved clearly better performance in the sulphide oxidation rate and the electromotive voltage of the fuel cell, further R&D works had to be carried out at lower temperature level (8° C), which corresponds to the real conditions in the deeper waters of the Black Sea. It was concluded to use appropriate catalysts in order to optimize the process, respectively to improve the FC efficiency [98].

10.4.2 Influence of the concentration at constant temperature

As already mentioned in previous chapters and shown in Figure 71 the temperature of the deeper Black See waters is around 8° C and the concentration of H2S in it there is around 10 mg/l. It was experimentally proved that this natural concentration of hydrogen sulphide is definitely not enough to enable effective reaction rates in the fuel cell, thus, a preliminary enrichment will be necessary [91, 98].

The team of prof. Beschkov carried out experiments with up to 100 times higher H2S concentration than this in the real conditions. Firstly, tests with increased initial concentration of 25 mg/l, 70 mg/l and 110 mg/l of sulphide ions in the simulated see water solution were performed. A comparison of the measured sulphide ions reducing rate is shown in Figure 91.

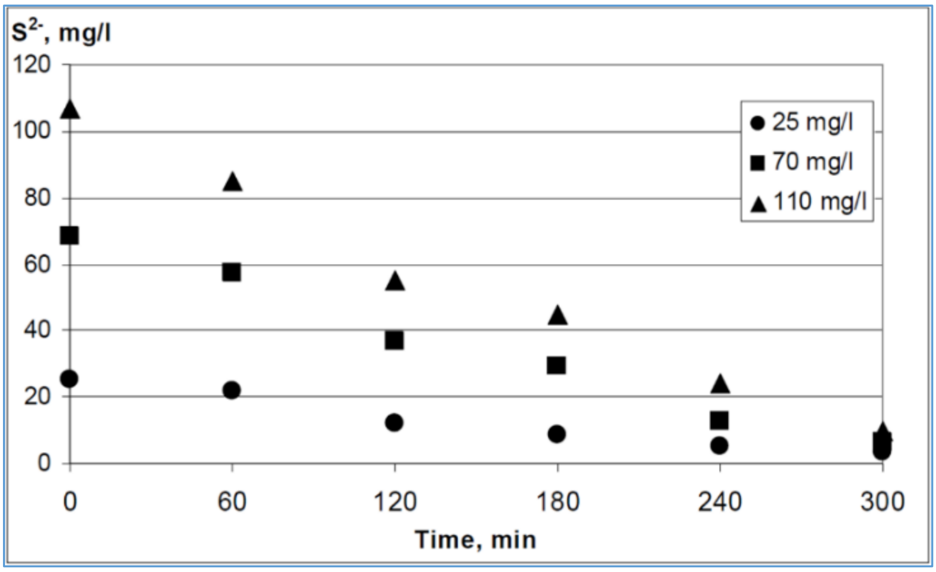


Figure 91. Influence of the initial sulphide concentration on the oxidation rate [100]

It was established that the sulphide oxidation rate does not depend on the initial concentration in this range as in all cases the reduction of the sulphide ions was about 50% at the second hour, about 80% at the fourth hour and 90% at the fifth hour [100]. Further fuel cell performance tests were carried out with two different initial sulphide concentrations in a much wider range (65 mg/l and 1.000 mg/l) at the real conditions temperature of 8°C. In the next Figure 92 is shown the impact of the initial H2S concentration on the SDFC voltage measured during these experiments.

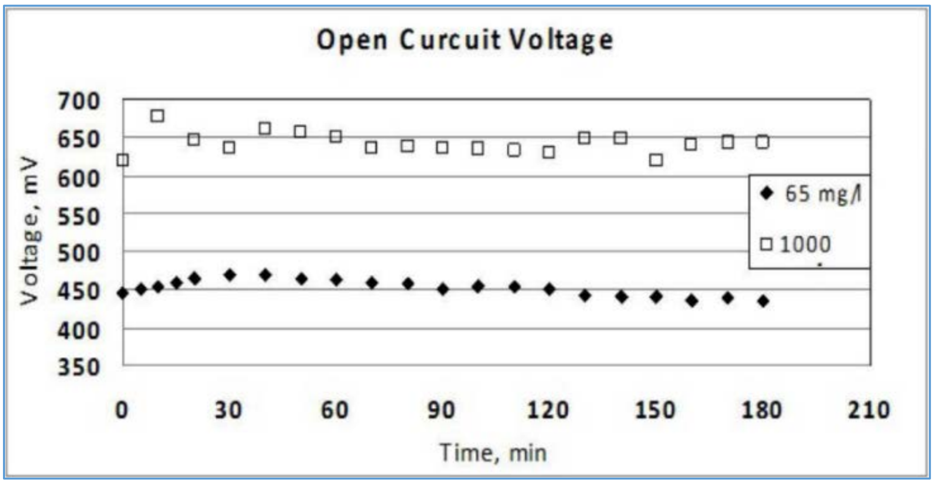


Figure 92. Effect of the initial co*ncentration on the cell* voltage [98]

The relatively constant voltage despite the sulphide's depletion was explained by the additional energy generated in the secondary reactions. However, it was observed that the 150-fold (65 mg/l compared to 1.000 mg/l) higher concentration of sulphide ions in the fuel solution led to *only a twofold* increase of the obtained voltage.

On the other hand, Figure 93 shows that the depletion rate of the sulphide ions is much higher per unit time at higher initial concentration.

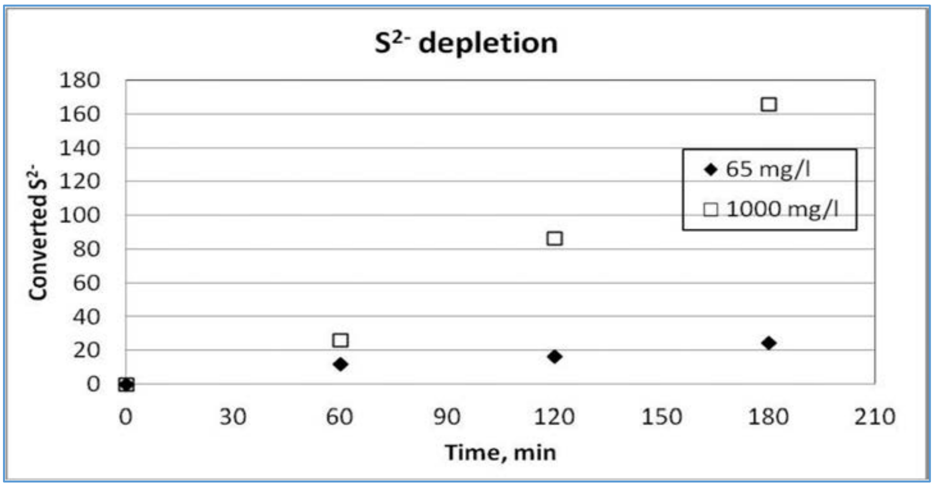


Figure 93. Initial concentration´s effect on the rate of depletion of sulphide ions [98]

So after 3 hours of operation an *eightfold higher* conversion rate of sulphides was established. This was a significant result as the higher oxidation rate defines the better efficiency of the cell. After the gained experience was decided an optimizing of the "*Concentration - Produced energy - Process Rate triangle*" for achieving financial benefits from the realization of the project in the future [98].

10.5 Experiments on a ship in the Black Sea

On the research and development way of reaching to the mature pilot-scale SDFC model various constructions, materials and conditions were realized and tested. Many experiments with different initial concentration of sulphide ions (10-1.000 mg/dm³), with diverse ion permeable membranes and with, based on some heavy metal oxides, catalysts, such as cobalt oxide, zirconia, etc., were carried out. Electrolyte solutions of sea salt with concentrations that simulates the real Black Sea water salt content (14-18 g/dm³) were used. But also sodium chloride was added in some experiments for improving the conductivity of the electrolyte. Both electrodes were mainly built out of graphite. The oxidizer, either air or pure oxygen, were blown into the cathode space during the experiments. Prototypes with two different cell constructions were proved. The one was cylindrically shaped with circular ion-exchange membrane and the other rectangular shaped and assembled in a stack [90].

Such a pilot-scale models were built and successfully tested in situ in July 27-31, 2014 (Figure 94). The experiments were conducted by an international team of researchers from Bulgaria, Rumania and Georgia on the ship "Akademik" (Figure 95) in the Black Sea waters (50 miles[30] (90 km) to the south from Varna[31]) [75, 88, 97].

Figure 94. SDFC pilot-scale model tested in situ on ship in the Black Sea [75]

---

[30] A nautical mile is a unit of measurement defined as 1,852 meters [32]

[31] The biggest city on the Bulgarian Black Sea coast [Author]

Figure 95. Research team on the ship “Akademik” in July 2014 [75]

Some of the in situ obtained experimental results are shown in the next Figure 96 and Figure 97. The well approved ion-exchange membrane Celgard 3501 was used in both prototypes. The ohmic resistance of the cell, which plays a significant role for the FC efficiency, is defined by the area of the used membrane and by the thickness of the cell. The reciprocal value of the resistance of the FC, its conductivity log, was experimental estimated above 2, even reaching values near to 3. This is a much better result compared to the traditional fuel cells operating in gaseous phase, since their conductivity log is below 2 [90].

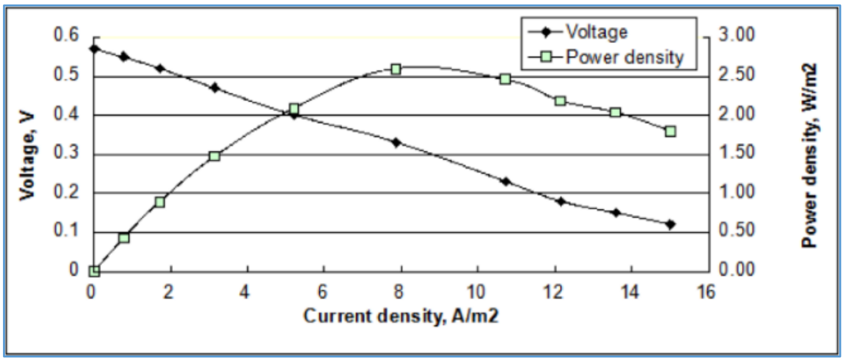


Figure 96. Polarization curves for SDFC_1 [90]
Membrane area: 7 cm²; Sulphide concentration: 241 mg/dm³; Maximum current density: 9.4 A/m²

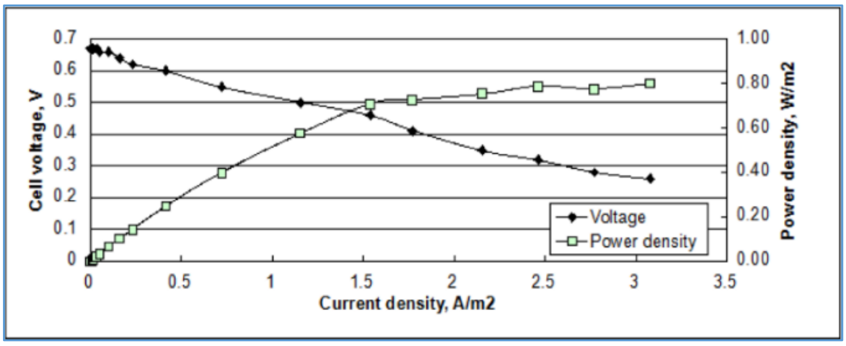
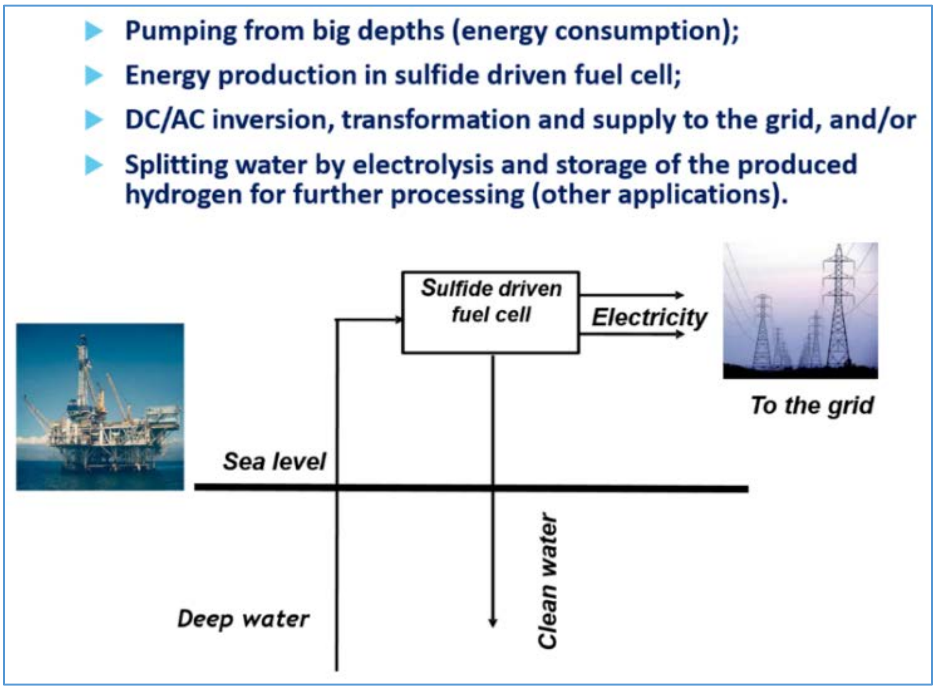


Figure 97. Polarization curves for SDFC_2 [90]
Membrane area: 650 cm²; Sulphide concentration: 230 mg/dm³; Max. current density: 3.4 A/m²

All in situ obtained results showed that the SDFC could be perspective for practical application. They led to the conclusion that 5-6 fuel cells coupled in stack and operating with increased sulphide concentrations would achieve the voltage and power levels necessary for realization of electrolysis, i.e. the electricity generation and production of hydrogen is feasible [97].

