

BIOGAS UPGRADING PROCESSES FOR THE PRODUCTION OF NATURAL GAS SUBSTITUTE

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Biogas from anaerobic digestion of biological wastes is a renewable energy resource. It has been used to provide heat, shaft power and electricity. Typical biogas contains 50-65% methane (CH₄), 30-45% carbon dioxide (CO₂), moisture and traces of hydrogen sulphide (H₂S). Presence of CO₂ and H₂S in biogas affects engine performance adversely. Reducing CO₂ and H₂S content will significantly improve quality of biogas. In this work, a method for biogas scrubbing and CH₄ enrichment is presented. Chemical adsorption of H₂S and chemical absorption of CO₂ by in a biomethane unit was experimentally investigated.

Key words: Biogas, CO₂ and H₂S reducing, CH₄ enrichment.

Poboljšanje procesa proizvodnje bioplina kao zamjenskog goriva za zemni plin. Bioplin iz anaerobne digestije biološkog otpada je obnovljivi izvor energije. Koristi se za dobivanje toplinske, mehaničke i električne energije. Tipični bioplin sadrži 50-65% metana (CH₄), 30-45% ugljičnog dioksida (CO₂), vlagu i u tragovima sumporovodik (H₂S). Prisutnost CO₂ i H₂S u bioplinu negativno utječe na karakteristike rada motora. Smanjenjem sadržaja CO₂ i H₂S značajno se poboljšava kvaliteta bioplina. U ovom radu opisana je metoda pročišćavanja bioplina i povećanja udjela CH₄. Eksperimentalno je ispitivana kemijska adsorpcija H₂S i kemijski apsorpcija CO₂ u biometanu.

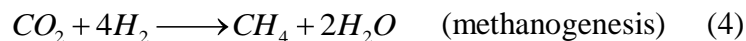
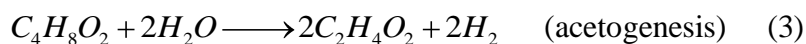
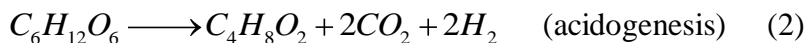
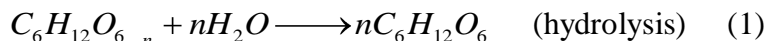
Ključne riječi: Bioplin, smanjenje udjela CO₂ i H₂S, povećanje udjela CH₄.

INTRODUCTION

Biogas is generated by microorganisms in the absence of air by a so called anaerobic metabolism. Industrial biogas is produced at sewage treatment plants (sludge fermentation stage), landfills, sites with industrial processing industry and at digestion plants for agricultural organic waste, both mesophilic (35 °C) and thermophilic (55 °C).

Biogas from anaerobic digestion and landfills consists primarily of CH₄ and CO₂. Trace components that are often present in biogas are water vapor, hydrogen sulphide, siloxanes, hydrocarbons, ammonia, oxygen, carbon monoxide and nitrogen.

The anaerobic digestion of organic material basically follows; hydrolysis, acidogenesis, acetogenesis and methanogenesis.



The research of biogas is a complex field of knowledge with high level of technology. It can be divided by practical aspect to two fields of research, namely research in the laboratory conditions and research in operative conditions.

The laboratory research is used for new technologies and device prototypes development, which are tested in operative

conditions and those devices are optimized for industrial operation.

In case, that the research of biogas production provided effective technologies, the present research of biogas technologies is dealing with raw biogas processing and upgrading as a energy resource for wide options of usage.

