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BIOWASTE AND HYDROGEN SULFIDE – PERSPECTIVE RENEWABLE FUELS**V.Beschkov, D.Yankov, I.Angelov, E.Razkazova-Velkova, M.Martinov***Institute of Chemical Engineering, Bulgarian Academy of Sciences
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The enormous economical growth on a global scale in the last century has lead to extensive use of fossil fuels, such as coal, oil and natural gas. The result was strong emissions of carbon dioxide and greenhouse effect with consequent climate changes. The extensive use of fossil fuels that developed and stored in Earth interior for millions of years has made it no possible to revive vegetation and process the emitted carbon dioxide with the help of photosynthesis.

One of the ways to cope with this global problem is to close the carbon cycle in the nature through the use of renewable fuels enabling to recycle the sources of biological origin for generating energy and absorbing emergent carbon by photosynthesis. Another perspective source of energy is the hydrogen sulfide accumulated in deep waters of the Black Sea. It can be converted into electric energy by sulfide-driven fuel cells. The generated energy could be directly used or employed for hydrogen generation by electrolysis fed by the produced electric energy.

The present work demonstrates all of these opportunities based on our experimental data and scientific results available.

Keywords: *hydrogen sulfide, carbon dioxide, renewable fuel, biomass, biogas, ethanol.*

Introduction

The building of future based on clean and sustainable energy sources is one of the most urgent contemporary tasks of mankind. Presently, worldwide research efforts and energy policy of industrially developed countries are focusing on the development of effective clean-up technologies and search for alternative fuels, whose utilization does not give rise to toxic and harmful emissions. The extensive use of fossil fuels which are formed and stored underground for millions of years deprived the present vegetation worldwide of the opportunity to treat the emitted carbon dioxide in a natural way.

Recently, the biomass-derived fuel (bio-ethanol, biodiesel, bio-glycerol and biogas)

has received a lot of research interest due to its innate advantages over conventional fossil fuels [3]. Biomass is renewable, clean, carbon neutral and widely available. Moreover, the carbon dioxide released by human activity could be more easily disposed by vegetation through the use of photosynthesis and, hence, to close the carbon cycle and thus reduce the greenhouse emissions considerably.

There are various types of biomass-derived fuels but the most important and the most abundant are ethanol, biogas and biodiesel.

In the present work we shall consider and compare their advantages and drawbacks with own results and data from the literature.

Ethanol

The interest in ethanol as alternative to the fossil fuels (like gasoline) came from its relatively high energy capacity and its anti-knocking effect on the engine operation. The fermentative way of ethanol production from

natural carbohydrate sources became important and superior to the synthetic methods after the climbing oil prices in the 1960s.

Using ethanol-blended fuel for automobiles can significantly reduce petroleum use and greenhouse emission.

The first step was to use cereals as raw materials (mostly corn) but this competed the use of cereals as food and lead to very high prices on the world market. That is why, the next step was to replace cereals by “second generation” raw materials, i.e. by lignocellulosic waste (grass, sawdust, wood

chips, straw). The conversion includes two processes: saccharification by hydrolysis of cellulose to fermentable reducing sugars, and fermentation of the sugars to ethanol. The first step is accomplished either by sulfuric acid or by enzymes. The enzyme hydrolysis is usually catalyzed by cellulase enzymes, and the fermentation is carried out by yeasts or bacteria. A flow-sheet of a typical ethanol production from lignocellulosic origin is shown in Fig. 1.

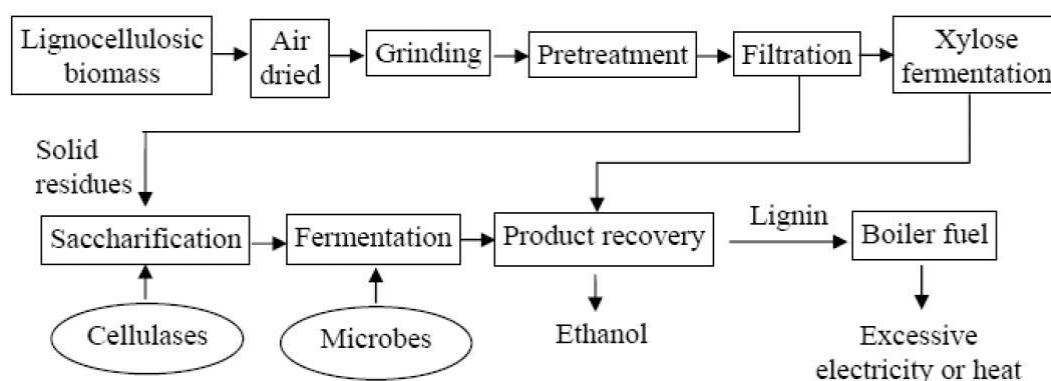


Fig. 1. Schematic overview of biomass-to-ethanol conversion process [1].