11 PRODUCTION STEPS

As described above, the feasibility of the project for electricity generation with the new invented SDFC by utilizing the hydrogen sulphide-containing seawater as a fuel was confirmed by the promising results obtained in situ in the Black Sea waters near to the Bulgarian coast. Based on it, the team of prof. Beschkov has proposed and calculated the following production steps presented on the Figure 98 and Figure 99:



- **Pumping from big depths (energy consumption);**
- **Energy production in sulfide driven fuel cell;**
- **DC/AC inversion, transformation and supply to the grid, and/or**
- **Splitting water by electrolysis and storage of the produced hydrogen for further processing (other applications).**

Figure 98. Production steps for electricity generation by SDFC_1 [89]

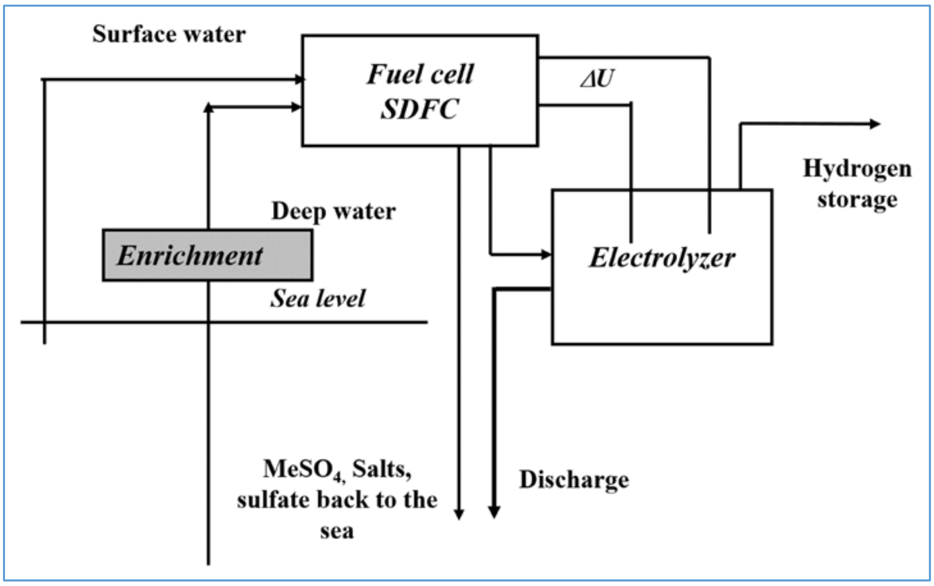


Figure 99. Production steps for electricity generation by SDFC_2 [75]

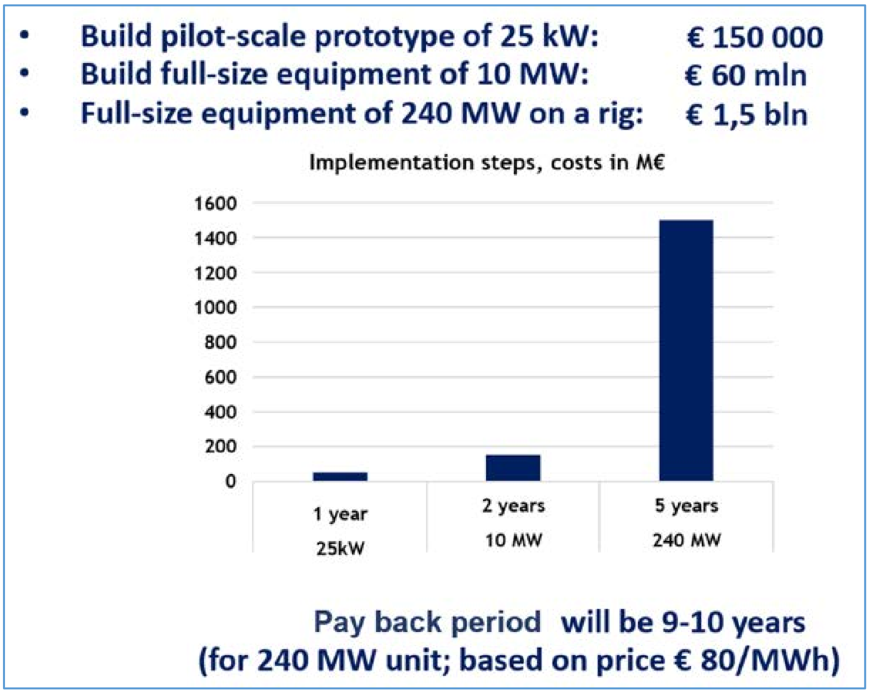
The low concentration of H2S and the depth of it´s location are the main challenges having significant impact on the investment cost. The issue with the storage of excess energy will be solved by using it for splitting the water in the process of electrolysis to hydrogen and oxygen. The latter will be reused as oxidizer in the SDFC. The hydrogen can be stored in situ i.e. in the form of metal hydrides[32] and used in the periods of higher electricity demand as energy carrier in fuel cells [98]. Another alternative could be the using of already existed methane transferring pipelines in the Black Sea (after connecting to them) for delivery of hydrogen to the coast. For filtering of the H2 out of the methane can be used the HylyPure® invention (see chapter 3.3) of the Institute for Chemical Engineering from the University of Technology in Vienna (TU Wien), presented in the first part of this thesis. One more TU Wien invention, called Heliofloat, also mentioned in chapter 3.3, coming from the Institute for Light Construction and Structural Biomechanics could partly or fully replace the massive production plant platforms in the sea and significantly decrease the investing cost presented in the next chapter.

---

[32] *Metal hydride is an intermetallic compound that traps hydrogen at moderate pressures. It stores large amounts of hydrogen in an exothermal diffusional process. Some drawbacks are its cost and its heavy weight, and its requirement for very pure hydrogen. Metal hydride advantages include convenience, compactness, stable storage, and intrinsic safety* [80]

12 INVESTMENT and OPERATIONAL COST

The cost and duration of the construction steps for three various scaled sulphide power plants, calculated by the team of prof. Beschkov, are presented in the Figure 100 below. The investment for the largest of them, namely the 240 MW sulphide power station placed on a rig in the Black Sea, were calculated to an amount of 1,5 billion of euro expenced in an estimated 5 year´s construction period. Despite this huge investment cost, their return is expected to take 9-10 years only (based on an average elctricity price of 80 €/MWh) [89].

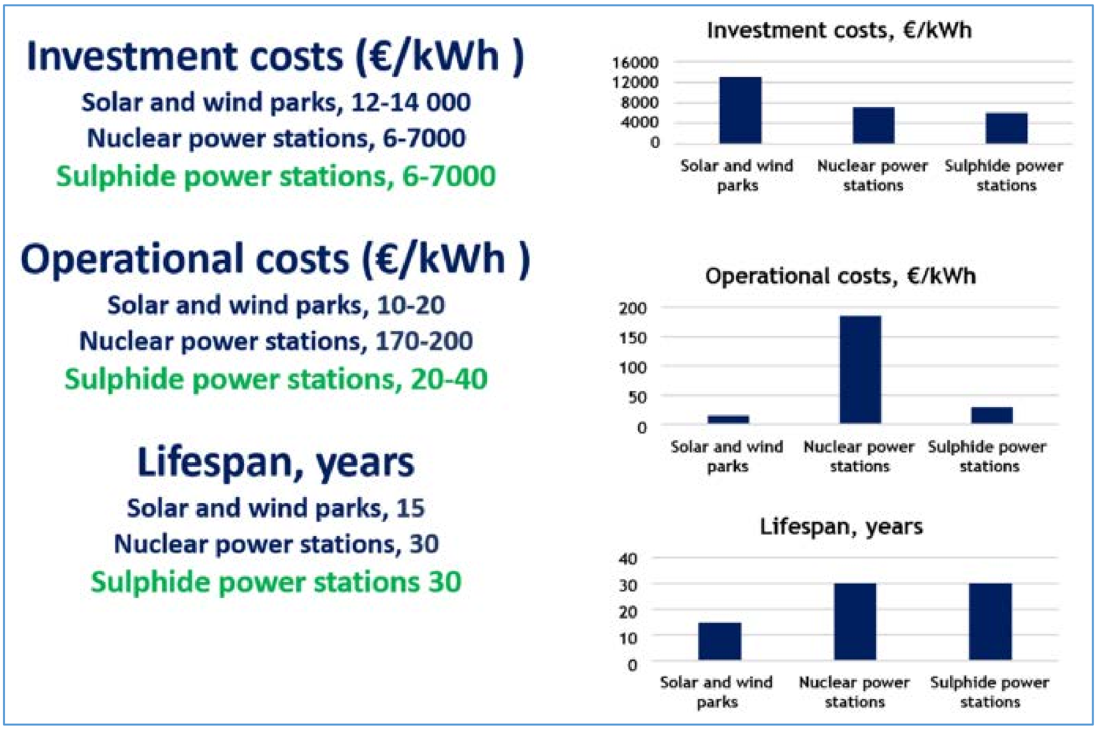


- Build pilot-scale prototype of 25 kW:	€ 150 000
- Build full-size equipment of 10 MW:	€ 60 mln
- Full-size equipment of 240 MW on a rig:	€ 1,5 bln

Pay back period will be 9-10 years
(for 240 MW unit; based on price € 80/MWh)

Figure 100. Cost of implementation steps for sulphide power stations [89]

In order to get a better view on the advantages of sulphide driven power plants their investment and operational coast per kWh, as well as the operation periods were compared with the same parameters of solar and wind (taken together) and nuclear power plants (Figure 101). For all the plants was assumed the same capacity of electricity generation, namely 8.500 kWh per year. As can be seen, in this range the sulphide power stations would have the same investment costs as the nuclear ones and twofold lower than these of solar and wind. The operational costs would be only double higher than these of the solar and wind parks, but up to tenfold lower than the nuclear ones, and the lifespan was estimated to be double as high as this of the wind power plants. A similar project for extraction of hydrogen sulphide containing in 1.000 m depths in the Black Sea waters was elaborated by M. Stavros in 2012 (103).



Investment costs (€/kWh)

Solar and wind parks, 12-14 000

Nuclear power stations, 6-7000

Sulphide power stations, 6-7000

Operational costs (€/kWh)

Solar and wind parks, 10-20

Nuclear power stations, 170-200

Sulphide power stations, 20-40

Lifespan, years

Solar and wind parks, 15

Nuclear power stations, 30

Sulphide power stations 30

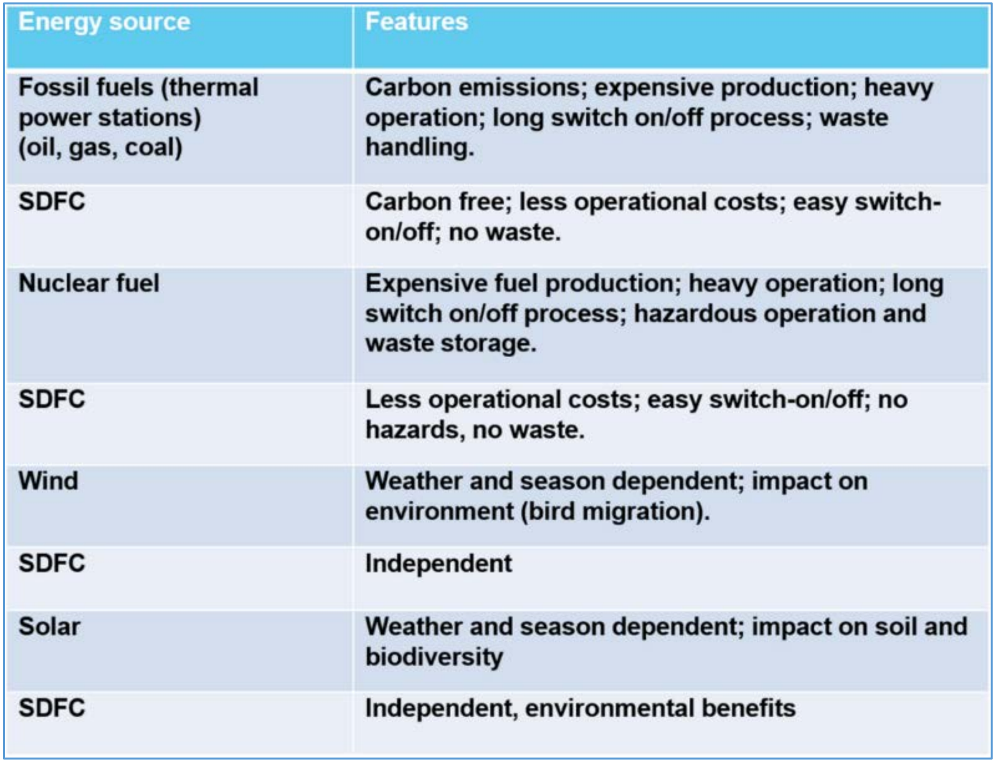
Figure 101. Comparison of costs for electricity generation of 8.500 kWh/a [89]

The difference there, which makes it even more cost intensive compared to the SDFC innovation of the Bulgarian team, is that solid oxide fuel cells, with such disadvantages as very high operating temperatures (700-1.000 K), lower efficiency (45% compared to the 60% of the SDFC) and using of *gaseous* state of H2S, were proposed and calculated there. All this required an additional investment and operational cost for systems like a vapour liquid separator for H2S extraction from the seawater in gaseous state (power demand 185 kW) and a heater with power demand of 107 kW. But even though and having similar equipment like this required in the Bulgarian project (powerful turbine pump, mechanical stable and anti-corrosive pipelines and concentration enrichment unit), the analysed and calculated economical parameters such as Net Present Value (NPV = 1.969.293 €), Internal Rate of Return (IRR = 23%) and Pay Back Period (PBP = 5.5 years) showed very encouraging profitable outcomes. These calculations and the promising economic results obtained by the Bulgarian researchers are a sustainable confirmation for the feasibility and profitability of the project.

13 ADVANTAGES of the SDFC POWER PLANT COMPARED to OTHER POWER PLANTS

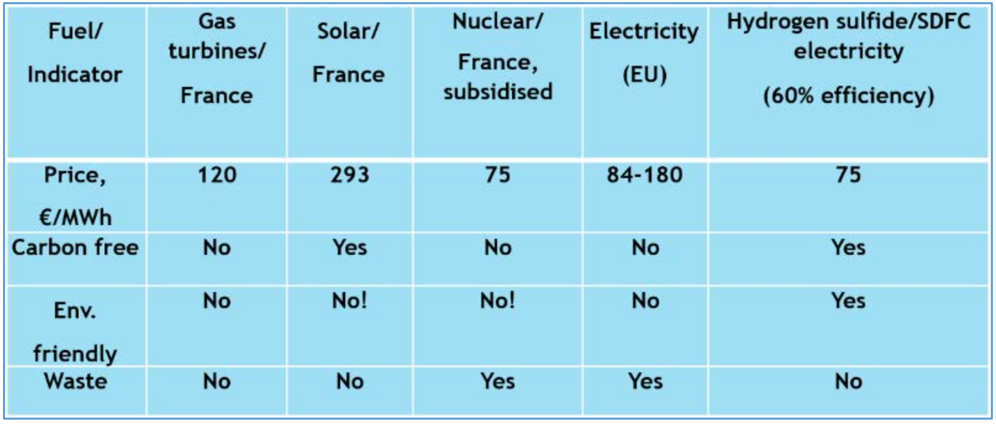
In the last chapter were presented the financial advantages of the sulphide driven power plants compared to power plants operating with other energy carriers. Further better performing characteristics of the SDFC power stations compared to plants utilizing renewable and non-renewable energy sources are shown in the Table 14 and Table 15 below:

Table 14. SDFC compared to power plants converting other energy sources_1 [89]



Energy source	Features
Fossil fuels (thermal power stations) (oil, gas, coal)	Carbon emissions; expensive production; heavy operation; long switch on/off process; waste handling.
SDFC	Carbon free; less operational costs; easy switch-on/off; no waste.
Nuclear fuel	Expensive fuel production; heavy operation; long switch on/off process; hazardous operation and waste storage.
SDFC	Less operational costs; easy switch-on/off; no hazards, no waste.
Wind	Weather and season dependent; impact on environment (bird migration).
SDFC	Independent
Solar	Weather and season dependent; impact on soil and biodiversity
SDFC	Independent, environmental benefits

Table 15. SDFC compared to power plants converting other energy sources_2 [89]



Fuel/ Indicator	Gas turbines/ France	Solar/ France	Nuclear/ France, subsidised	Electricity (EU)	Hydrogen sulfide/SDFC electricity (60% efficiency)
Price, €/MWh	120	293	75	84-180	75
Carbon free	No	Yes	No	No	Yes
Env. friendly	No	No!	No!	No	Yes
Waste	No	No	Yes	Yes	No

Shortly summarized, the advantages of the SDFC power plants utilizing hydrogen sulphide as a fuel are as follow:

- Direct energy production by using of enormous source of renewable energy
- Carbon and waste free technology
- Low operational cost
- Easy switch on/off electricity generation process
- Weather and season independent [104]

However, the strongest advantage of the sulphide power plants is the utilizing of hazardous H2S by converting it into electricity and non-hazardous by-products. Thus, taking care of the environment and restore the eco-balance in the seawater by rescuing them from the poisonous substance.