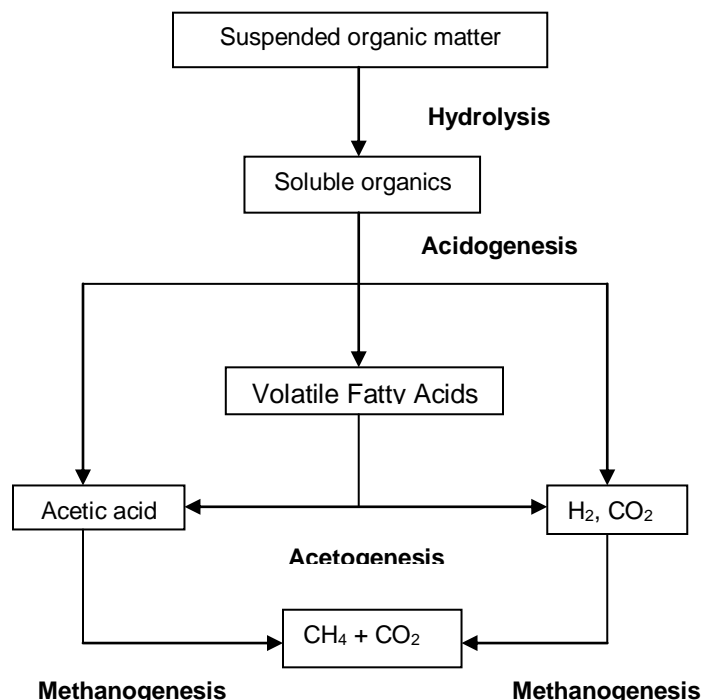


Figure 1. Subsequent steps in the anaerobic digestion process.

Slika 1. Pojedini koraci u procesu anaerobne digestije.

Currently the most common way of biogas processing in Slovakia is its combustion in cogeneration units and their direct distribution of electric power produced into the grid. However, thermal power which is produced by this process is often unused. Not every biogas station is located nearby industrial center with potential of sampling thermal power.

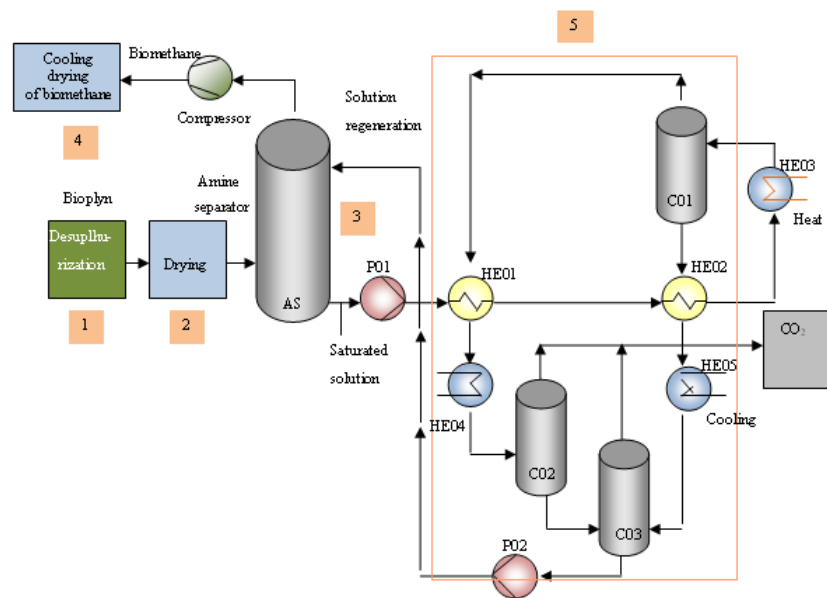
Biogas contains 50 per cent up to 60 per cent of methane, which is a major component of natural gas, and pipeline network represents ideal way of transporting refined biogas. Mentioned law defines the term biomethane as aligned biogas that has technical parameters compared with natural gas.

There exists several well-known, resp. developing ways for biogas modification:

- Pressure water absorption (DWW)
- Pressure swing absorption (PSA)
- Chemical adsorption (activated carbon)
- Chemical separation (MEA, DEA, MDEA)
- Physical absorption by special removers CO₂ and H₂S
- Segregation through polymer membranes
 - dry
 - wet
- Cryogenic segregation
- Procedural refinement

Peculiar attention in refinement of biogas is given to chemical segregation, which creates new ways in areas of science and research.

Description of technology



HE = Heat Exchanger, P = Pump, C = Column, AS = Amine Separation

Figure 2. The principal scheme of chemical purification of biogas.

Slika 2. Osnovna shema kemijskog pročišćavanja bioplina

Biogas purification at the level of natural gas quality (content of cca. 99 % CH₄) means the removal of humidity, H₂S,

NH₃ and CO₂. The rest of the components are of minority character and in the mixture of natural gas they are not problematic.