Cellulases are usually produced by fungi, like *Sclerotium rolfii*, *P. chrysosporium* and species of *Trichoderma*, *Aspergillus*, *Schizophyllum* and *Penicillium*[2-4]. Of all these fungal genera, *Trichoderma* has been most extensively studied for cellulase production [4].

The second step is the fermentation of the hydrolysed carbohydrates to ethanol, usually accomplished by yeast *Saccharomyces cerevisiae* and the bacterium *Zymomonas mobilis*, suitable for hexoses, like glucose as a substrate. Another strain i.e. the yeast *Pachysolen tannophilus* was isolated [5] to digest xyloses (i.e.

penthose) which is product of hemicellulose saccharification.

In our work we have used dry distiller grains with high cellulose content after ethanol distillation as a substrate and we have tested different hydrolytic methods: hydrolysis by sulfuric acid, sodium hydroxide (for lignin removal), ammonium hydroxide and enzymes (α -amylase, amyloglucosidase and cellulase) and combination of these methods. Some of the results obtained after treatment with 1% sulphuric acid samples previously hydrolyzed by NaOH or NH_4OH are shown below, cf. Fig. 2.

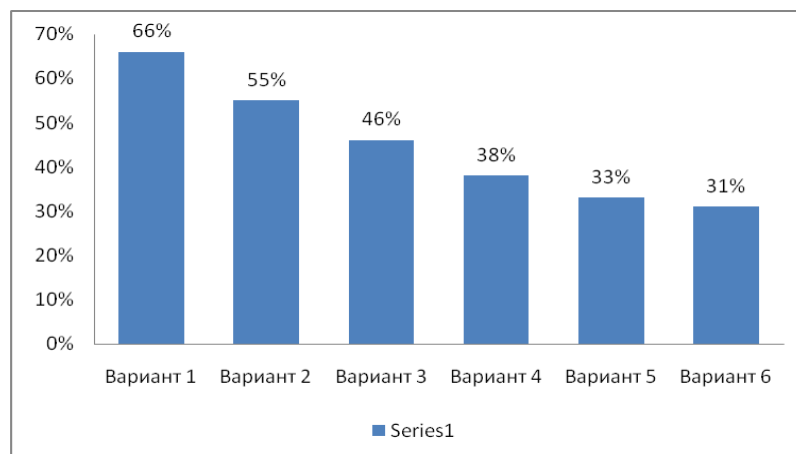


Fig. 2. Increase of reducing sugars yields after acid treatment of samples treated by NaOH and NH_4OH . Variant 1 – 1% NaOH; variant 2 – 2% NaOH; variant 3 – 3% NaOH; variant 4 – 1% NH_4OH ; вариант 5 – 2% NH_4OH ; вариант 6 – 6% NH_4OH .

Obviously, sodium hydroxide is preferred to ammonium hydroxide and especially at lower concentrations where 70% increase is observed. There are data for the effect of enzyme treatment after chemical

hydrolysis, shown in Fig. 3 and 4. Figure 3 shows data for the treatment by amylolytic enzymes and Figure 4 – the reducing sugars after treatment by cellulase.

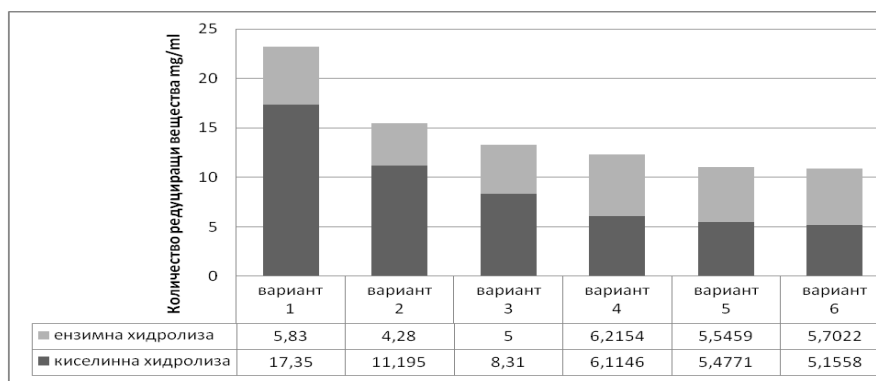


Fig. 3. Reducing sugars after treatment by α -amylase and amyloglucosidase. Comparizon with asid hydrolysis.