14 TRANSFER and UTILIZATION of the H2S-SEAWATER MIXTURE

Hydrogen from the sea

In this chapter, several concepts for transportation of seawater containing hydrogen sulphide from the depths of the Black Sea and following electricity generation and industrial production of hydrogen are proposed.

14.1 Concept 1 – open pipelines

The first idea suggests laying of open ends pipelines from the deeper seawater layers to the e.g. Bulgarian coast. The return of the processed seawater, free from the poisonous sulphide, to a certain depth, is provided by a shorter pipeline (Figure 102).

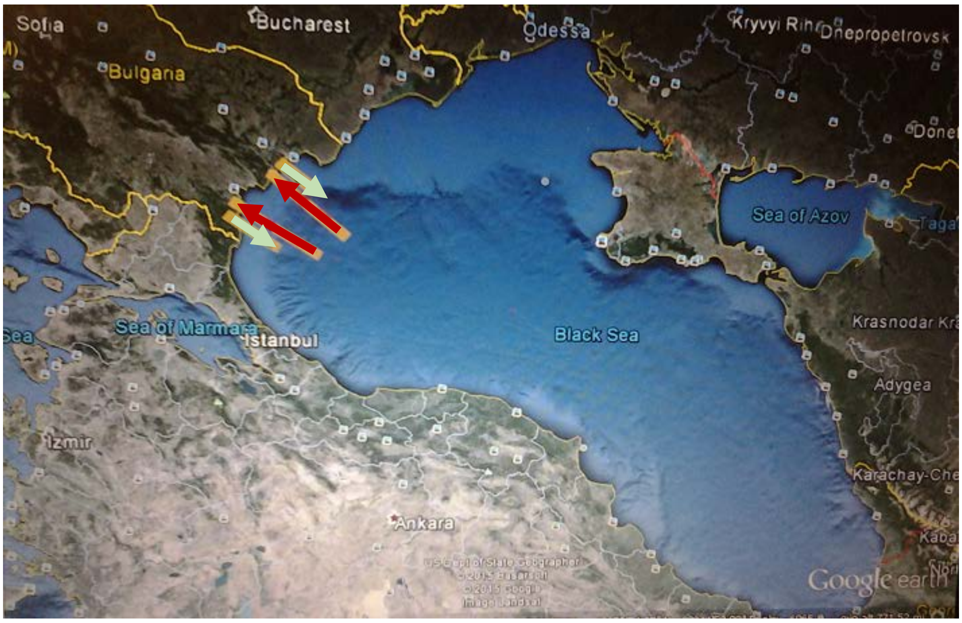


Figure 102. Seawater pipelines [105]

On this way, as a positive side effect, an environmentally friendly purge process of the sea is initiated in addition to the electricity generation out of the energy accumulated in the H2S. The detoxification can be accelerated through similar plants built by all countries bordering to the Black Sea. The upward seawater transport is facilitated by the principle of pressure difference between the lower water layers and its surface. This means, on one side, low energy costs for the pumping out of the H2S-containing seawater and on the other, lighter conditions for the wall thickness of the pipelines. This is explained by the fact that at any height of the pipeline the external pressure executed on the walls of the tube is equal to the internal pressure formed by the water column in the connected sea-open-pipeline vessel. This also allows an increase in the diameter of the pipe. Of course, the materials from which the pipes will be made of, must demonstrate mechanical stability and strength as well as resistance against the high corrosive impact of the sulphide-containing seawater. According to the observed literature (Stavros, 2012) [103], stainless steels alloys and especially these containing 6% of molybdenum would be the most proper choice despite their higher costs compared to the copper nickel alloys, which are much cheaper, but do not have that sufficient high resistance level against the corrosive hydrogen sulphide.

A note:

The former international project "South Stream" for transfer of natural gas from Russia to Europe via on the Black Sea ground laid pipeline, planned the coming out of the pipeline to be realized on the coast of Bulgaria near the city of Varna. In the Bulgarian seawater, these construction works could have been combined with the parallel laying of a pipeline for transfer of the seawater containing H2S. The pipeline could have reached to the industrial zone of Varna. Unfortunately, due to political decisions in 2015 the layout of the project was changed. The EU sanctions against Russia have resulted in a new route of the "South Stream" - not via Bulgaria, but through the European territory of Turkey. The pipelines already laid on the seabed towards Varna have been rerouted to the south. For strength reasons the entire gas pipeline is constructed in a bundle form of four pipes with a diameter of 65 cm each. It is desirable that the EU and Bulgaria came to an agreement with Russia for detouring of one of the pipes (from the already into “Turkey Stream” renamed project) towards the cities of Varna or Burgas on the Bulgarian coast. A construction of a bundle with a parallel pipeline for transfer of seawater containing H2S could be combined with these sidelining works (Figure 103).

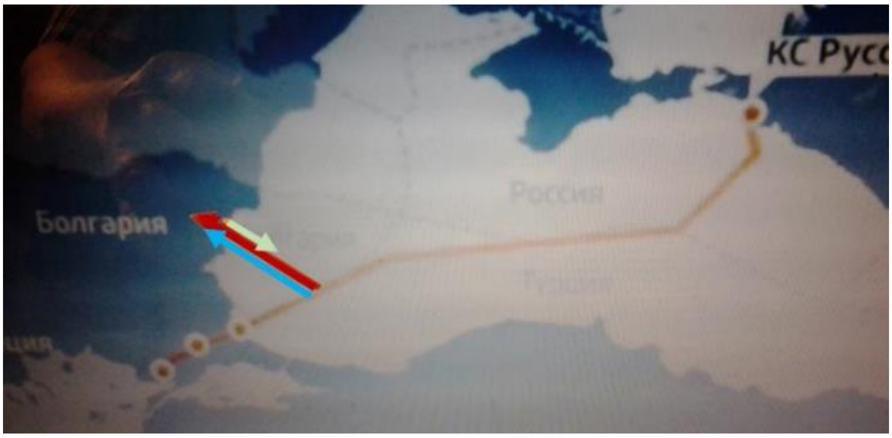


Figure 103. Gas pipeline project „Turkey Stream“ on the Black Sea bed [106]

In the industrial zone of Burgas, a gas distribution hub could be built near the oil refinery "Lukoil Neftochim Burgas[33]". It would be effective to integrate the construction of a sulphide power plant into the hub´s building works. The government of Bulgaria has already launched constructive talks about the natural gas distribution facility “Balkan” on the Black Sea coast. During his visit in Paris in April 2015, the Bulgarian Prime Minister Boyko Borisov discussed this topic with the former president of France François Hollande. Bulgaria's chances have increased significantly in recent months. It has got indirect support from Serbia, Hungary and the Austrian industrial giant OMV[34]. In July 2017, the European Commission has given its approval to Bulgaria for starting the negotiations with Russia for sidelining a pipeline from the “Turkey stream” to the Bulgarian coast [108]. Bulgaria (and Europe) have been waiting for the Russian decision now.

14.2 Concept 2 – mobile platforms for H2 production in the sea

The research carried out by the Bulgarian Institute of Oceanology has shown that in the middle territories of the Black Sea basin exist areas with higher concentrations of hydrogen sulfide in depths much less than the established 200 m below the surface. It means, that mobile production platforms, such as ships or the *Heliofloat* invention of TU Wien presented in previous chapters of this work (p.30, p.118), can be positioned over such zones and use much shorter pipelines for lifting the H2S-sewater mixture to the surface. This would significantly reduce the project costs.

The produced hydrogen can be stored in the form of metal hydrides (chapter 11) i.e. the H2 absorption value of Palladium is 600-3.000 of its volume units [110]. Prof. Beschkov proposes using of such metals in specially designed containers for storing and transporting of the generated hydrogen [111]. Further research work is being carried out in this field. Other possibilities for storage of hydrogen would be the use of active carbon nanowires or glass microspheres [110].

---

[33] *The largest oil refinery in South-Eastern Europe and the largest industrial enterprise in Bulgaria* [107]

[34] *An international, integrated oil and gas company, headquartered in Vienna. It is active in the Upstream and Downstream businesses. OMV defines its business reason as follows: OMV is producing and marketing oil & gas, innovative energy and high-end petrochemical solutions – in a responsible way. With group sales of EUR 19 bn, a global workforce of 22.500 employees in 2016 OMV is one of the largest listed industrial companies in Austria* [109].

14.3 Concept 3 – fuel transportation to the power plants on the coast

As a third concept for electricity generation and hydrogen production from the H2S-sewater mixture the following is proposed. On the mobile platforms mentioned in concept 2, the seawater containing hydrogen sulphide can be transferred to the surface and the concentration of H2S in it enhanced to a defined proportion. The latter can be fulfilled i.e. by using of the flash drum suggested by Stavros, 2012 [103]. The working principle is based on the Henry’s Law saying that ”*At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid*” [103]. The energy required for this process can be gained by PV panels placed on additional *Heliofloat* platforms mentioned above. The seawater with the increased H2S concentration can be shipped in special H2S-resistant and secured vessels (containers) to the processing facilities on the coast. The sulphide power plant built in the area of Lukoil Neftochim Burgas (mentioned in concept 1) will operate much more efficient with the enhanced concentration of H2S in the fuel liquid (see chapter 10.4.2). The generated electricity will be fed in directly into the existing electricity distribution network of the city. And the produced hydrogen can be injected into the existing natural gas transmission infrastructure and filtered out at the desired places (i.e. H2 fuel stations or industrial and household fuel cell electricity generators running on hydrogen) by using of the *HylyPure*® innovation mentioned in chapters 3.3 and 11.

14.4 Concept 4 – cooperation

The fourth concept is derived from the fact that the seabed on the western and northern sides of the Black Sea, which are coastal areas of Bulgaria, Romania and Ukraine, is gradually sinking. Therefore, long distances have to be overcome in order to reach to the deeper waters with suitable concentrations of hydrogen sulfide. This would significantly increase the pipeline installation costs. On the other hand, the coastal seabed of Georgia and partly of Turkey (the east side of the Black Sea) is quite steep. It means, that here, due to the shorter distances from the sulphide power plant to the suction point in the sea, the installation of the open pipeline described in the concept 1 will be more cost-efficient. An additional advantage of Georgia is the fact that, because of the cracks in the seabed (chapter 7.1) in front of the Georgian shore, the concentration of hydrogen sulfide is higher there. The above mentioned circumstances lead to an idea of a possible cooperation between Bulgaria and Georgia. In the Georgian territorial waters H2S-sewater mixture can be extracted and then be further processed in situ or/and in Bulgaria according to the other concepts procedures.

15 METHANE HYDRATES

Talking about the energy resources in the Black Sea some words have to be mentioned about the Methane Hydrates, especially due to the fact that as a potential energy source, their large natural deposits were worldwide firstly discovered 1971 in the seabed layers of the Black Sea. In the early 1980´s followed the find spots in the coastal area of Alaska. Today, it is known that methane hydrate deposits are stored in large quantities in certain regions on or in the seabed and occur in the coastal areas in all seas and on the edges of the continents. Experts estimate that there are ten times more natural gas stored in the form of methane hydrate than in all conventional natural gas sources. According to current knowledge, methane hydrate deposits are the largest stocks of fossil fuel [113, 114].

Methane hydrate ($CH_4 \cdot 5.75H_2O$) is a solid compound in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice [112] (Figure 104).

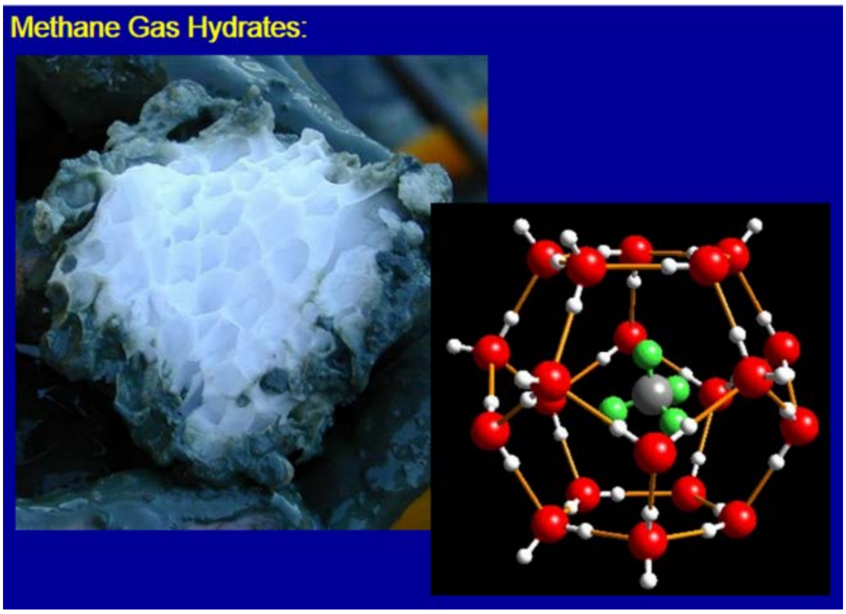


Figure 104. Methane hydrate structure [117]

Gas hydrates can be formed at depths below 500 meters, where the pressure rises above 50 atmospheres. It is estimated that 1 m^3 of gas hydrate contains about 155 - 168 m^3 of methane [116]. At the seabed, the methane hydrates are in stable state due to the low temperature and high pressure (Figure 105). The water molecules acts as cages in which the methane molecules are trapped. If a white lump of methane hydrate is brought to the surface i.e. on board of a research vessel - it can be easily ignited. It burns with a blue-reddish flame (Figure 106). On this way the methane hydrate received the name "*burning ice*" [113].