Desulphurization, chemical adsorption

Before entering the amine separator, it is necessary to remove the residual sulphureted hydrogen in raw biogas whatsoever. Biogas flows through the system of filters with activated carbon whose surface is adjusted. The system has an enormous capacity. The alternation of

sulphureted hydrogen to elementary sulphur leads to obstruction of sulphur in the system of filters.

The depleted filter is diffused on the fields together with fermentation substrate from the biogas station. The circulation of sulphur is closed.

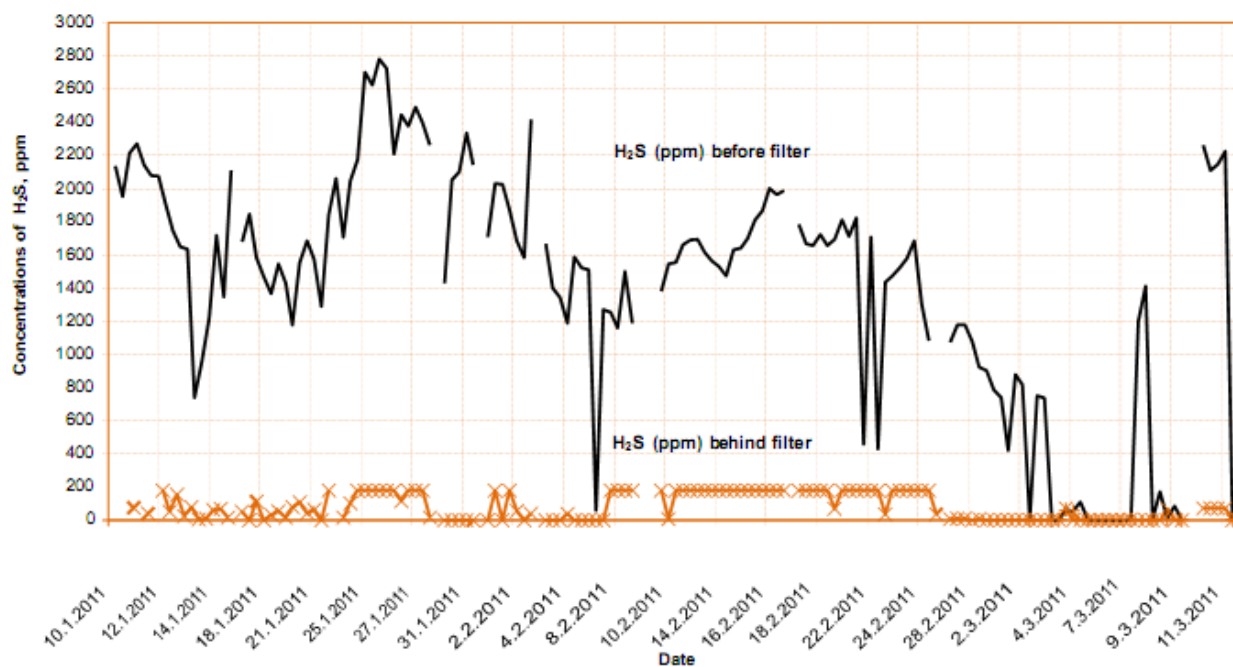
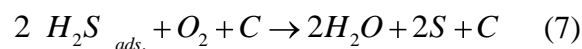
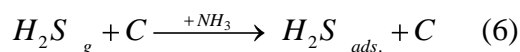


Figure 3. Graph of input and output concentrations of H₂S.

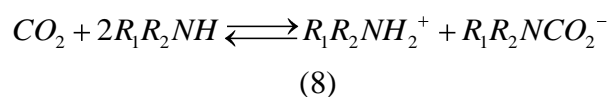
Slika 3. Grafički prikaz ulaznih i izlaznih koncentracija H₂S.

Drying

The raw biogas is saturated by aqueous vapors. The cooling and subsequent heating of biogas in the heat exchangers cause its drying. The biogas cooling leads to precipitation of water and the relative humidity is increased by the heating. Biogas is cooled by cooling aggregates in the heat exchangers and consequently the water separation is removed from the gas. The gas is again heated by a hot part of the cooled aggregate. The process of biogas drying guarantees that the next biogas purification out of CO₂ will not alter the concentration of amine - based solvent.