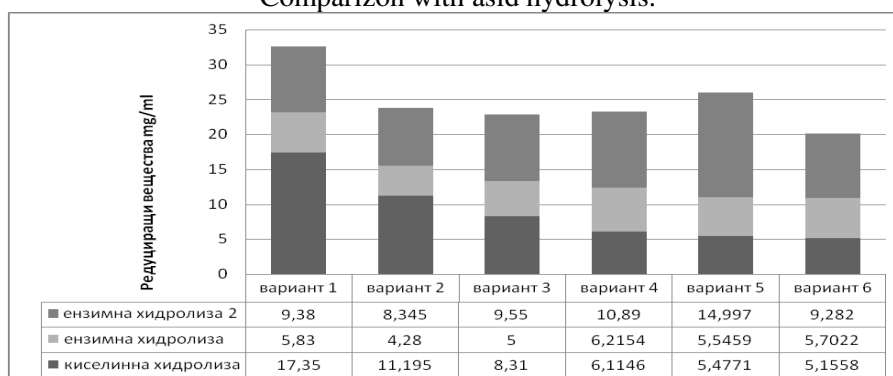


Fig. 4. Reducing sugars after consecutive treatment by α -amylase, amyloglucosidase and cellulase. Comparison with acid hydrolysis

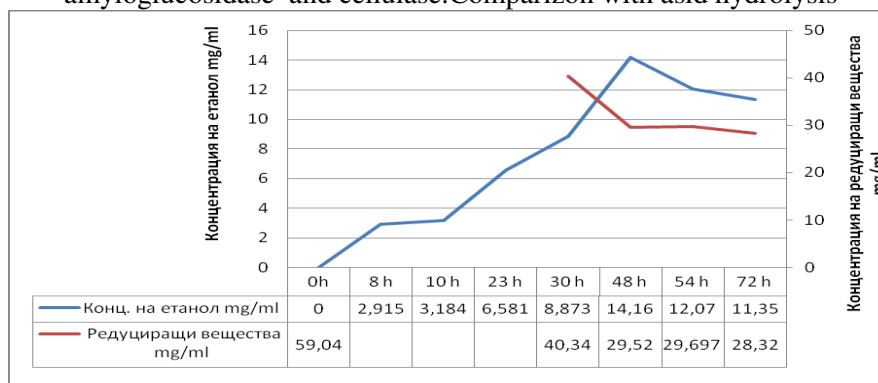


Fig. 5. Ethanol and reducing sugars at fermentation after acid hydrolysis.

There are data on ethanol fermentation of sample after acid hydrolysis only are shown in Fig. 5. In our work the yeast *Saccharomyces cerevisiae* was used. Although the concentrations are not too high there are indications for the perspectives of this process.

There are two main drawbacks to this ethanol fermentation: first, the very low product concentrations due to product

inhibition and second, problems with the waste disposal.

The first one is usually solved by genetic manipulations giving ethanol-resisting strains enabling higher concentrations. The second one is solved when the ethanol plant is coupled to biogas equipment based on anaerobic digestion of organic waste.

Biogas production

The process of anaerobic digestion employs specialized bacteria to break down organic waste, converting it to a stable solid and biogas, a mixture of carbon dioxide and methane. AD takes place naturally and it is frequently used to solve two big problems simultaneously: to get rid of organic waste and to solve partially the problem of energy shortage. The biogas generated at these sites is used to produce electricity and heat that is then sold to utilities, making the facilities profitable. Additional environmental gains include improvements in water and air quality over current practices of waste management.

In the recent practice, as substrates of cattle manure, poultry litter and activated sludge are the most commonly used ones. In our case we tested the possibilities for use of the stillage resulting of ethanol distillation as a substrate. The biogas production is a very sensitive process comprising several consecutive steps, Fig. 6. Methanogenic bacteria operate in

neutral media, namely at pH within 6 and 8. Overloading by organic substrate may lead to over-acidification and inhibition of the target process of methanogenesis. That is why, suitable bioreactor and stream optimization is required to avoid the undesired acidification.

We have chosen a cascade bioreactor with separated compartments and a substrate feed at the one end, cf. Fig. 7. A feed-batch strategy was employed. The bioreactor volume was 270 liters. It was separated to 8 compartments of equal size. The produced biogas was collected in the common gas space and transferred to gas holder where its volume was measured and samples were taken for analysis.

Hence, the consecutive processes are more or less distributed along the reactor starting with hydrolysis in compartment 1 and ending with methanogenesis in compartments 7 and 8. So one can minimize or even to avoid the undesired acidification in the last two or three compartments.