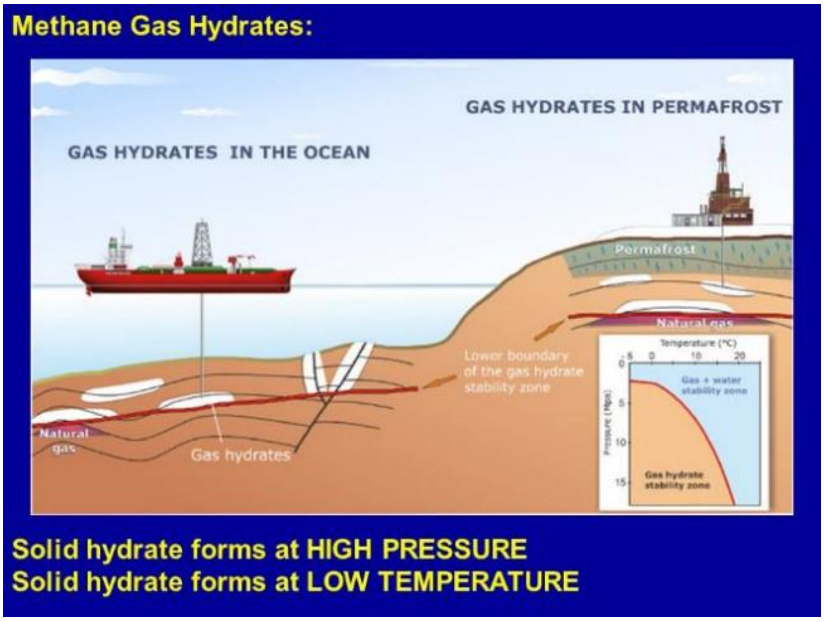


Figure 105. Methane hydrate deposits [117]

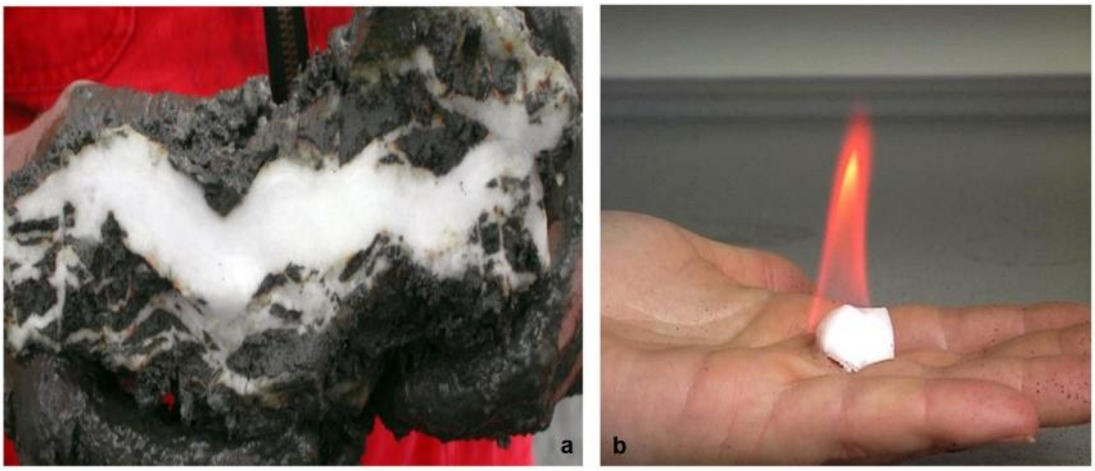


Figure 106. Methane hydrate lump (a) [113]; Burning of methane hydrate (b) [119]

Today, methane hydrates are one of the fastest growing scientific areas. A number of countries have been conducting intensive research. "*There is currently some kind of leap from technologies for exploration to technologies for extraction*," says associate professor Atanas Vassilev from the Bulgarian Institute of Oceanology belonging to the Bulgarian Academy of Sciences [116].

Since the end of March 2017, China has already begun to extract methane from hydrates in the South China Sea. It has been drilled at a depth of approximately 1.300 m in the ocean floor, with an average yield of 16.000 m³ of methane gas per day. Jiang Daming, China's Minister of Resources, called it "*a major breakthrough*" that could "*lead to a global energy revolution*" [113].

Not only China, but also Japan, South Korea and India have high hopes for the extraction of methane hydrate, especially due to the fact of having only little or no natural gas resources at their countries. Already in 2013, with the "Chikyu" research-drilling vessel, Japan extracted large quantities of methane from the hydrates in its territorial waters in the seabed in front of the Honshu Island [113].

And how does the situation in the Black Sea, the pioneer of the methane gas hydrate deposits, look like? It is encouraging that the results of the German-Bulgarian research expedition carried out within the SUGAR[35] project on the German ship "Maria S. Merian" in 2014 in the Black Sea have proved enormous amounts of gas hydrates not only in the Black Sea as a whole but especially in the vicinity of the Bulgarian coast (Figure 107). 2D and 3D seismic and electromagnetic recordings, measurements of the heat flow dencity and extraction of geochemical samples were carried out. According to Dr. Atanas Vassilev, a member of this expedition, it was the first comprehensive and detailed exploration of methane hydrates deposits in the exclusive economic zone of Bulgaria and the preliminary results have exceeded the expectations of the researchers [115].

Figure 107. Location of methane hydrates in the Black Sea
Source: Institute of Oceanology, Bulgaria, 2014

---

[35] SUGAR (**su**bmarine **ga**s hydrate deposits: explo**r**ation, extraction and transport) is a project led by the Helmholtz Center for Ocean Research Kiel (GEOMAR). Nearly 30 partners from industry and science are joint together to develop new technologies for extracting of natural gas (methane) from methane hydrates deposits in the seabed and safely storage of the industrial exhaust carbon dioxide (CO2) in the same places [118].

The deposits of methane hydrates in the Bulgarian economic zone of the Black Sea cover an area of about 1.500 km². They are located about 200 meters below the sea ground, which is at a depth of 800 to 1.900 meters below the sea level. The experts estimate that the amount of methane in it can reach up to several hundreds of thousands of cubic kilometers. In addition, the Bulgarian fields are considered as the most advantageous for extraction, because of their location in sand collectors [116]. As seen from Figure 107 other huge methane hydrate deposits in the Black Sea exist in the coastal areas of Georgia, Russia and to the south of the Crimea peninsula (the most promising area). An interesting fact is that exactly in this area, 50 miles to the east from Sevastopol, 90 years ago, on the 11 September 1927, during the strong Crimea earthquake, was observed a huge column of flames, now known as a result of the self-ignition of the released methane gas [5].

Since, 1 m³ of gas hydrate contains about 155 - 168 m³ of methane [116] a rough calculation showed that on the bottom of the Black Sea in the form of hydrates are stored about € 8.280 billion. In order to illustrate this huge amount of money should be mentioned that it corresponds to the Bulgarian gross domestic product for 407 years. According to the preliminary estimates of the Bulgarian Institute of Oceanology, between 10% and 20% of this energy treasure is stored in the Bulgarian seawater [115]. According to Dr. Vassilev, for a period of a century Bulgaria will be able not only to cover its energy demand but also to be the one of the largest exporters in Europe [116].

According to the results of the first SUGAR research expedition mentioned above, in the seabed of the Bulgarian section are hiding thousands of cubic kilometers of methane in the form of a solid gas hydrate. Very soon, in November and December 2017, in the Black Sea waters a second joint German-Bulgarian scientific expedition within the SUGAR project will be carried out. Taking out of samples of methane hydrate stored in the seabed for examining the results of the geophysical studies conducted so far, will be the goal of the international research team [116].

The project SUGAR was launched in 2008 and is funded by Germany. Due to the good prospects, the project has been extended three times by the government in Berlin. On the Figure 108 are shown scientists presenting a methane hydrate experiment to former ministers from Schleswig-Holstein and Chancellor Angela Merkel at the Helmholtz Center for Ocean Research GEOMAR in Kiel in 2012.

Figure 108. German government members at presentation of hydrate experiments [113]

The main purpose of SUGAR is the development of safety and efficient technology for extraction of methane hydrates from the seabed, but there is another, no less important. Especially, if it's going about a fossil fuel extraction and its utilization, the main question will be the CO2 emissions and the need of environment protection. With an H:C ratio of 4.0 (4 atoms of hydrogen and only 1 carbon atom in its molecular structure – CH4) methane is the environment friendliest hydrocarbon fossil fuel in comparison i.e. to crude oil which has an H:C ratio of 1.5 [120]. Nevertheless, the air combustion of methane produces CO2 emissions, although much less than those caused by the combustion of oil based fuel products such as gasoline and diesel.

In this way, explained by prof. Vassilev, the new technology developed in Germany allows that methane extracted from the hydrates will be replaced by carbon dioxide. This means that the more methane will be extracted, the more CO2 will be reduced in the atmosphere [116].

With the extraction of gas hydrate deposits in the own coastal area the countries aim an independence from the energy imports. However, it still has to be clarified whether the methane hydrates extraction could entail hazards to the environment, climate and the marine flora and fauna. The research activities should be moved towards inventions of new technologies. The above-mentioned German lead is a very well initiative for others to be followed. Producing of hydrogen from the extracted methane by the steam reforming process could be another approach for an environment friendly utilization of the worldwide methane hydrate deposits.

16 CONCLUSIONS to PART II

In part I of the thesis were calculated and described various power plant projects for the city of Burgas, a municipality on the Bulgarian Black Sea coast. Three technologies for transport fuel production based on renewable energy sources such as biomass, solar and wind were compared. Having in mind the legal and market situation and the obtained negative Net Present Values for all these REN power plants, investment could not be recommended for anyone of the observed projects.

Following these results, an alternative and inovative new energy technology especially applicable in the Black Sea region was presented in part II. Due to the geographic (closed basin), biologic (activities of the sulphur reducing bacteria) and tectonic (fractures and mud volcanoes, as well as the destroyed gas hydrate deposits) characteristics, Black Sea is an enormous natural reservoir of hydrogen sulphide. Its annual generation in the basin amounts to 75 million tons. In the Black Sea waters, hydrogen sulphide is provided as a mixture of 85% of sulphide anions and only 15% of pure H2S gas [74, 76]. This explains why for decades, despite the many attempts to utilize the toxic substance, there have not been developed practically realizable technologies for extraction of H2S gaseous form from the seawater yet. Therefore, in the last years, studies have been focused on the utilization of the prevailing ionic form of hydrogen sulphide in the Black Sea.

The invention of a new environment friendly technology for electricity generation by utilizing of hydrogen sulphide in the Black Sea as a fuel and at the same time rescue its waters from this poisonous substance and improvement of the ecological situation in the basin has been the main goal of the Bulgarian team of scientists led by prof. Venko Beschkov from the Institute of Chemical Engineering in Sofia. Their research work was supported by the project “Hydrogen production from Black Sea water by the sulphide-driven fuel cell HYSULFCEL” a part of the BS-ERA.NET networking project financed by the European Commission.

The goal of the Bulgarian team was to invent an energy efficient, sustainable, environment friendly and in the Black Sea waters applicable fuel cell technology enabling an operation under ambient conditions and closing of the fuel-final product circle, hence, make it renewable. The idea was to generate electricity from the H2S by electrochemical conversion of toxic sulphides down to harmless sulphates. Thus, on the one hand side gaining more energy and avoiding sulphur accumulation, and on the other, make the process renewable by releasing the sulphates into the sea, where they get converted back into hydrogen sulphide through the anaerobic respiratory of the sulphur reducing bacteria. By closing of this bio-electro-chemical natural cycle, the humanity obtains a new sustainable and renewable energy source and simultaneously maintains the ecological balance in the natural waters.

The initial project of the Bulgarian researchers in 2011 was to utilize the H2S from the Black Sea as a raw material for hydrogen production by electrolysis. However, the energy input (187-223 MJ/kg) was higher than the energy yield from the produced H2 (144,2 MJ/kg) [8]. So the further experimental works have been targeted into optimization of the already existed H2S oxidizing fuel cell technology. The goal was to overcome the well-known disadvantages such as sulphur accumulation and low enthalpy of sulphide-to-sulphur conversion (263 kJ/mole). Within the last 4 years has been developed the new sulphide driven fuel cell with increased efficiency, which generates electricity by using H2S-containing seawater as a fuel and transforming the sulphide forms in it into sulphate ones. Thus, yielding more energy by increasing the enthalpy to 788 kJ/mole and resolving the sulphur accumulation problem. The final product - the harmless sulphates, do not poison the catalysts used in the process and even more get entered back into the sea closing on this way the natural microbial cycle, hence, making the process renewable [90, 93].

The leading intention at the construction process has been the efficiency improvement of the fuel cell. The milestones in the minimizing of the internal losses (in order to ensure a higher electromotive force) were choosing of proper electrodes, catalysts and optimal design. The experimental works were carried out with different prototypes. Various sizes, materials and positions of sulphide and oxygen compartments, their electrodes as well as the electrical connections between SR and OR sections were investigated. For optimization of the electrochemical characteristics of the sulphide driven fuel cell were created electrodes with bigger specific surface and with tightly incorporated catalyst in them. The energy efficiency of the fuel cell was improved by optimizing the material, design, number and position of the electrodes as well as by selecting of catalysts with the best-achieved acceleration of the oxidation rate [92, 95-98].

It was observed that the depletion rate of the sulphide ions is much higher per unit time at higher initial concentration of sulphides in the water, which led to higher oxidation rate respectively better efficiency of the cell. After the gained experience was decided an optimization of the “*Concentration - Produced energy - Process Rate* *triangle*" for achieving financial benefits from the realization of the project in the future [98].

During the years 2011-2014, the fuel cell design had been optimized and finally reached to an operating pilot-scale industrial model. The feasibility of the project for electricity generation with the new invented SDFC by utilizing the seawater containing hydrogen sulphide as a fuel and production of hydrogen was confirmed by the promising results obtained with the pilot-scale industrial model tested in real conditions in the Black Sea waters near to the Bulgarian coast.

This technology based on the electrochemical oxidation of hydrogen sulphide into sulphate has several advantages such as higher energy converting efficiency, environmental compatibility, ability for automation, versatility and cost effectivity [84]. Further research activities have been targeted into increasing of the current and power density of the sulphide driven fuel cells.

Related to the obtained results, the team of prof. Beschkov has proposed and calculated production steps for electricity generation and production of hydrogen based on the new technology. The low concentration of H2S and the depth of its location are the main challenges having significant impact on the investment cost. Some inventions of the TU Wien, described here, could be used and essential decrease the investing cost presented in the work.