Non-pressure amine separator – Removal of CO₂

The biogas which is desulphurated and dried flows to the packed column from



where **R** represents the functional groups (for MEA, **R**₁ = -H, **R**₂ = -CHCH₂OH; for DEA, **R**₁ = **R**₂ = -CH₂CH₂OH). The Dankwerts' zwitterion mechanism has recently become one of the most widely accepted mechanisms for primary and secondary amine reaction with CO₂ (Blauwhoff et al., 1984; Versteeg and Van Swaaij, 1988; Versteeg et al., 1990; Versteeg and Oyevaar, 1989; Glasscock et al., 1991; Little et al., 1992).

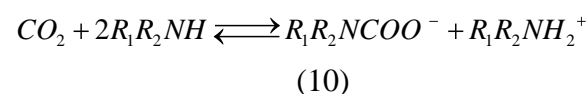
The reaction equilibrium constant K_{eq} is as follows:

$$K_{eq} = \frac{R_1R_2NCO_2 \left[R_1R_2NH_2^+ \right]}{CO \ R_1R_2NH^2} = \frac{k_1k_3}{k_2k_4} \quad (9)$$

the bottom. An aqueous solution flows from the top against the flow of the biogas. The packed column serves for an augmentation of an active surface, which will guarantee CO₂ reaction in the biogas with solution intensively. The combination of methane and solution does not react and it is diverted from the upper part of column with a high purity. The system provides a maximum content of CO₂ at the level of 0,1 % in a purified gas.

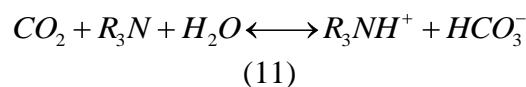
Theory

Several authors have investigated the chemistry of CO₂-amine solutions over the years due to its important industrial application for the removal of CO₂ from gas streams. The overall reaction between CO₂ and primary or secondary amines is:



$$K_{eq} = \frac{k_1k_3}{k_2k_4} \quad k_r = \frac{k_1}{K_{eq}}$$

MDEA being a tertiary amine has an extremely small value of k_1 , which is perhaps the reason for the lowest CO₂ permeance among the amines tested. The overall reaction can be represented by:



MDEA is considered to be a sterically hindered amine due to the presence of 3-bulky alkyl groups attached to the amino group as seen in Figure 4.