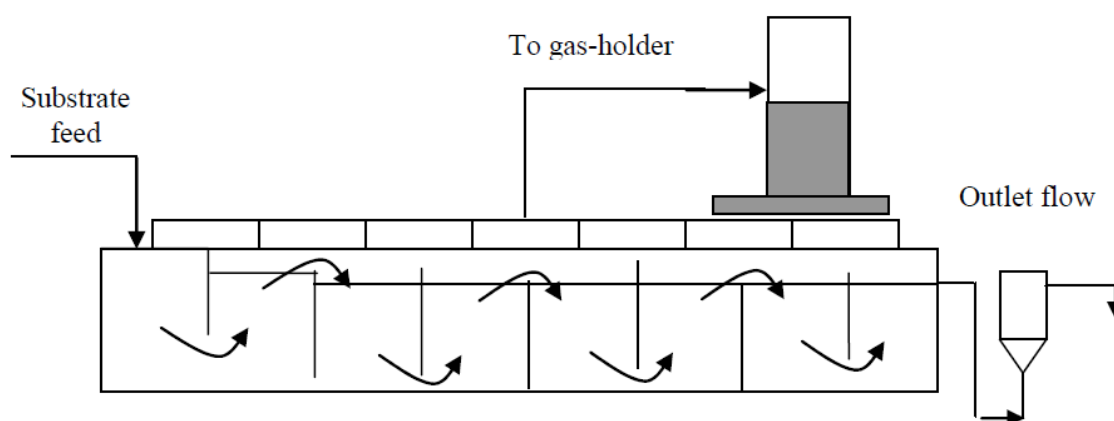
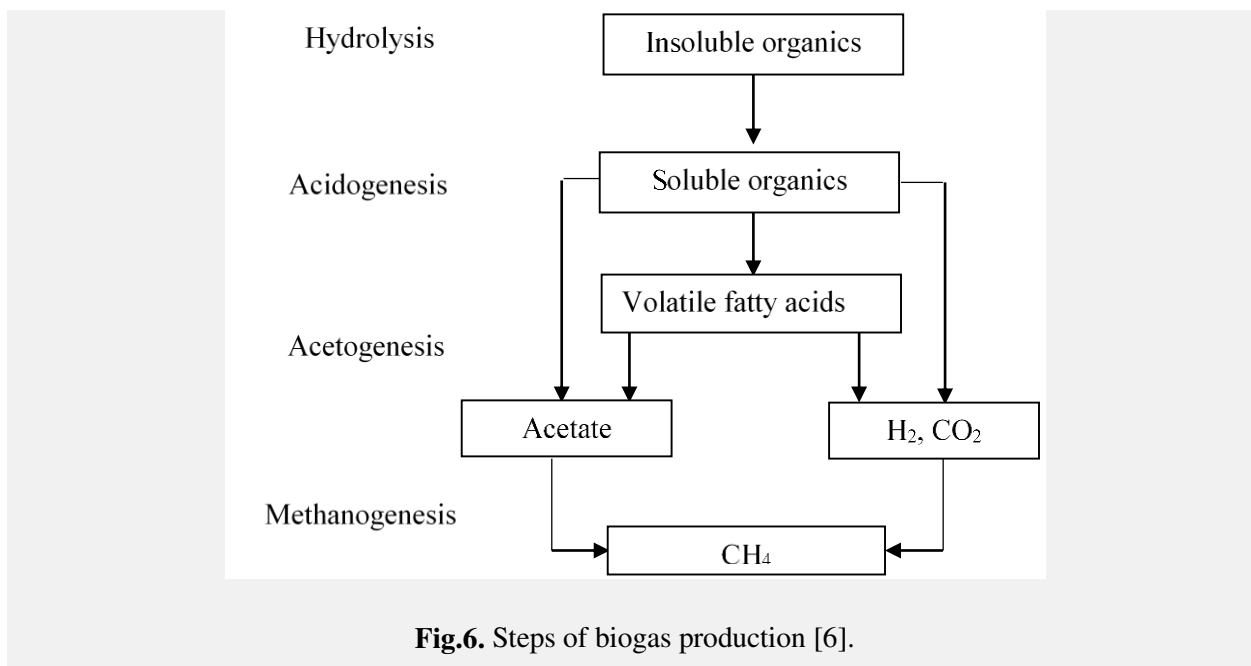


Fig. 7. Multi-stage bioreactor for biogas production.

Some results of the experiments with alcohol stillage are shown in Fig. 8. More important are the data for the intermediate product profile and the microbial profile along the bioreactor, cf. Fig. 9. One can see that volatile fatty acids (acetic and propionic ones) are in considerable concentrations in the first three compartment where hydrolysis, acidogenesis and acetogenesis take place. Methanogenic bacteria prevail in

compartments 5, 6 and 7, where acids are too low and therefore methane formation should be expected. There are practically no active microbes in compartment 8, i.e. it is useless.

The biogas production rate was pretty high, reaching 4 l/l/day. The COD decrease was up to 95%. The methane content in the produced biogas was between 65 and 80% (vol.) which is a very good achievement, compared to the traditional 50-55%.