The investment and operational cost calculations and the promising results obtained by the Bulgarian researchers are sustainable confirmation for the feasibility and profitability of the project.

Shortly summarized, the advantages of the SDFC power plants utilizing hydrogen sulphide as a fuel are as follow:

- Direct energy production by using of enormous source of renewable energy
- Carbon and waste free technology
- Low operational cost
- Easy switch on/off electricity generation process
- Weather and season independent [104]

However, the strongest advantage of the sulphide driven power plants is the utilizing of hazardous H2S by converting it into electricity and non-hazardous by-products. Thus, taking care of the environment and restore the eco-balance in the seawater by rescuing them from the poisonous substance.

The author proposed several concepts for transportation of seawater containing hydrogen sulphide from the depths of the Black Sea and following electricity generation and industrial production of hydrogen.

Talking about the energy resources in the Black Sea some attention was paid to the Methane Hydrates. Their large natural deposits were worldwide firstly discovered 1971 in the seabed layers of the Black Sea. The German SUGAR project and the German-Bulgarian joint initiative for detailed exploration of methane hydrates deposits in the exclusive economic sea zone of Bulgaria were presented. Especially the new environment saving technology developed by German researchers for storing of carbon dioxide by replacing the extracted methane hydrates in the seabed with the CO2 was pointed out.

Developing of such an effective energy converting and environment protecting technology as the SDFC power plants that use the oxidation energy, contained in the enormous and constantly growing amounts of H2S in the Black Sea, would provide not only Burgas and Bulgaria, but also all the countries around the sea and other water basins containing H2S, with a new electricity and hydrogen generating method based on a sustainable and renewable energy source.

REFERENCES

[1] Saksa Fuels, Regulation on the quality of liquid fuels, the terms and manner of their control (2014), Bulgaria, p. 24, http://saksa-bg.com/pdf/NKTG.pdf (10.05.2016)

[2] Energy Content of Biodiesel, Directive 2009/28/EC of the European Parlament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, p. 34, http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0016:0062:EN:PDF (10.05.2016)

[3] Leitfaden über den Kraftstoff verbrauch, die CO2-Emissionen und den Stromverbrauch aller neuen Personenkraftwagenmodelle die in Deutschland zum Verkauf angeboten werden (2016), p. 59, DAT Deutsche Automobil Treuhand GmbH, http://www.dat.de/uploads/media/LeitfadenCO2.pdf (10.05.2016)

[4] Zobaa F. Ahmed, Bansal C. Ramesh (2011): Handbook of renewable energy technology, p. 4ff, 397ff, World Scientific Publishing Co. Pte. Ltd.

[5] Mittelbach M. (2015): Biofuels/Biodiesel Part 1. Lecture script, p. 95, MSc Program – Renewable Energy in Central and Eastern Europe, TU Wien

[6] Mittelbach M. (2015): Biofuels/Biodiesel Part 2. Lecture script, pp. 6, 36, 55ff, MSc Program – Renewable Energy in Central and Eastern Europe, TU Wien

[7] Moudsale D. (2008): Biofuels: Biotechnology, Chemistry and Sustainable Development, Taylor & Francis Group, LLC

[8] Jungmeier G. (2015): General introduction on environmental challenges for bioenergy, Lecture script, p. 43, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[9] Bulgarian Ministry of Agriculture and Food, “Agrarian report 2013”, p. 28f

[10] Bulgarian Ministry of Agriculture and Food, “Agrarian report 2014”, p. 28f

[11] Bulgarian agrarian stock exchange, http://agro.bg/financies/ (30.04.2016)

[12] Firrisa M. (2011): Energy efficiency of rapeseed biofuel production in different agro-ecological systems. pp. 5f, 53, master thesis, University of Twente, NL

[13] Melamed A. (2012): Comparison of different technologies for transport fuel production for the region of Vienna. p. 12, CEC REN11, TU Wien

[14] Connemann J., Fischer J. (1998): Biodiesel in Europe 1998, International Liquid Biofuels Congress 1998, Curitiba-Parana, Brazil

[15] Friedrich S. (2004): A worldwide review of the commercial production of biodiesel – a technological, economic and ecological investigation based on case studies. Institut für Technologie und nachhaltiges Produktmanagement der Wirtschaftsuniversität Wien

[16] UFOP – Union zur Förderung von Öl- und Proteinpflanzen E.V. (2016), http://www.ufop.de/biodiesel-und-co/biodiesel-preis/ (17.05.2016)

[17] WON, Waste Oil Net Bulgaria, http://www.wasteoilnet.bg/en/services (17.05.2016)

[18] Eurostat News Release, Renewable energy in the EU, Share of renewables in energy consumption, (30/2016 from 10 February 2016), http://ec.europa.eu/eurostat/documents/2995521/7155577/8-10022016-AP-EN.pdf/38bf822f-8adf-4e54-b9c6-87b342ead339 (24.05.2016)

[19] Fechner H. (2016): Introduction on Photovoltaics, physical basis, semiconductors. Lecture slides, p. 11, p. 30, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[20] Fechner H. (2016): Photovoltaics. Lecture script, pp. 8-40, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[21] Fraunhofer ISE, PSE AG (2016): Photovoltaics Report. p. 24, p. 40, Freiburg, https://www.ise.fraunhofer.de/de/downloads/pdf-files/aktuelles/photovoltaics-report-in-englischer-sprache.pdf (25.06.2016)

[22] National Renewable Energy Laboratory, http://www.nrel.gov/workingwithus/re-photovoltaics.html (25.06.2016)

[23] Solargis, Global Horizontal Irradiation (GHI) for Bulgaria, Average annual sum (1994-2013), GHI Solar Map © 2015 GeoModel Solar http://solargis.com/assets/graphic/free-map/GHI/Solargis-Bulgaria-GHI-solar-resource-map-en.png (25.06.2016)

[24] Photovoltaic Geographical Information System (PVGIS) 2016, http://re.jrc.ec.europa.eu/pvgis/apps4/pvest.php# (01.07.2016)

[25] SMA Solar Technology AG, Brochure: “Performance ratio – quality factor for the PV plant”, p. 2, Version 1.1, http://files.sma.de/dl/7680/Perfratio-TI-en-11.pdf (01.07.2016)

[26] Diermann R. (2016): Pumpspeicher: Forscher planen Windkraft-Akkus am Meeresgrund. Spiegel Online Wissenschaft. http://www.xing-news.com/reader/news/articles/206163 (05.07.2016)

[27] TU Wien News (2015): Combination of Power-to-Gas with Biogas Plant. Doubling of biogas production through the use of excess electricity for electrolysis and methanation. https://www.tuwien.ac.at/fileadmin/t/tuwien/fotos/pa/download/2015/HM2015/Flyer_Power_to_Bio--Gas_EN.pdf (05.07.2016)

[28] TU Wien News, Press Release 19/2016: Hydrogen makes the natural gas network greener. https://www.tuwien.ac.at/en/news/news_detail/article/10033/ (05.07.2016)

[29] TU Wien News, Press Release 23/2016: More space to soak up the sun. https://www.tuwien.ac.at/en/news/news_detail/article/10060/ (18.08.2016)

[30] TU Wien News, Press Release 18/2016: New concrete tower construction method for wind turbines. https://www.tuwien.ac.at/en/news/news_detail/article/10031/ (18.08.2016)

[31] IRENA / IEA PVPS (2016): End-of-Live Management. Solar Photovoltaic Panels. June 2016, p. 47, p. 75,

http://iea-pvps.org/index.php?id=3&no_cache=1&tx_damfrontend_pi1[showUid]=3222&tx_damfrontend_pi1[backPid]=3 (04.08.2016)

[32] IEA-PVPS-TASK 12 (2015): Life Cycle Inventories and Life Cycle Assessments of Photovoltaic Systems. p. 9ff, http://iea-pvps.org/index.php?id=56 (04.08.2016)

[33] Velinov K, Stefanov R. (2014): Ue of PV for lighting road tunnels. Paper, University of Mining and Geology in Sofia, Bulgaria, Conference of the Bulgarian National Committee on Illumination, p. 5, June 2014, http://www.bnci.eu/konfer/light-2014/36%20%20Velinov%20Stefanov-2014.pdf (10.08.2016)

[34] New rules for wind and solar energy producers in Bulgaria, January 2014, http://www.lexology.com/library/detail.aspx?g=8e409dc6-4c5e-470d-9599-4b7feac75905 (10.08.2016)

[35] Renewable Energy Snapshot Bulgaria (2013), http://www.eurasia.undp.org/content/dam/rbec/docs/Bulgaria.pdf (11.08.2016)

[36] Bulgarian Energy and Water Regulatory Commission (2016): “res-c19-2016”, Resolution from 30. June 2016, p. 34ff, https://www.energo-pro.bg/uploads/files/2016/res-c19-2016.pdf (11.08.2016)

[37] Interviews with Tsalo Parvanov, CTO in “VETs Svoge AD” (a cascade of small hydro power plants on the river Iskar in Bulgaria) and former wind power plant`s field engineer. Carried out in June-August, 2016

[38] Petz A. (2014): Windkraft Anlagentechnik. Lecture script, FH Campus Wien

[39] Umair N. Mughal (2014): Wind Energy Systems. Lecture, p. 24, Narvik University College, http://www.slideshare.net/aero958/lecture-2-wind-energy-course (13.08.2016)

[40] Bulgarian Alternative Energy Company (BAEC), http://www.baec.bg/sector_info.html (14.08.2016)

[41] Wikipedia: Wind Power by Country. https://en.wikipedia.org/wiki/Wind_power_by_country (13.08.2016)

[42] International Energy Agency, Wind Power Generating, October 2013, http://www.iea.org/newsroomandevents/news/2013/october/wind-power-seen-generating-up-to-18-of-global-power-by-2050.html

[43] Ventus Bulgaria: Wind Potential in Bulgaria. http://ventus.bg/wind-potency/en/ (14.08.2016)

[44] Wikipedia: Energy in Bulgaria, Wind Power, https://en.wikipedia.org/wiki/Energy_in_Bulgaria#Wind_power (14.08.2016)

[45] Bulgarian Wind Energy Association (BWEA), http://bgwea.eu/English/Installed_Wind_in_Bulgaria_EN.html# (14.08.2016)

[46] Wind Turbines, Bulgaria, http://wind.bghot.com/index.php (14.08.2016)

[47] Krenn A. (2015): Wind Measurement. Lecture script, p. 26, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[48] Krenn A. (2015): Aerodynamics. Lecture script, p. 7, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[49] Wikipedia: Betz´s Low. https://en.wikipedia.org/wiki/Betz%27s_law (14.08.2016)

[50] Neubauer M. (2015): Development and planning of wind projects. Lecture script, p. 69ff, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[51] Bulgarians largest wind power farm "Saint Nicola", 156 MW, http://aes.bg/our-business/saint-nicola-wind-farm/?lang=en (18.08.2016)

[52] Freris L., Infield D. (2008): Renewable energy in power systems, p. 30ff, John Wiles and Sons Ltd., Publication

[53] Technical specification of wind turbine Vestas V90-3.0 MW, https://www.vestas.com/en/products/turbines/v90-3_0_mw#!technical-specifications (18.08.2016)

[54] Quaschning V., Online-Tools: Windpark-Ertragsanalyse. http://www.volker-quaschning.de/software/windertrag/index.php#Windgeschwindigkeit (18.08.2016)

[55] The Windpower, Wind Energy Market Intelligence, Technical specification of Kavarna NW (Saint Nikola) wind farm in Bulgaria,http://www.thewindpower.net/windfarm_en_7152_kavarna-nw.php (18.08.2016)

[56] Garrett P., Rønde K. (2013): Life cycle assessment of electricity production from an onshore V90-3.0 MW wind plant. Vestas Wind Systems A/S Denmark, October 2013. https://www.vestas.com/~/media/vestas/about/sustainability/pdfs/lca_v903mw_version_1_1.pdf (19.08.2016)

[57] Vestas Wind Systems A/S Denmark (2006): Life cycle assessment of offshore and onshore sited wind power plants based on Vestas V90-3.0 MW turbines", pp. 27-35, June 2006. https://www.vestas.com/~/media/vestas/about/sustainability/pdfs/lca_v90_june_2006.pdf (19.08.2016)

[58] Vestas Sustainability (2016), http://www.vestas.com/en/about/sustainability#!sustainable-products (19.08.2016)

[59] CO2-eq emissions, „Technischer Anhang der Anleitung für die SEAP-Vorlage: die Emissionsfaktoren", http://www.energyagency.at/fileadmin/dam/pdf/projekte/klimapolitik/3_SEAP-Vorlage-Technischer-Anhang.pdf (22.08.2016)

[60] Burgas Bus, The Bus company of the municipality of Burgas, 173 vehicles (2014), http://burgasbus.info/burgasbus/?page_id=42 (20.05.2016)

[61] Ajanovic A. (2015): International Survey on Transport. Lecture script, p. 49f, p. 71ff, MSc Program Renewable Energy in Central and Eastern Europe, TU Wien

[62] World Watch Institute (2014): Biofuel Production. http://www.worldwatch.org/biofuel-production-declines-1 (23.08.2016)

[63] Charging stations for electrical vehicles on the territory of Bulgaria (2015), http://www.vsichkotok.bg/en/ (22.08.2016)

[64] Ministry of Foreign Affairs of Denmark (2016): Energy Sector Report for Bulgaria. Issued by the Danish Embassy in Sofia, Bulgaria

[65] NREAP, National Renewable Energy Action Plan of Bulgaria (2011), https://ec.europa.eu/energy/en/topics/renewable-energy/national-action-plans (21.10.2016)

[66] National Statistical Institute of Bulgaria: Average Monthly Wages and Salaries. http://www.nsi.bg/en/content/6412/statistical-regions-district (10.05.2016)

[67] Di Chio A, Tschiesche U., Tsenov A. (2017): Retrofitting of two schools and a hospital, and replacement of an oil-fired by a biomass-fired boiler in a local heat power plant in the city of Burgas. Business Plan Project AUA o.o.d, CEC REN15, TU Wien

[68] Black Sea, https://en.wikipedia.org/wiki/Black_Sea (06.09.2017)

[69] Location of the Black Sea, http://www.sldinfo.com/the-black-sea-as-a-flashpoint-in-managing-maritime-security/ (06.09.2017)

[70] Dermendzhieva N., Razkazova-Velkova E., Martinov M., Ljutzkanov L., Beschkov V. (2013): Oxidation of sulphide ions in model solutions of sea water using metal catalysts built in carbon matrix. Journal of Chemical Technology and Metallurgy, 48, 5, 2013, pp. 465-468