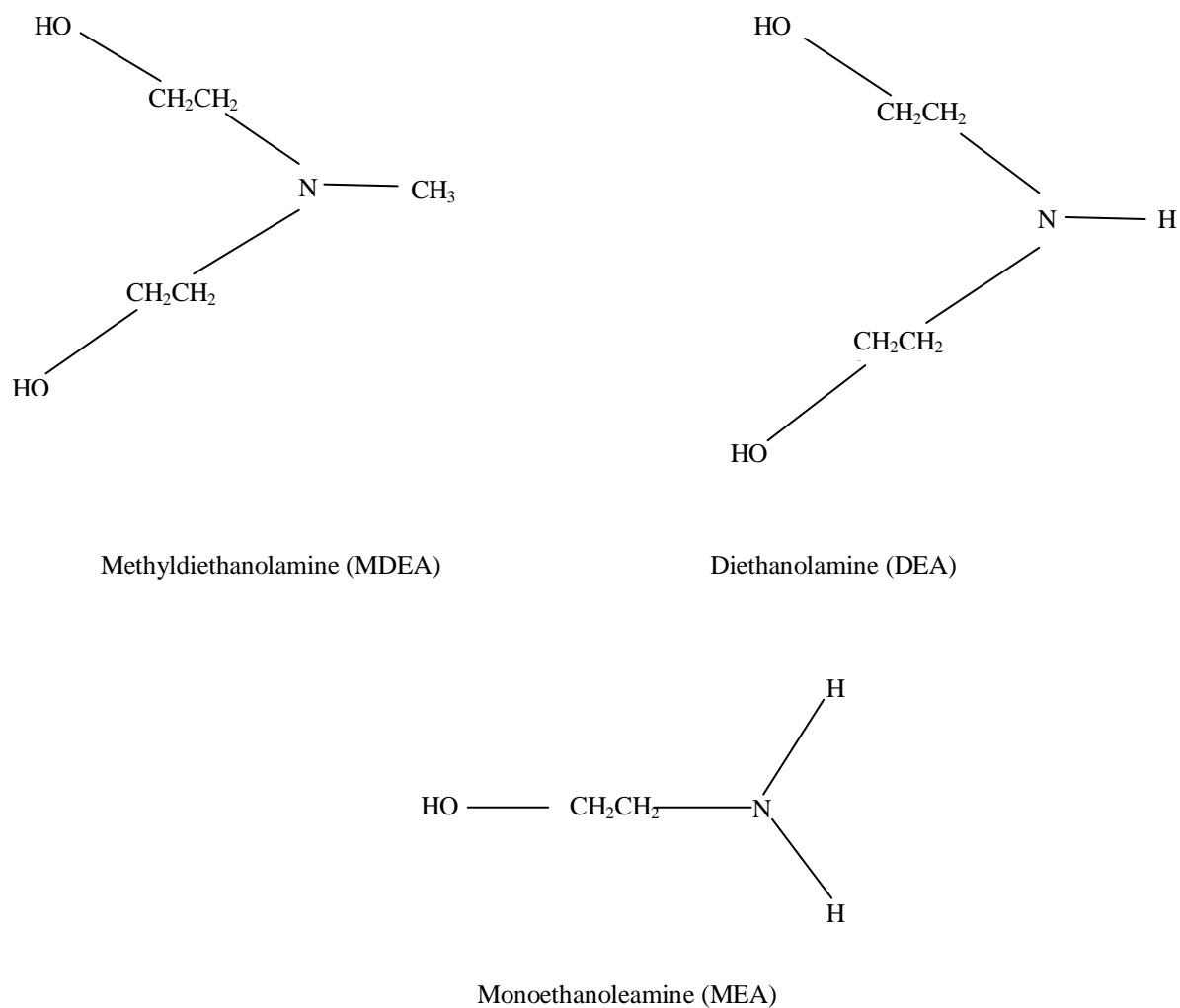


Figure 4. Molecular structures of different alkanolamines.

Slika 4. Molekularna struktura različitih alkanolamina.

Experiment

The first batch of simulated biogas purification experiments used 40% MDEA as the absorbent at a simulated biogas flow rate of 12.0 L/min. The amine working solution flow rate was 2.0 L/min using a 6.0 L recycle reservoir. As shown in Figure 5a,

carbon dioxide concentration decreased from 22% to 12% in the first 5 minutes. The pH of the solution dropped quickly from 11.67 to 10 in the first 5 minutes (Figure 5b). After the initial drop, pH slowly continued to descend from 10 to 9.1 over the next 35 minutes.