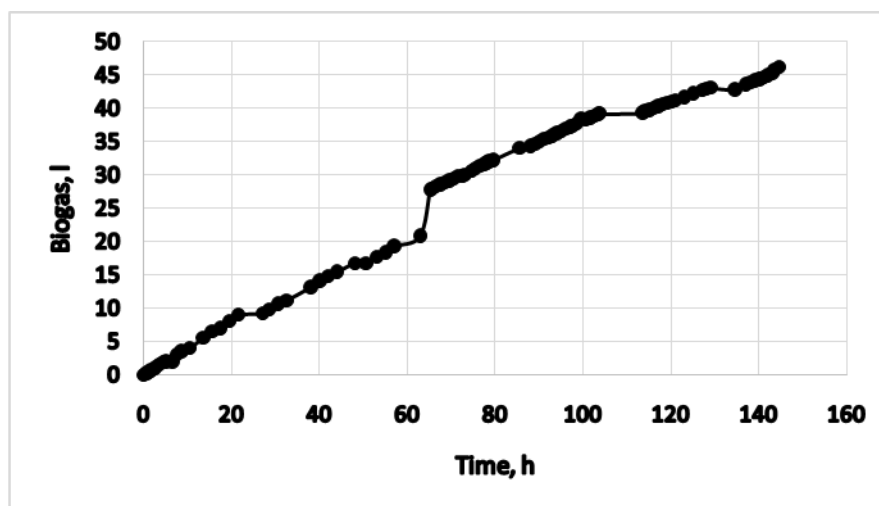


Fig. 8. Partial time profile of accumulated biogas with corn stillage as substrate.

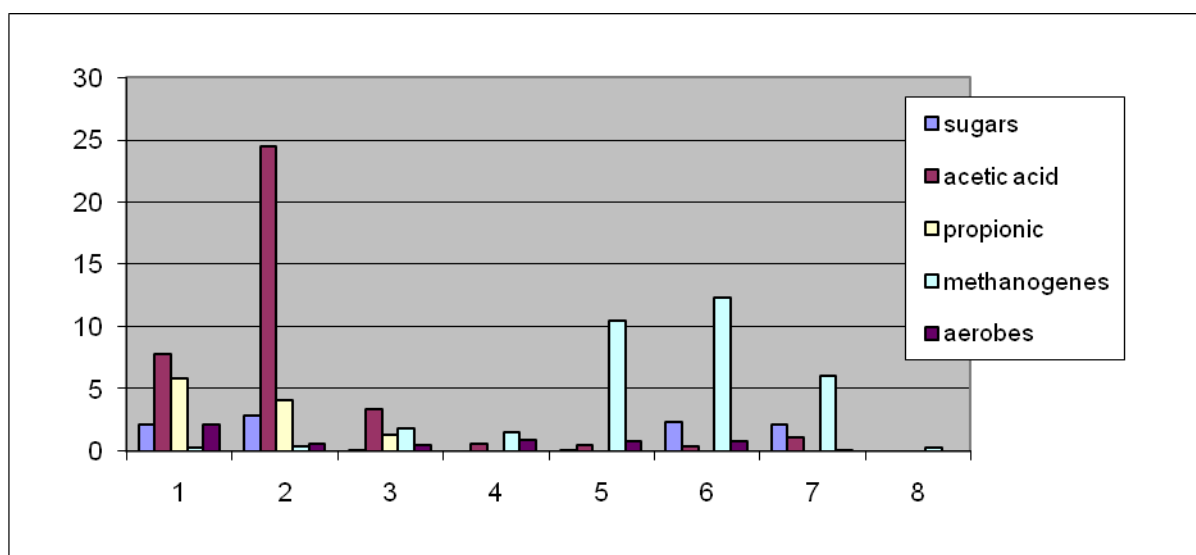


Fig. 9. Acid and microbial profiles along the compartments in the bioreactor.

Waste glycerol from biodiesel production

Crude glycerol is the main waste product from biodiesel manufacturing. Its amount is about 10% of the produced biodiesel and exceeds the traditional market demands. On the other hand this waste product contains about 20% water and it is contaminated by the catalyst (potassium hydroxide) and some methanol. Since the market is interested only in pure glycerol new applications of this waste product as a source for value-added chemicals are considered [7,8]. Many of them study the production of various chemicals by chemical conversions, like 2,3-butanediol, 1,3-propanediol, some derivatives suitable as additives to gasoline and diesel, e.g., glycerol

tertiary butyl ether (GTBE) [9], etc.. Also, some carboxylic acids used as monomers for biodegradable polymers, like lactic acid, are available [10].

Another way of waste glycerol utilization is biogas production by anaerobic digestion as described above. The advantage is that along with the biogas production some useful chemicals could be produced.

We studied the possibility of the use of crude glycerol treatment for simultaneous biogas and target chemicals production, like 2,3-butanediol [11]. Experiments have been carried out in a fed-batch mode in the bioreactor shown in Fig. 7, and samples taken

from each compartments and analysed for 2,3-butanediol and carboxylic acids by HPLC. Acetic and propionic were present in the reactor. No other acids have been detected in measurable concentrations.

Some concentration profiles with the pH variations along the reactor compartments are shown in Fig. 10.