[71] Gutsevich E.I., Rusanov V.D. (1995): Problems of Hydrogen sulphide and its treatment in the Black Sea. Publication, Hydrogen Energy & Plasma Technology Institute, Kurchatov sq. 1, Moscow, 123182 Russia

[72] Dimitrov D., Genov I., Kozhuharov E. (2003): Alternative Resources and Energetic Sources from the Black Sea Bottom. Publication, Institute of Oceanology, Bulgarian Academy of Sciences (BAS), Part IV, Varna, Bulgaria

[73] Namana S.A., Engin Tureb I., Veziroglu Nejat T. (2008): Industrial extraction pilot plant for stripping H2S gas from Black Sea water. International Journal of Hydrogen Energy 33, 2008, 6577-6585

[74] Dimitrov P.S., Dimitrov D.P. (1999): Alternative Energy Resources from the bottom of the Black Sea. Publication, Department of Marine Geology and Archaeology, Institute of Oceanology, Bulgarian Academy of Sciences, Varna, Bulgaria

[75] Beschkov V., Razkazova-Velkova E., Martinov M., Stefanov S. (2015): Energy Production from Black Sea Water by Sulphide-Driven Fuel Cell. 15th International Multidisciplinary Scientific Conference SGEM 2015 Book, Part Energy and Clean Technologies, Albena, Bulgaria, pp. 207-212

[76] Bondarenko G.N., Koljabina I.L., Marinitch O.V. (2009): Problems of extraction of hydrogen sulphide from the Black Sea depth waters. Publication, Institute of Environmental Geochemistry of NAS and Ukranian Ministry of Emergency Situations, Kiev, Ukraine

[77] Beschkov V., Yankov D., Angelov I., Razkazova-Velkova E., Martinov M. (2017): Biowaste and hydrogen sulphide – perspective renewable fuels. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[78] Martinov M., Razkazova-Velkova E., Stefanov S. (2016): Energy efficiency of an electrochemical fuel cell for treatment of wastewaters contaminated with sulphides and nitrates. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[79] Fuel Cell, http://www.intelligent-energy.com/technology/technology-faq/, (10.09.2017)

[80] International Atomic Energy Agency IAEA (1999): Hydrogen as an energy carrier and its production by nuclear power. Vienna, Austria

[81] O'Hayre R., Cha S. W., Colella W. G., Prinz F. B. (2016): Fuel Cell Fundamentals. 3rd ed., Wiley, Hoboken, New Jersey

[82] Vanitha M. U., Natarajan M., Sridhar H. (2017): Microbial fuel cell characterisation and evaluation of *Lysinibacillus macroides* MFC02 electrigenic capability. In: World Journal of Microbiology and Biotechnology. 33 (91)

[83] Reimers C. E., Girguis P., Stecher III H. A., Tender L. M., Ryckelynck N., Whaling P. (2006): Microbial fuel cell energy from an ocean cold seep. In: Geobiology Journal. 4, pp. 123-136

[84] Dutta P. K., Rabaey K., Yuan Z., Keller J. (2008): Spontaneous electrochemical removal of aqueous sulfide. In: Water Research Journal. 42, pp. 4965-4975

[85] Kwiyong K., Jong-In H. (2014): Performance of direct alkaline sulfide fuel cell without sulfur deposition on anode. In: International Journal of Hydrogen Energy. 39, pp. 7142-7146

[86] Wikipedia: Platinum on carbon, https://en.wikipedia.org/wiki/Platinum_on_carbon (16.09.2017)

[87] Martinov M., Razkazova-Velkova E., Stefanov S. (2017): Sulphite driven fuel cell for environmental purposes: Optimization of the operating condition. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[88] Interviews with prof. Venko Beschkov (February & July 2017), carried out by author in the Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[89] Beschkov V. (2016): Hydrogen Sulphide Power Plant. PPT Presentation, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[90] Beschkov V., Yankov D., Angelov I., Razkazova-Velkova E., Martinov M. (2017): Biowaste and Hydrogen Sulphide - Perspective Renewable Fuels. In: Kimya ProblemlƏri. № 1, UDC 550.4, 541.15

[91] Uzun D., Razkazova-Velkova E., Petrov K., Beschkov V. (2016): H2S/O2 fuel cells using hydrogen sulfide from Black Sea waters. In: Journal of Applied Electrochemistry. 46, pp. 943-949

[92] Razkazova-Velkova E., Martinov M., Beschkov V., Stefanov S., Dermendzhieva N. (2015): Fuel cells based on sulphides and sulphites. Problems, perspectives and possibilities. In: J. Int. Sc. Publ., Ecology & Safety, ISSN 1314-7234, Volume 9

[93] Beschkov V., Razkazova-Velkova E., Martinov M., Stefanov S. (2015): Energy Production from Black Sea Water by Sulphide-Driven Fuel Cell. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[94] Martinov M., Razkazova-Velkova E., Beschkov V. (2013): Energy efficiency of an electrochemical fuel cell for oxidation of sulphide ions from deep Black Sea water: Part I. Design of the fuel cell. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[95] Razkazova-Velkova E., Martinov M., Ljutzkanov L., Dermendzhieva N., Beschkov V. (2013): Energy efficiency of an electrochemical fuel cell for oxidation of sulphide ions from deep Black Sea water: Part II. Design of the electrodes. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[96] Razkazova-Velkova E., Martinov M., Stefanov S., Beschkov V. (2014): Energy efficiency of an electrochemical fuel cell for oxidation of sulphide ions from deep Black Sea water: Part III. Final design and lab-scale model. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[97] Martinov M., Razkazova-Velkova E., Stefanov S., Beschkov V., Vaszilcsi N., Marsagishvili T. (2014): Energy efficiency of an electrochemical fuel cell for oxidation of sulphide ions from deep Black Sea water: Part IV. Pilot-scale equipment and test in real conditions. Publication, Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria

[98] Stefanov S., Panajotova P., Beschkov V. (2014): Influence of temperature and initial concentration on the oxidation rate of sulphide from sea water in a fuel cell. In: Journal of Chemical Technology and Metallurgy. 49 (5), pp. 455-458

[99] Wikipedia: Nautical mile, https://en.wikipedia.org/wiki/Nautical_mile (20.09.2017)

[100] Razkazova-Velkova E., Martinov M., Ljutzkanov L., Dermendzhieva N., Beschkov V. (2013): Catalytic oxidation of sulphide ions in Black Sea water. In: Journal of Int. Sc. Publ., Materials, Methods & Technologies. 7 (1), pp. 456-463

[101] Wikipedia: Spinel, https://en.wikipedia.org/wiki/Spinel_group (22.09.2017)

[102] Wikipedia: Electromotive force, https://en.wikipedia.org/wiki/Electromotive_force (23.09.2017)

[103] Stavros M. (2012): Feasibility study of hydrogen production and power in fuel cell reactors from the H2S-rich Black Sea waters. Master thesis, School of Science and Technology, Thessaloniki, Greece

[104] Beschkov V., Hristov V., Petkov P. (2017): Energy yield from sulfide containing marine water. Presentation on the 9th International Invention Fair in the Middle East, Kuwait

[105] Picture of the Black Sea, Google Earth, reworked by author

[106] Picture of the changed layout of the South Stream gas pipeline, the 1st Russian state TV channel, reworked by author

[107] Lukoil Neftochim Burgas, https://en.wikipedia.org/wiki/LUKOIL_Neftochim_Burgas (28.09.2017)

[108] Bulgarian daily paper “Standart” from July 19th and 28th, 2017

[109] OMV, https://en.wikipedia.org/wiki/OMV (28.09.2017)

[110] Delchev P. (2009): Study of the processes for natural gas reforming and hydrogen production. Diploma thesis, Burgas University of Technology, Burgas, Bulgaria

[111] Bulgarian magazine “Theme”, 2014

[112] Wikipedia: Methan hydrate, https://en.wikipedia.org/wiki/Methane_clathrate (29.09.2017)

[113] Lossau N. (2017): Methanhydrate „Brennendes Eis“ soll die Energie der Menschheit revolutionieren. In: Die Welt. Issue from 24.05.2017

[114] Lehmköster J. (2014): World Ocean Review 2014 - Rohstoffe aus dem Meer-Chancen und Risiken. Maribus, Hamburg, Germany

[115] Interview with Dr. Atanas Vasilev, Institute of Oceanology, Bulgarian Academy of Sciences, Varna, Bulgaria. Published in the Bulgarian weekly paper “168 Chasa” on 21.08.2014

[116] Bulgarian online news platform Varnautre.bg, Експедиция вади от Черно море метан за милиони. Published on 24.07.2017

[117] Methane Gas Hydrates, online presentation, slides 51&55, http://slideplayer.com/slide/9465488/ (30.09.2017)

[118] Wikipedia: SUGAR project, https://de.wikipedia.org/wiki/SUGAR_(Projekt) (30.09.2017)

[119] SUGAR Project, Natural gas from methane hydrate, Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Germany, http://www.umsicht.fraunhofer.de/de/presse-medien/2015/sugar-erdgas-methanhydrate.html (01.10.2017)

[120] Big Chemical Encyclopedia, H:C ratio,[c.127], Chempedia.info (2015), http://chempedia.info/page/018097023076226172212235004063066015207135053253/ (04.11.2017)

[OC] Own Calculations

List of tables

List of figures

List of abbreviations

AFC	Alcaline Fuel Cell
BD	Biodiesel
BS	Black Sea
BAS	Bulgarian Academy of Sciences
BEV	Battery Electric Vehicle
BMFC	Benthic Microbial Fuel Cell
BOS	Balance of Systems (construction elements of a PV power plant)
CH4	Methane
CHP	Combined Heat and Power
CNG	Compressed Natural Gas
CO	Carbon Monoxide
Co	Cobalt
CO2	Carbon Dioxide
DASFC	Direct Alkaline Sulphide Fuel Cell
DMFC	Direct Methanol Fuel Cell
emf	Electromotive force
EPBT	Energy Payback Time
EROEI	Energy Return on Energy Investment
EV	Electric Vehicle
EWEA	European Wind Energy Agency
FAME	Fatty Acid Methyl Ester
FAO	Food and Agricultural Organization
FC	Fuel Cell
FCV	Fuel Cell Vehicle
FIT	Feed In Tariff
FLH	Full Load Hours
GHG	Greenhouse Gas
GHI	Global Horizontal Irradiation
GWEC	Global Wind Energy Council
HAWT	Horizontal Axis Wind Turbine
H2S	Hydrogen sulphide
HS^-	Sulphide anion
ICE	Internal Combustion Engine
IRR	Internal Rate of Return
KOH	Potassium Hydroxide
LUC	Land Use Change
LCA	Life Cycle Assessment
M	Mole (unit)
MCFC	Molten Carbonate Fuel Cell
MFC	Microbial Fuel Cell
MPP	Maximum Power Point
Na2S	Sodium Sulphide
NaOH	Sodium Hydroxide
NG	Natural Gas
Ni	Nickel
NOx	Nitrogen Oxides

NPV	Net Present Value
NREAP	National Renewable Energy Action Plan
OC	Own Calculations
O&M	Operation and Maintenance
OR	Oxygen Reactor
PAFC	Phosphoric Acid Fuel Cell
PEFC	Polymer Electrolyte Fuel Cell
PEM	Proton Exchange Membrane
ppm	parts per million
PR	Performance Ratio
PV	Photovoltaic
PVGIS	Photovoltaic Geographical Information System
RES	Renewable Energy Sources
S^{2-}	Polysulphide anion
SCR	Selective Catalytical Reduction
SDFC	Sulphide Driven Fuel Cell
SOx	Sulphur Oxides
SOB	Sulphur Oxidizing Bacteria
SOFC	Solid Oxid Fuel Cell
SPFC	Solid Polymer Electrolyte Fuel Cell
SR	Sulphide Reactor
SRB	Sulphur Reducing Bacteria
TU Wien	University of Technology in Vienna
UCO	Used Cooking Oil
VAWT	Vertical Axis Wind Turbine
WACC	Weighted Average Cost of Capital
WECS	Wind Energy Conversion System
WT	Wind Turbine
ZrO2	Zirconium Oxide

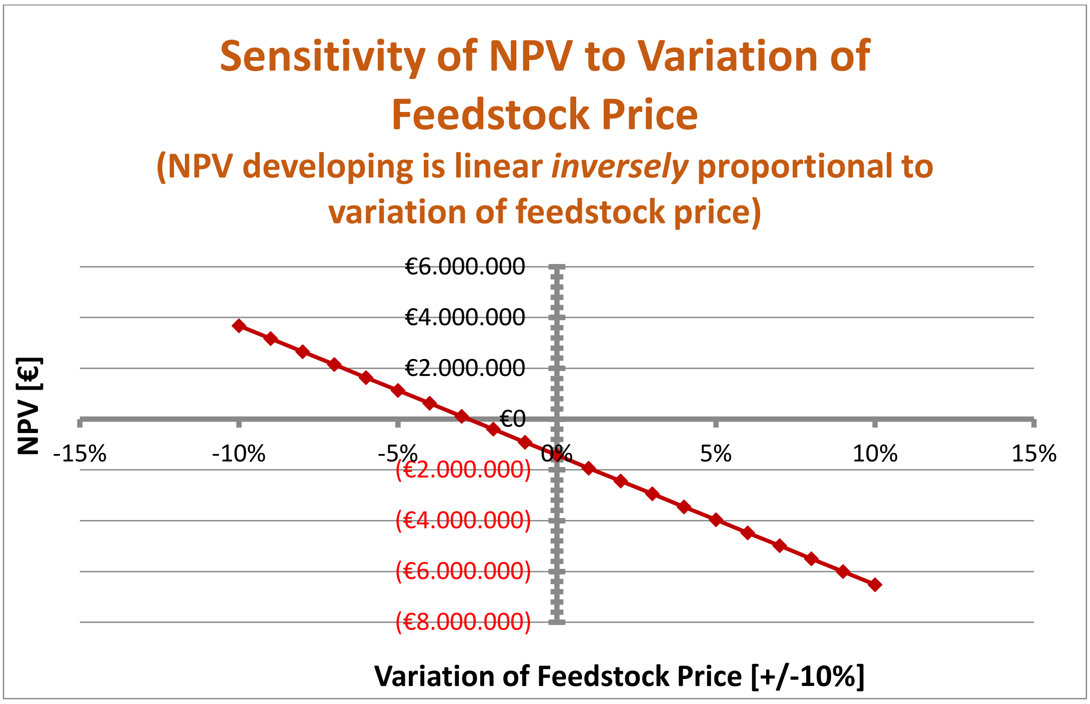
APPENDICES

Appendix 1.1. NPV analysis of the small-scale biodiesel plant (15.000 t/a) [OC]