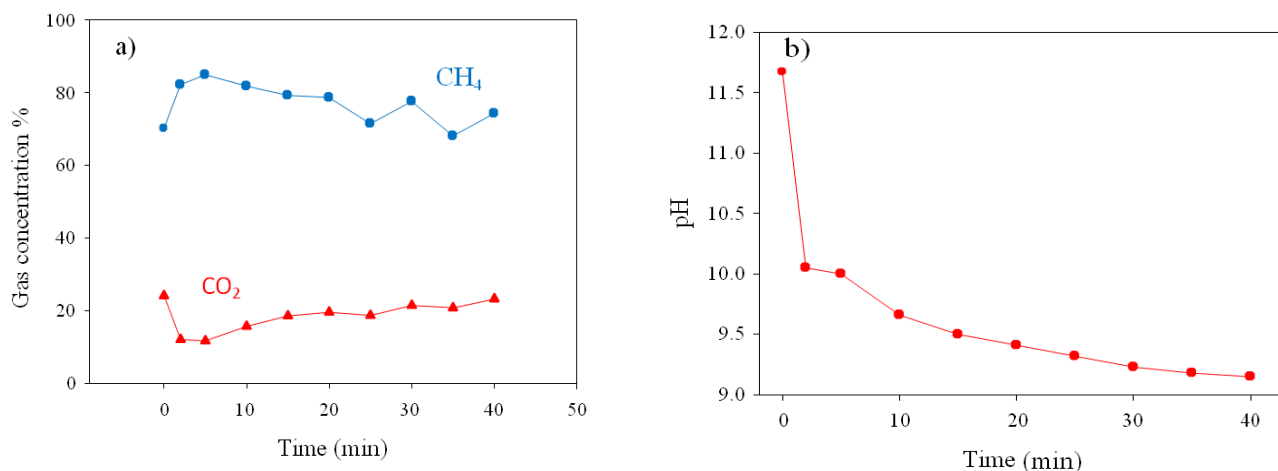


Figure 5. Biogas purification results with 40% MDEA.
Slika 5. Rezultati pročišćavanja bioplina s 40% MDEA.