One can see that pH-values in compartments 2-5 are below pH 6. This fact

coincides with the high concentrations of propionic acid in these compartments. Probably, the low values of acetic acids is due to its decarboxylation to methane although at low reaction rate. The supplementary product, i.e. 2,3-butanediol is accumulated in compartments 4-6 with sharp decrease in compartments 7 and 8, possibly due to degradation processes.

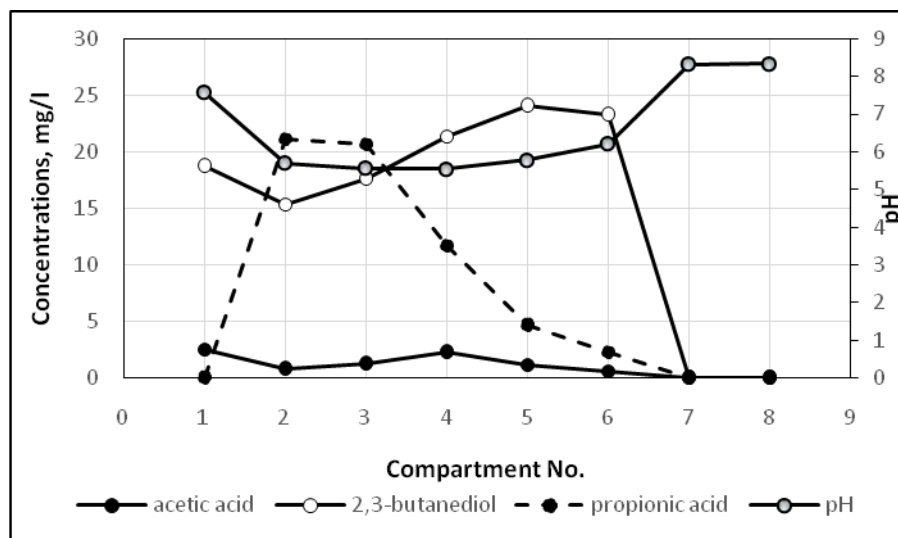


Fig. 10. Concentration profiles along the bioreactor compartments. 14 days after inoculation. Fed-batch process, 1 kg glycerol weekly.

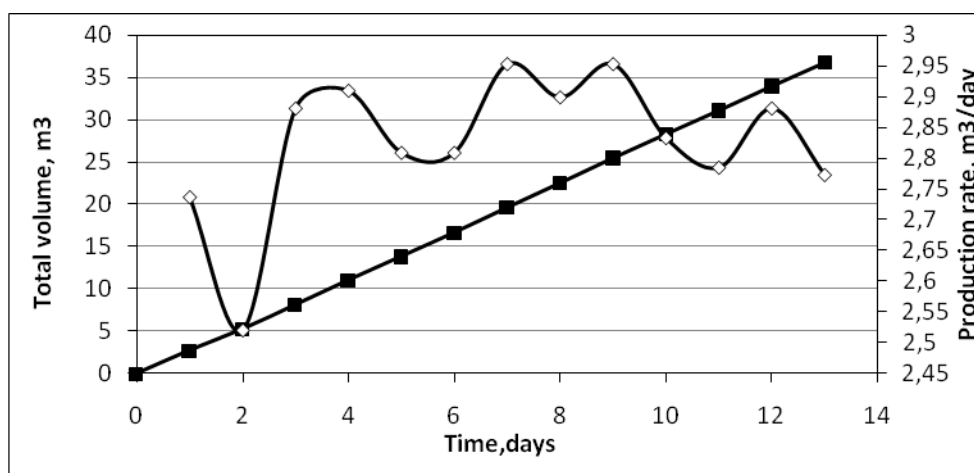


Fig.11. Rate of biogas production and accumulation from crude glycerol, Fed-batch process, 1 kg glycerol weekly.

The time evolution of the obtained biogas and the production rate are shown in Fig. 11. It

can be seen, that production rate is oscillating but around one constant value.

The general conclusion of this research is that glycerol maybe used for energy and

chemicals production simultaneously in the selected bioreactor type.

Hydrogen sulfide as renewable energy source

The Black Sea water contains significant amount of hydrogen sulfide at depths below 150 m. Its amount is estimated around 4.6 billion tons [12]. Due to the very high toxicity of hydrogen sulfide, beneath this depth the sea is practically dead. A lot of efforts were made to utilize and decompose it to harmless products [13-19]. Some of them propose the decomposition of hydrogen sulfide to hydrogen and elemental sulfur by photolysis [15,16], thermolysis [12,17] or by plasma methods [18]. However, in all of these cases the energy consumption is comparable or even higher than the gained energy as produced hydrogen. On the other hand the accumulation of sulfur as a sideproduct is inconvenient because of the necessity of suitable market for it.

There are some articles for the use of the oxidation energy of sulfide to elemental sulfur in fuel cells [19,20]. The problem in such a set-up is the accumulation of sulfur which is inhibitor and passivates the anode. Another drawback of this process is the relatively low enthalpy of sulfide-to-sulfur conversion (263 kJ/mole).