Small-scale BD Plant													
	Cash Flow		Costs								Revenues		
Year	Discounted CF	Nominal CF	O&M	Personnel	Methanol	Energy	Overheads	Loss of oil	Feedstock	UCO	Biodiesel	Glycerol	Fatty acids
0	-€ 8.000.000	-€ 8.000.000											
1	€ 908.179	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
2	€ 840.906	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
3	€ 778.617	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
4	€ 720.942	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
5	€ 667.539	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
6	€ 618.091	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
7	€ 572.307	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
8	€ 529.914	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
9	€ 490.661	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
10	€ 454.316	€ 980.833	-€ 300.000	-€ 52.500	-€ 270.000	-€ 630.000	-€ 150.000	-€ 270.000	-€ 7.596.522	-€ 2.543.478	€ 11.833.333	€ 825.000	€ 135.000
NPV	-€ 1.418.528												

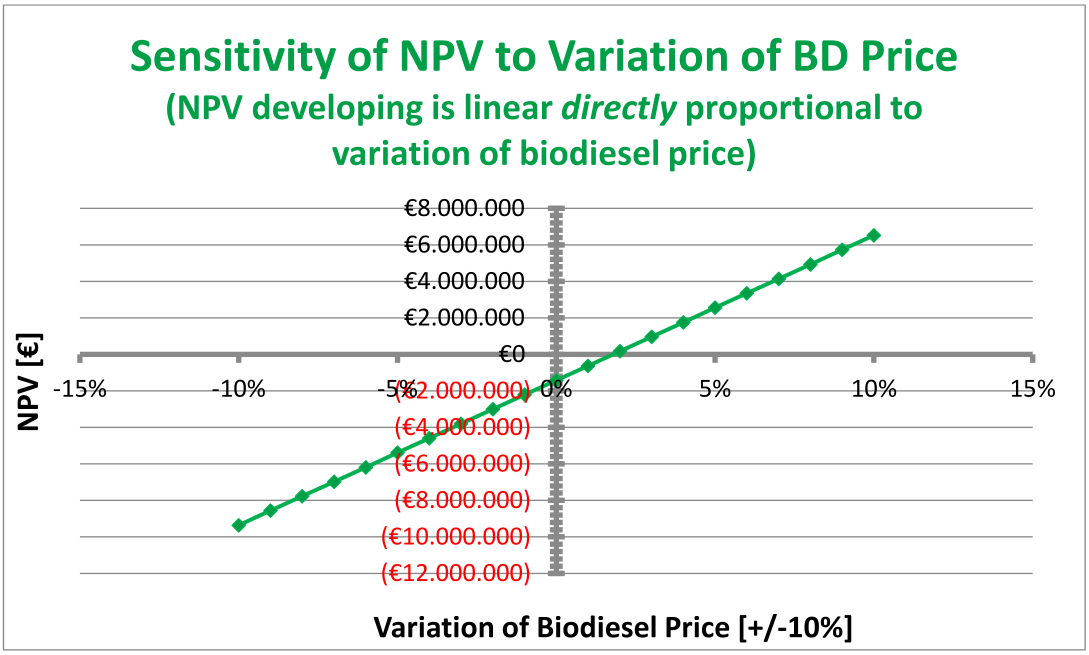
Appendix 1.1.1. Sensitivity analysis of NPV to variation of feedstock price (small-scale BD plant) [OC]

Variation of Feedstock Price	NPV [€]
-10%	€ 3.678.799
-9%	€ 3.169.067
-8%	€ 2.659.334
-7%	€ 2.149.601
-6%	€ 1.639.868
-5%	€ 1.130.135
-4%	€ 620.403
-3%	***€ 110.670***
-2%	***-€ 399.063***
-1%	-€ 908.796
0%	**-€ 1.418.528**
1%	-€ 1.928.261
2%	-€ 2.437.994
3%	-€ 2.947.727
4%	-€ 3.457.460
5%	-€ 3.967.192
6%	-€ 4.476.925
7%	-€ 4.986.658
8%	-€ 5.496.391
9%	-€ 6.006.124
10%	-€ 6.515.856



Appendix 1.1.2. Sensitivity analysis of NPV to variation of biodiesel price (small-scale BD plant) [OC]

Variation of Biodiesel Price	NPV [€]
-10%	-€ 9.358.791
-9%	-€ 8.564.765
-8%	-€ 7.770.739
-7%	-€ 6.976.713
-6%	-€ 6.182.686
-5%	-€ 5.388.660
-4%	-€ 4.594.634
-3%	-€ 3.800.607
-2%	-€ 3.006.581
-1%	-€ 2.212.555
0%	**-€ 1.418.528**
1%	***-€ 624.502***
2%	***€ 169.524***
3%	€ 963.550
4%	€ 1.757.577
5%	€ 2.551.603
6%	€ 3.345.629
7%	€ 4.139.656
8%	€ 4.933.682
9%	€ 5.727.708
10%	€ 6.521.734

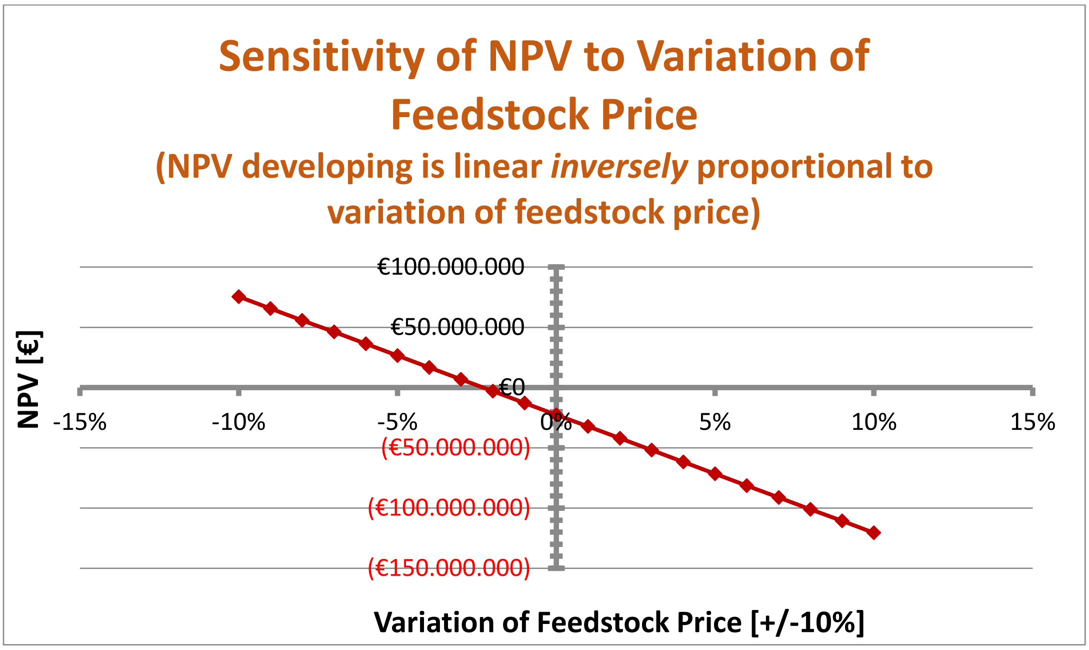


Appendix 1.2. NPV analysis of the large-scale biodiesel plant [OC]

Large-scale BD Plant												
	Cash Flow		Costs							Revenues		
Year	Discounted CF	Nominal CF	O&M	Personnel	Methanol	Energy	Overheads	Loss of oil	Feedstock	Biodiesel	Glycerol	Fatty acids
0	-€ 50.000.000	-€ 50.000.000										
1	€ 3.787.797	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
2	€ 3.507.220	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
3	€ 3.247.426	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
4	€ 3.006.876	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
5	€ 2.784.144	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
6	€ 2.577.911	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
7	€ 2.386.955	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
8	€ 2.210.143	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
9	€ 2.046.429	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
10	€ 1.894.842	€ 4.090.821	-€ 1.200.000	-€ 200.000	-€ 3.000.000	-€ 6.000.000	-€ 1.000.000	-€ 4.600.000	-€ 146.086.957	€ 157.777.778	€ 6.200.000	€ 2.200.000
NPV	-€ 22.550.256											

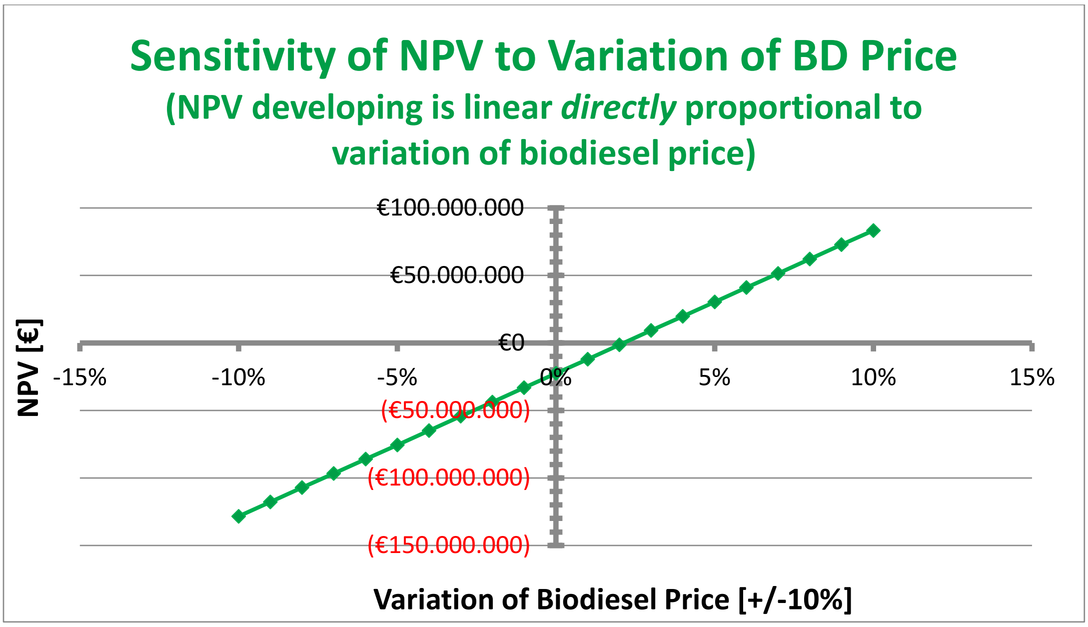
Appendix 1.2.1. Sensitivity analysis of NPV to variation of feedstock price (large-scale BD plant) [OC]

Variation of Feedstock Price	NPV [€]
-10%	€ 75.475.281
-9%	€ 65.672.727
-8%	€ 55.870.173
-7%	€ 46.067.619
-6%	€ 36.265.066
-5%	€ 26.462.512
-4%	€ 16.659.958
-3%	***€ 6.857.405***
-2%	***-€ 2.945.149***
-1%	-€ 12.747.703
0%	**-€ 22.550.256**
1%	-€ 32.352.810
2%	-€ 42.155.364
3%	-€ 51.957.917
4%	-€ 61.760.471
5%	-€ 71.563.025
6%	-€ 81.365.579
7%	-€ 91.168.132
8%	-€ 100.970.686
9%	-€ 110.773.240
10%	-€ 120.575.793



Appendix 1.2.2. Sensitivity analysis of NPV to variation of biodiesel price (large-scale BD plant) [OC]

Variation of Biodiesel Price	NPV [€]
-10%	-€ 128.420.430
-9%	-€ 117.833.412
-8%	-€ 107.246.395
-7%	-€ 96.659.378
-6%	-€ 86.072.360
-5%	-€ 75.485.343
-4%	-€ 64.898.326
-3%	-€ 54.311.308
-2%	-€ 43.724.291
-1%	-€ 33.137.274
0%	**-€ 22.550.256**
1%	-€ 11.963.239
2%	***-€ 1.376.222***
3%	***€ 9.210.796***
4%	€ 19.797.813
5%	€ 30.384.830
6%	€ 40.971.848
7%	€ 51.558.865
8%	€ 62.145.882
9%	€ 72.732.899
10%	€ 83.319.917

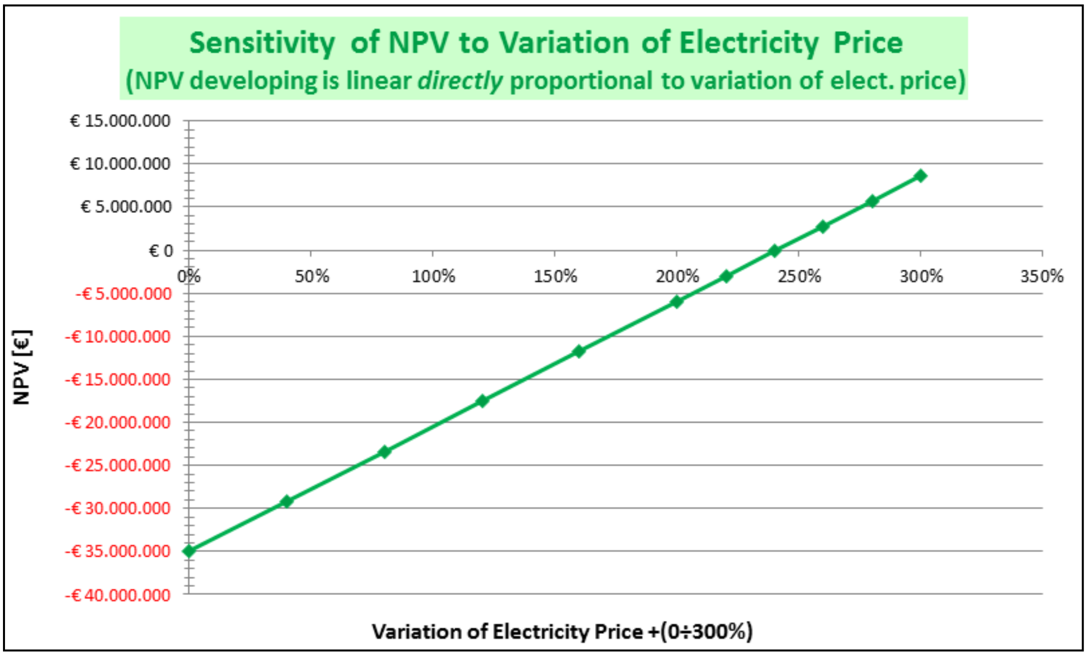


Appendix 2.1. NPV analysis of the small-scale PV plant (36 MW) [OC]