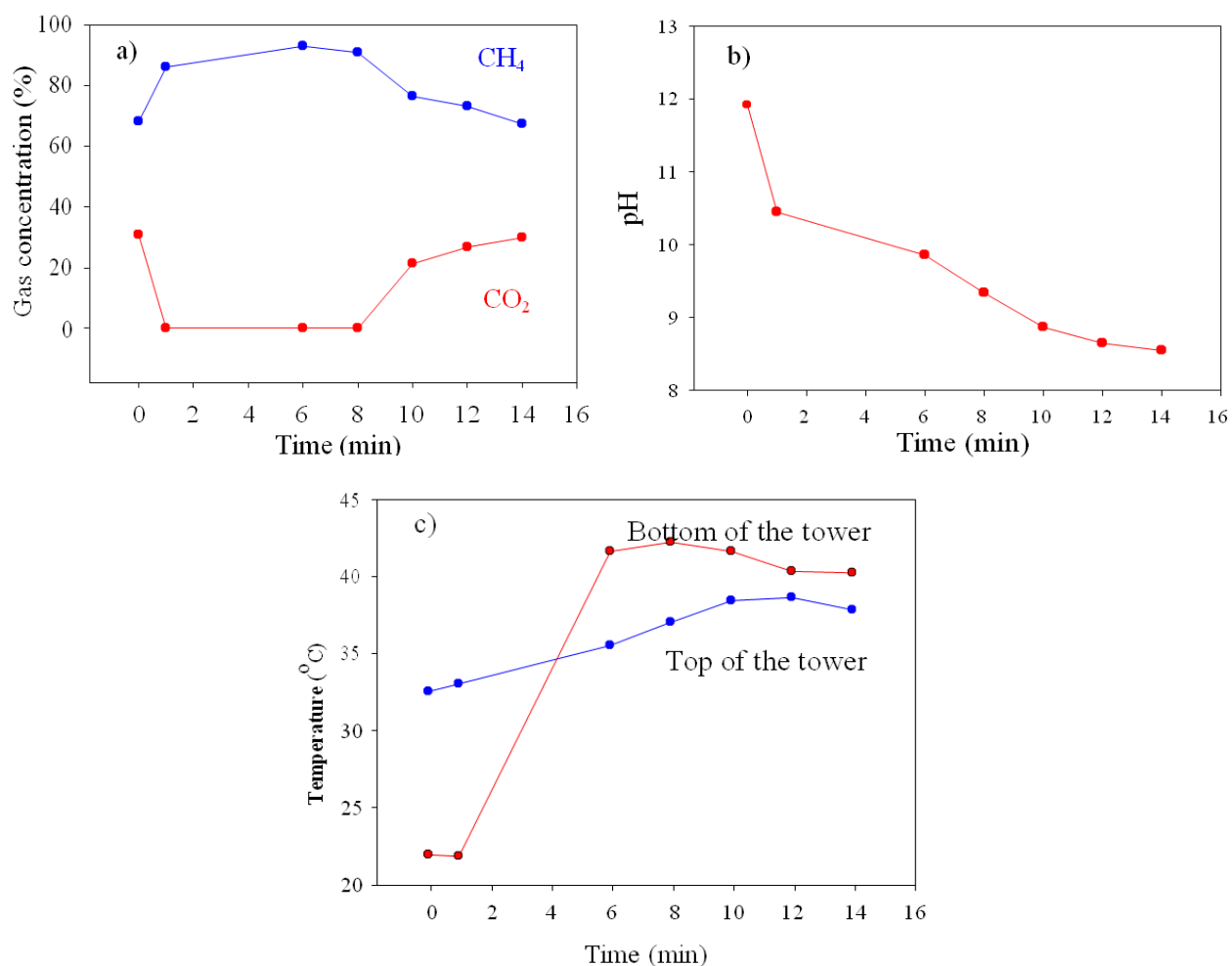


Figure 6. Biogas purification results with 10% MEA.
Slika 6. Rezultati pročišćavanja bioplina s 10% MEA.

The second batch of biogas purification experiments used 10% MEA solution as the absorbent (Figure 6). The simulated biogas flow rate and the amine working solution flow rates were 7.5 L/min and 1.6 L/min, respectively. The carbon dioxide concentration decreased from 32% to 0% in 1 minute. The carbon dioxide concentration remained at 0% for 7 minutes.

Results and discussion

As shown in Figure 6, MEA showed better carbon dioxide removal efficiency than MDEA. Using 10% MEA as an absorbent resulted in 100% carbon dioxide removal. By using 10% MEA, CO₂ was completely removed in 1 minute. 100% removal can only be achieved before the amine solution approaches carbon dioxide saturation, which takes about 7 minutes; after 7 minutes the pH falls to 9.5 and inhibits the reaction.

The experimental results demonstrate that of the various amine solutions and amine concentrations tested, successfully removing 100% of the CO₂. Further, results showed that pH can be an excellent indicator for amine saturation, thereby offering a technical approach towards optimizing reaction time and sequencing of absorption/desorption flows. Heat captured from the exothermic reaction could be used to reduce the heating costs required in the regeneration phase.

After 7 minutes the carbon dioxide concentration increased to 30%. The temperature of the absorbent increased from 21°C to 42°C (Figure 6c). The temperature of the simulated biogas increased from 32°C to 38°C. After 8 minutes the absorbent was nearly saturated with carbon dioxide, the reaction rate decreased, and the temperature of the solvent decreased.

Cooling and drying of biomethane

It is necessary to cool and dry a biomethane after separation repeatedly. The gas is led to the heat exchanger where an aqueous vapor and a vapor which contains amines condensates at the top of a cooler formerly as it is led back to the separation process. Condensed steam is led back to the column. Biomethane is transferred through the pipes to the unit of biomethane transport into the pipe network of natural gas. Biomethane is mixed with a natural gas in the pipe.

Solution regeneration

Amine-based solution which contains CO₂ is withdrawn from the bottom of the column. CO₂ is removed from the used solution by the heat in the process of regeneration. This step is totally sufficient for the subsequent needs of solution usage.

Advantages of utilization of chemical segregation for refined biogas:

- It occurs in normal pressure (economy of expenses)
- Purification occurs in separator
- Gas contains higher rates of purity than in conventional systems
- Oscillation of methane is minimized – high ecological and economical effectiveness
- Stable process of purification and constant quality of methane
- Comparatively low operational expenses

Table 1. System comparison of biogas modification on biomethane.**Tablica 1.** Sustav usporedbe modifikacije bioplina na biometan.

| Weight factor | Pressure water absorption (DWW – Druckwasserwa sche) | Physical selexol absorption | Chemical separation (MEA) | Pressure Swing Absorption (PSA) | Membrane separation |
|--|--|-----------------------------|---------------------------|---------------------------------|---------------------|
| CH ₄ enrichment | high+ | high+ | very high ++ | high + | high + |
| Concentration increase of O ₂ , N ₂ | yes - | yes - | yes - | no + | yes - |
| CH ₄ loss | medium +/- | medium +/- | very low ++ | medium +/- | medium +/- |
| Need of drying the gas | yes - | no + | yes - | no + | no + |
| Desulphurization before modification | no + | yes - | yes - | yes - | yes - |
| Processing of waste gas | yes - | no + | no + | no + | no + |
| Need of raw materials (el. current, water, heat, cooling water, chemicals) | medium +/- | high - | high - | medium +/- | very high - |
| Need of the power energy kWh.m ⁻³ | ~ 0,28 | ~ 0,30 | ~ 0,13 | ~ 0,24 | ~ 0,5 |
| Need of heat energy kWh.m ⁻³ | none | ~ 0,30 | ~ 0,50 | none | none |
| Emission (water, air, wastes) | medium +/- | low+ | low + | low + | low + |
| Initial costs | medium +/- | medium +/- | medium +/- | medium +/- | high - |
| Overall assessment | - 1 | 0 | - 1 | + 4 | - 3 |