The possibility of using the oxidation energy of H_2S into a fuel cell oxidizing the sulfide to sulfate in genuine marine water has been analyzed by us within the last 4 years. The purpose is to transform the sulfide species into sulfate ones, thus gain more energy (788 kJ/mole), resolving the problems with the elemental sulfur and returning harmless sulfate ions into the sea entering again into their natural cycle. A scheme of the proposed fuel cell is shown in Fig. 12.

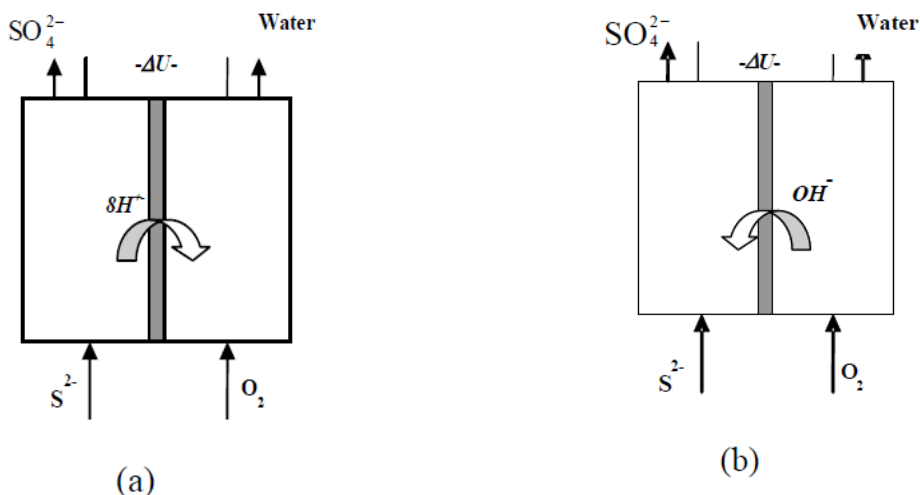


Fig. 12. A sketch of the proposed fuel cell with proton exchange (a) and hydroxylic anion exchange (b).

We have made a lot of experiments at different initial concentrations ($10\text{--}1000\text{ mg dm}^{-3}$), testing different ion-exchange membranes and catalysts, based on some heavy metal oxides (cobalt oxide, zirconia, etc.). As supporting electrolytes solutions of sea salt (i.e. crystallized from marine water) with concentrations $14\text{--}18\text{ g dm}^{-3}$, similar to the one of the genuine marine water, were

used. In some experiments sodium chloride was added to improve the electrolyte conductivity.

Mainly graphite was used as electrode material both for anode and cathode. Two different types of cell construction were tested: cylindrically shaped with circular membrane and ones of rectangular shape coupled in a stack. Air or pure oxygen were used as

oxidizer blown in the cathode space. A pilot-scale stack is shown in Fig. 13.



Fig. 13. Pilot equipment of stack of two parallel fuel cells.

In situ experiments with genuine Black Sea water have been carried out and the results indicated in [21].

Some experimental results are shown in Fig. 14 and 15. In both cases membrane Celgard 3501 was used.

The cell ohmic resistance depends on the membrane area and the cell thickness. The cell conductivity $\log(\sigma T)$ in our experiments was estimated above 2 reaching values close to 3. For a reference, those values for traditional fuel cells operating in gaseous phase are below 2 [22].

Overpotentials were estimated from the polarization curves. In all of our experiments

overpotentials proved to be lower than 10 mV, i.e. the Butler-Volmer equation could be used in its linear approximation:

$$\eta = \frac{RT}{(\alpha_a + \alpha_c)Fi_0} i, j_0 = i_0/A$$

The exchange current densities j_0 were calculated dividing the exchange current i_0 by the membrane area A .

The product $(\alpha_a + \alpha_c)j_0$ was estimated between 10^{-5} and 10^{-4} A/cm². Assuming that the sum of symmetry coefficients $\alpha_a + \alpha_c$ is about unity we can suppose similar exchange current densities j_0 to those estimated for the traditional fuel cells [22].