Small-scale PV Plant										
	Cash Flow		Costs							Revenues
Year	Discounted CF	Nominal CF	Investment	Grid connection	Gr. Access&Transm.	Land	Personnel	O&M	Insurance	Electricity sale
0	-€ 40.206.813		-€ 39.699.000	-€ 56.688		-€ 451.125				
1	€ 461.842	€ 498.790			-€ 333.323		-€ 52.000	-€ 238.194	-€ 238.194	€ 1.360.500
2	€ 426.740	€ 497.750			-€ 333.323		-€ 53.040	-€ 238.194	-€ 238.194	€ 1.360.500
3	€ 394.288	€ 496.689			-€ 333.323		-€ 54.101	-€ 238.194	-€ 238.194	€ 1.360.500
4	€ 364.286	€ 495.607			-€ 333.323		-€ 55.183	-€ 238.194	-€ 238.194	€ 1.360.500
5	€ 336.550	€ 494.503			-€ 333.323		-€ 56.286	-€ 238.194	-€ 238.194	€ 1.360.500
6	€ 310.911	€ 493.377			-€ 333.323		-€ 57.412	-€ 238.194	-€ 238.194	€ 1.360.500
7	€ 287.211	€ 492.229			-€ 333.323		-€ 58.560	-€ 238.194	-€ 238.194	€ 1.360.500
8	€ 265.303	€ 491.058			-€ 333.323		-€ 59.732	-€ 238.194	-€ 238.194	€ 1.360.500
9	€ 245.054	€ 489.863			-€ 333.323		-€ 60.926	-€ 238.194	-€ 238.194	€ 1.360.500
10	€ 226.337	€ 488.645			-€ 333.323		-€ 62.145	-€ 238.194	-€ 238.194	€ 1.360.500
11	€ 209.038	€ 487.402			-€ 333.323		-€ 63.388	-€ 238.194	-€ 238.194	€ 1.360.500
12	€ 193.051	€ 486.134			-€ 333.323		-€ 64.655	-€ 238.194	-€ 238.194	€ 1.360.500
13	€ 178.275	€ 484.841			-€ 333.323		-€ 65.949	-€ 238.194	-€ 238.194	€ 1.360.500
14	€ 164.620	€ 483.522			-€ 333.323		-€ 67.268	-€ 238.194	-€ 238.194	€ 1.360.500
15	€ 152.002	€ 482.177			-€ 333.323		-€ 68.613	-€ 238.194	-€ 238.194	€ 1.360.500
16	€ 140.342	€ 480.804			-€ 333.323		-€ 69.985	-€ 238.194	-€ 238.194	€ 1.360.500
17	€ 129.568	€ 479.405			-€ 333.323		-€ 71.385	-€ 238.194	-€ 238.194	€ 1.360.500
18	€ 119.613	€ 477.977			-€ 333.323		-€ 72.813	-€ 238.194	-€ 238.194	€ 1.360.500
19	€ 110.416	€ 476.521			-€ 333.323		-€ 74.269	-€ 238.194	-€ 238.194	€ 1.360.500
20	€ 101.918	€ 475.035			-€ 333.323		-€ 75.754	-€ 238.194	-€ 238.194	€ 1.360.500
21	€ 94.068	€ 473.520			-€ 333.323		-€ 77.269	-€ 238.194	-€ 238.194	€ 1.360.500
22	€ 86.815	€ 471.975			-€ 333.323		-€ 78.815	-€ 238.194	-€ 238.194	€ 1.360.500
23	€ 80.116	€ 470.399			-€ 333.323		-€ 80.391	-€ 238.194	-€ 238.194	€ 1.360.500
24	€ 73.928	€ 468.791			-€ 333.323		-€ 81.999	-€ 238.194	-€ 238.194	€ 1.360.500
25	€ 68.212	€ 467.151			-€ 333.323		-€ 83.639	-€ 238.194	-€ 238.194	€ 1.360.500
NPV	-€ 34.986.308									

Appendix 2.2. Sensitivity analysis of NPV to variation of electricity price (small-scale PV plant) [OC]

Variation of Electricity Price	NPV [€]
0%	-€ 34.986.308
40%	-€ 29.177.095
80%	-€ 23.367.881
120%	-€ 17.558.668
160%	-€ 11.749.455
200%	-€ 5.940.242
220%	-€ 3.035.635
240%	***-€ 131.029***
260%	***€ 2.773.578***
280%	€ 5.678.185
300%	€ 8.582.791

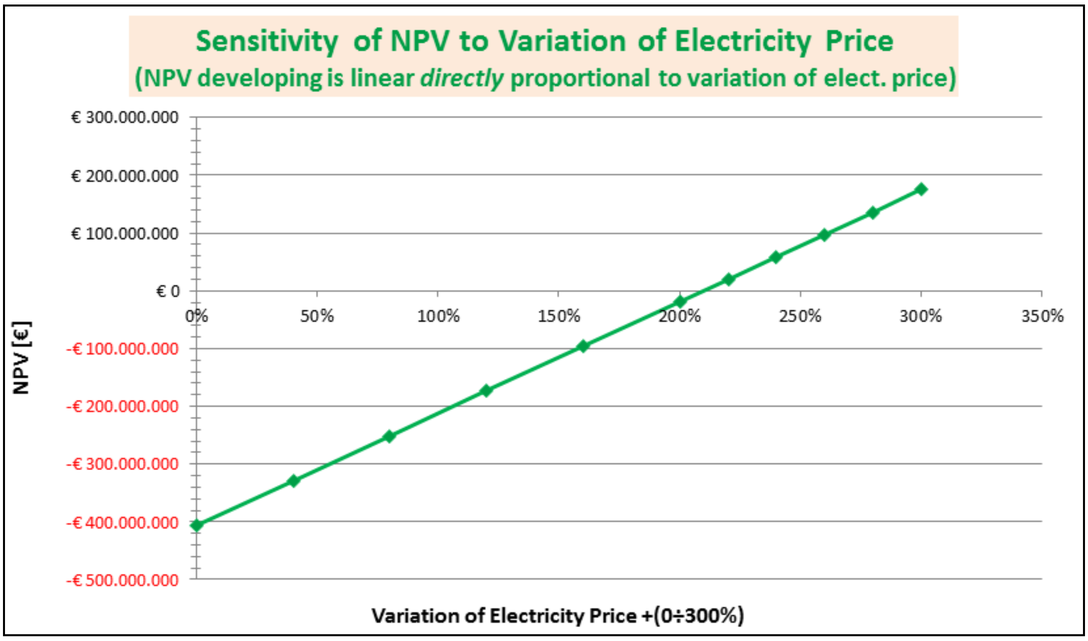


Appendix 2.3. NPV analysis of the large-scale PV plant (481 MW) [OC]

Large-scale PV Plant										
	Cash Flow		Costs							Revenues
Year	Discounted CF	Nominal CF	Investment	Grid connection	Gr. Access&Transm.	Land	Personnel	O&M	Insurance	Electricity sale
0	-€ 488.021.500		-€ 481.250.000	-€ 755.875		-€ 6.015.625				
1	€ 7.154.125	€ 7.726.455			-€ 4.444.545		-€ 195.000	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
2	€ 6.620.846	€ 7.722.555			-€ 4.444.545		-€ 198.900	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
3	€ 6.127.255	€ 7.718.577			-€ 4.444.545		-€ 202.878	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
4	€ 5.670.402	€ 7.714.519			-€ 4.444.545		-€ 206.936	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
5	€ 5.247.556	€ 7.710.381			-€ 4.444.545		-€ 211.074	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
6	€ 4.856.187	€ 7.706.159			-€ 4.444.545		-€ 215.296	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
7	€ 4.493.957	€ 7.701.853			-€ 4.444.545		-€ 219.602	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
8	€ 4.158.699	€ 7.697.461			-€ 4.444.545		-€ 223.994	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
9	€ 3.848.406	€ 7.692.981			-€ 4.444.545		-€ 228.474	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
10	€ 3.561.222	€ 7.688.412			-€ 4.444.545		-€ 233.043	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
11	€ 3.295.429	€ 7.683.751			-€ 4.444.545		-€ 237.704	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
12	€ 3.049.435	€ 7.678.997			-€ 4.444.545		-€ 242.458	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
13	€ 2.821.768	€ 7.674.148			-€ 4.444.545		-€ 247.307	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
14	€ 2.611.064	€ 7.669.202			-€ 4.444.545		-€ 252.253	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
15	€ 2.416.062	€ 7.664.157			-€ 4.444.545		-€ 257.298	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
16	€ 2.235.592	€ 7.659.011			-€ 4.444.545		-€ 262.444	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
17	€ 2.068.574	€ 7.653.762			-€ 4.444.545		-€ 267.693	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
18	€ 1.914.007	€ 7.648.408			-€ 4.444.545		-€ 273.047	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
19	€ 1.770.963	€ 7.642.947			-€ 4.444.545		-€ 278.508	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
20	€ 1.638.586	€ 7.637.377			-€ 4.444.545		-€ 284.078	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
21	€ 1.516.080	€ 7.631.695			-€ 4.444.545		-€ 289.760	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
22	€ 1.402.712	€ 7.625.900			-€ 4.444.545		-€ 295.555	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
23	€ 1.297.801	€ 7.619.989			-€ 4.444.545		-€ 301.466	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
24	€ 1.200.716	€ 7.613.960			-€ 4.444.545		-€ 307.495	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
25	€ 1.110.876	€ 7.607.810			-€ 4.444.545		-€ 313.645	-€ 2.887.500	-€ 2.887.500	€ 18.141.000
NPV	-€ 405.933.178									

Appendix 2.4. Sensitivity analysis of NPV to variation of electricity price (large-scale PV plant) [OC]

Variation of Electricity Price	**NPV [€]**
0%	-€ 405.933.178
40%	-€ 328.472.732
80%	*-€ 251.012.286*
120%	-€ 173.551.840
160%	-€ 96.091.394
200%	***-€ 18.630.948***
220%	***€ 20.099.275***
240%	€ 58.829.498
260%	€ 97.559.721
280%	€ 136.289.944
300%	€ 175.020.167



Appendix 3.1. NPV analysis of the small-scale wind farm [OC]

Small-scale wind farm											
	Cash Flow		Costs								Revenues
Year	Discounted CF	Nominal CF	Investment	Grid connection	Gr. Access&Transm.	Land	Personnel	O&M	Insurance	20% tax on FIT	Electricity sale
										Cancelled	
										by	
0	-€ 189.823.188		-€ 186.000.000	-€ 56.688		-€ 3.766.500				BG constitutional	
										court	
1	-€ 1.757.475	-€ 1.898.073			-€ 333.323		-€ 130.000	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
2	-€ 1.629.520	-€ 1.900.673			-€ 333.323		-€ 132.600	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
3	-€ 1.510.920	-€ 1.903.325			-€ 333.323		-€ 135.252	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
4	-€ 1.400.989	-€ 1.906.030			-€ 333.323		-€ 137.957	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
5	-€ 1.299.090	-€ 1.908.789			-€ 333.323		-€ 140.716	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
6	-€ 1.204.634	-€ 1.911.603			-€ 333.323		-€ 143.531	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
7	-€ 1.117.077	-€ 1.914.474			-€ 333.323		-€ 146.401	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
8	-€ 1.035.912	-€ 1.917.402			-€ 333.323		-€ 149.329	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
9	-€ 960.672	-€ 1.920.388			-€ 333.323		-€ 152.316	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
10	-€ 890.922	-€ 1.923.435			-€ 333.323		-€ 155.362	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
11	-€ 826.261	-€ 1.926.542			-€ 333.323		-€ 158.469	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
12	-€ 766.315	-€ 1.929.711			-€ 333.323		-€ 161.639	-€ 3.720.000	-€ 1.116.000		€ 3.401.250
13	-€ 1.461.119	-€ 3.973.694			-€ 333.323		-€ 164.871	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
14	-€ 1.354.011	-€ 3.976.991			-€ 333.323		-€ 168.169	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
15	-€ 1.254.774	-€ 3.980.355			-€ 333.323		-€ 171.532	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
16	-€ 1.162.829	-€ 3.983.785			-€ 333.323		-€ 174.963	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
17	-€ 1.077.639	-€ 3.987.285			-€ 333.323		-€ 178.462	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
18	-€ 998.707	-€ 3.990.854			-€ 333.323		-€ 182.031	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
19	-€ 925.573	-€ 3.994.495			-€ 333.323		-€ 185.672	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
20	-€ 857.808	-€ 3.998.208			-€ 333.323		-€ 189.385	-€ 3.720.000	-€ 1.116.000		€ 1.360.500
NPV	-€ 213.315.434										

Appendix 3.2. NPV analysis of the large-scale wind farm [OC]

Large-scale wind farm											
	Cash Flow		Costs								Revenues
Year	Discounted CF	Nominal CF	Investment	Grid connection	Gr. Access&Transm.	Land	Personnel	O&M	Insurance	20% tax on FIT	Electricity sale
										Cancelled	
										by	
0	-€ 2.028.413.875		-€ 1.977.600.000	-€ 755.875		-€ 50.058.000				BG constitutional	
										court	
1	-€ 10.032.079	-€ 10.834.645			-€ 4.444.545		-€ 325.000	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
2	-€ 9.294.534	-€ 10.841.145			-€ 4.444.545		-€ 331.500	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
3	-€ 8.611.314	-€ 10.847.775			-€ 4.444.545		-€ 338.130	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
4	-€ 7.978.409	-€ 10.854.538			-€ 4.444.545		-€ 344.893	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
5	-€ 7.392.110	-€ 10.861.435			-€ 4.444.545		-€ 351.790	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
6	-€ 6.848.980	-€ 10.868.471			-€ 4.444.545		-€ 358.826	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
7	-€ 6.345.836	-€ 10.875.648			-€ 4.444.545		-€ 366.003	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
8	-€ 5.879.729	-€ 10.882.968			-€ 4.444.545		-€ 373.323	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
9	-€ 5.447.929	-€ 10.890.434			-€ 4.444.545		-€ 380.789	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
10	-€ 5.047.906	-€ 10.898.050			-€ 4.444.545		-€ 388.405	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
11	-€ 4.677.318	-€ 10.905.818			-€ 4.444.545		-€ 396.173	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
12	-€ 4.333.997	-€ 10.913.742			-€ 4.444.545		-€ 404.097	-€ 39.552.000	-€ 11.865.600		€ 45.352.500
13	-€ 14.021.544	-€ 38.133.324			-€ 4.444.545		-€ 412.179	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
14	-€ 12.985.718	-€ 38.141.567			-€ 4.444.545		-€ 420.422	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
15	-€ 12.026.463	-€ 38.149.976			-€ 4.444.545		-€ 428.831	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
16	-€ 11.138.118	-€ 38.158.552			-€ 4.444.545		-€ 437.407	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
17	-€ 10.315.436	-€ 38.167.300			-€ 4.444.545		-€ 446.155	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
18	-€ 9.553.563	-€ 38.176.223			-€ 4.444.545		-€ 455.078	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
19	-€ 8.848.000	-€ 38.185.325			-€ 4.444.545		-€ 464.180	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
20	-€ 8.194.585	-€ 38.194.609			-€ 4.444.545		-€ 473.464	-€ 39.552.000	-€ 11.865.600		€ 18.141.000
NPV	-€ 2.197.387.444										