CONCLUSIONS

Special attention is given to the Act No. 309/2009 Coll. in Slovak Republic by which biomethane producers would be able to require an issuance of confirmation from Regulatory Office for Network Industries (RONI) of biomethane origin, from the operator of gas system the confirmation about the quantity of supplied biomethane and would also have the rights to prefer the distribution of biomethane.

However, they would be obliged to take care of the fact that biomethane,

provided by them, would conform to parameters of natural gas and provide measuring of its quantity and quality. Quantity of biomethane would be re-counted according to the index specified by RONI that would depend on the portion of biomass used by biogas production which was grown on the soil.

Within an overall systems view, this research confirms a potentially viable and economically preferable mechanism for biogas upgrade, be it for fuel production or simply improved engine/generator performance.

Acknowledgement

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REFERENCES

1. M. Gerardi, *The microbiology of anaerobic digesters*, Wiley, New York, 2003.
2. E. Weidner, *Technologien und Kosten der Biogasaufbereitung und Einspeisung in das Erdgasnetz In Ergebnisse der Markterhebung 2007 – 2008*, Institut Umwelt-, Sicherheits-, Energietechnik, 2008.
3. S. Klinski, *Einspeisung von Biogas in das Erdgasnetz*. In: IE-Leipzig, Leipzig, 2006.
4. A. Makaruk, M. Miltner, M. Harasek, *Membrane biogas upgrading processes for the production of natural gas substitute, Separation and Purification Technology*, 2010, 83–92.
5. W. Kleinjan, *Biologically Produced Sulphur Particles and Polysulphide Ions Effects on a Biotechnological Process for the Removal of Hydrogen Sulphide from Gas Streams*, Ph.D. Thesis. Wageningen Universiteit, Wageningen, 2005.
6. P. M. M. Blauwhoff, G. F. Versteeg, W. P. M. van Swaaij, *A Study of the reaction between CO₂ and Alkanolamines in Aqueous Solutions*, *Chemical engineering science* 1984, 207-225.
7. P. V. Dankwerts, *The Reaction of CO₂ with Ethanolamines*, *Chem. Eng. Sci.* 34, 1979, 443-445.
8. G. F. Versteeg, W. P. M. van Swaaij, *On the Kinetics between CO₂ and Alkanolamines both in Aqueous and Non-aqueous Solutions*, *Chem. Eng. Sci.* 43, 1988, 573-585.
9. G. F. Versteeg, J. A. M. Kuipers, F. P. H. van Beckum, W. P. M. van Swaaij, *Mass Transfer with Complex Reversible Reactions-1. Parallel Reversible Chemical Reactions*, *Chem. Eng. Sci.* 45, 1990, 183-197.
10. D. A. Glasscock, J. E. Critchfield, R. T. Rochelle, *CO₂ Absorption/Desorption in Mixtures of Methyl-diethanolamine with Monoethanolamine or Diethanolamine*, *Chem. Eng. Sci.* 46, 1991, 2829-2845.
11. R. J. Littel, G. F. Versteeg, W. P. M. Van Swaaij, *Kinetics of CO₂ with Primary and Secondary Amines in Aqueous Solutions, Influence of Temperature on Zwitterion Formation and Deprotonation Rates*, *Chem, Eng. Sci.* 47, 1992, 2037-2045.
12. H. R. Godini, D. Mowla, *Selectivity study of H₂S and CO₂ absorption from gaseous mixtures by MEA in packed beds*, *Chemical Engineering Research & Design.* 2008, 401-409.