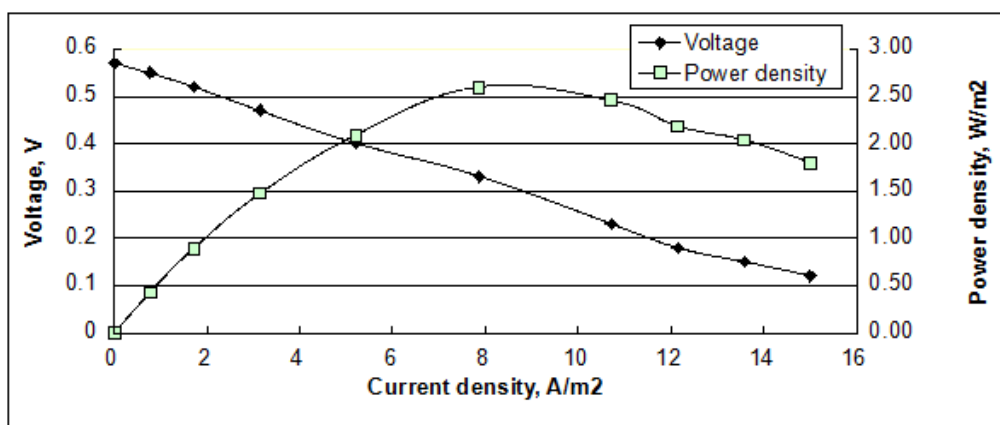


Fig. 14. Polarization curves for sulfide-driven fuel cell. Membrane area – 7 cm². Sulfide concentration 241 mg dm⁻³). Maximum current density 9,4 A/m².

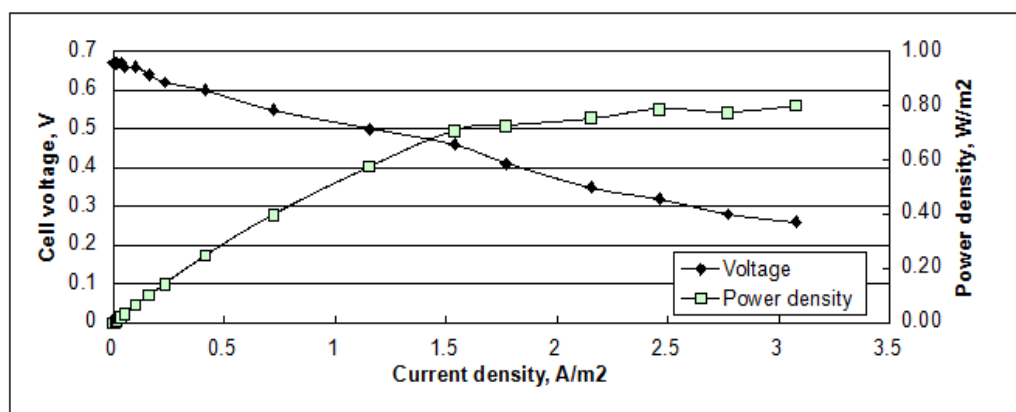


Fig. 15. Polarization curves for sulfide-driven single fuel cell. Membrane area – 650 cm². Sulfide concentration 230 mg dm⁻³. Maximum current density 3,4 A/m².

All these results showed that the new sulfide-driven fuel cells could be perspective for

practical applications if higher power densities would be attained.

Conclusion

The results cited above illustrate the advantages of the renewable fuel sources based on biomass and natural hydrogen sulfide. One can say that biomass-based fuels are quite distributed throughout the world; however, all these are related to much expenses when growing crops and investing funds in equipment (except biogas). Moreover, their use is concerned with carbon dioxide emissions to be considered further.

For a comparison, hydrogen sulfide taken from the marine water is carbon-free fuel independent of the climate changes to produce clean electricity which could be used for different purposes: connection to the grid, hydrogen production by splitting water, etc. The problem is to improve the cell power density. It is a matter of new selective catalysts and more appropriate membranes with higher ion conductivities.

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БИООТХОДЫ И СУЛЬФИД ВОДОРОДА – ПЕРСПЕКТИВНОЕ ВОЗОБНОВЛЯЕМОЕ ТОПЛИВО

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Значительный рост экономики в глобальном масштабе в последнем столетии привел к интенсивному использованию ископаемых горючих материалов, таких, как уголь, нефть и природный газ. Результатом этого явились сильная эмиссия диоксида углерода и парниковый эффект с последующим изменением климата. Интенсивное потребление ископаемых горючих материалов, образовавшихся и хранящихся в недрах в течение миллионов лет, сделало невозможной настоящую вегетацию на земле с переработкой выделившегося диоксида углерода с помощью фотосинтеза. Одним из путей для того, чтобы справиться с этой глобальной проблемой, является замыкание углеродного цикла в природе с использованием возобновляемого топлива, позволяющего переработку источников биологического происхождения с производством энергии и поглощением образующегося углерода с помощью фотосинтеза. Другим перспективным источником энергии является сульфид водорода, аккумулированный в глубинных водах Черного моря. Он может быть конвертирован в электрическую энергию с помощью сульфид-содержащих топливных элементов. Генерированная энергия может быть непосредственно использована для генерации водорода с помощью электролиза, питаемого полученной электрической энергией. Настоящая работа демонстрирует все эти возможности, базирующиеся на наших экспериментальных данных и доступных научных результатах.

Ключевые слова: *сульфид водорода, диоксид углерода, возобновляемое топливо, биомасса, биогаз, этанол.*

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