

Process Control of Biogas Purification Using Electronic Nose

Edyta Słupek, Patrycja Makoś, Dominik Dobrzyniewski, Bartosz Szulczyński, Jacek Gębicki*

Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Gabriela Narutowicza Street, 80-233 Gdańsk, Poland
jacek.gebicki@pg.edu.pl

Nowadays, biogas produced from landfills and wastewater treatment plants or lignocellulosic biomass is important sustainable and affordable source of energy. Impurities from biogas stream can cause a serious odor problem, especially for residents of areas immediately adjacent to production plants. Therefore, biogas pre-treatment is necessary to protect engines that convert biogas into energy and in order to increase the specific heat. Currently, there are many well-known methods of purifying biogas streams i.e. physical and chemical absorption, adsorption, membrane separation, cryogenic separation, pressure swing adsorption, advanced oxidation processes and biological separation. Among these technologies, methods based on the use of physical absorption show a high efficiency of the impurities removal from the gas phase using appropriately selected absorbents. In the presented study the purification of model biogas mixtures contaminated with cyclohexane, toluene, propionaldehyde, 1-butanol and dimethyl disulfide. Three absorbents were used in the research: hexadecane and two deep eutectic solvents: choline chloride with urea in 1:2 molar ratio and camphor with guaiaicol in 1:1 molar ratio. For process efficiency monitoring the electronic nose was used. The obtained results were compared with gas chromatography analysis.

1. Introduction

Currently, biogas is considered to be modern form of bioenergy, which an alternative to conventional energy carriers, i.e.: coal, crude oil or natural gas. Waste products from various industries and agriculture (agri-food and animal waste) are increasingly used for biogas production. This is consistent with the theory of sustainable development and “green” technologies. However, biogas produced from waste materials contains (apart from the basic ingredients i.e. CH_4 and CO_2), numerous compounds that can be classified as problematic impurities, i.e.: ammonia, hydrogen sulfide, organosulfur compounds, siloxanes, aromatic and aliphatic hydrocarbons, halogenated and other volatile organic compounds (VOCs) (Andres et al., 2019). These impurities can cause a serious odor problem, especially for residents of areas immediately adjacent to production plants as well as can have environmental impacts i.e. stratospheric ozone depletion, the greenhouse effect, and effect damage to power equipment. Therefore, biogas pre-treatment is necessary to protect engines that convert biogas into energy and in order to increase the specific heat. There are many technologies to remove impurities from biogas that differ in functioning. Biogas purification methods include physical and chemical absorption, adsorption, pressure swing adsorption, membrane separation, cryogenic separation, and biological separation (Sun et al., 2019; Allegue and Hinge, 2014). The absorption process (also known as scrubbing) consists of transferring contaminants from a gas phase to a liquid phase (absorbent). This technique can select the absorbent so that it meets the designated criteria i.e. high absorption capacity of impurity, high-boiling and low vapor pressure, low viscosity and a high diffusion coefficient, safety and no toxicity, and a low cost. In addition, the development of sustainable absorbents represents one of the main challenges of “green” chemistry (Abbott et al., 2003).

Until newly, the research has been focused on Ionic Liquids (ILs) as an absorption material due to their unique properties. Recently, Deep Eutectic Solvents (DESs) have been introduced as a green alternative to ILs, due to their environmental-friendly composition, simple synthesis, low cost, and biodegradability. The literature has reported stable DESs based on natural compounds, particularly primary metabolites, such as organic acids,

polyphenols, amino acids, terpenes, and sugars (Makoś et al, 2018). Liquid DESs are obtained by the complexation of a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD). The hydrogen bonding and electrostatic interactions are responsible for the decrease in the melting point of the mixture relative to the melting points of the raw materials. The physicochemical properties of the DESs (i.e.: viscosity, density, melting points or thermal stability) depend on the chemical nature of components and on their intermolecular interactions (Xin et al., 2017). Moreover, by appropriate selection of the components for the synthesis of DES it is possible to create a "perfect" absorbent which will allow selective removal impurities from a complex matrix i.e. biogas. Till now, DES have been successfully used to remove CO₂, H₂O, H₂S, NH₃ from biogas (Aissaoui et al., 2016). However, only a small number of works describe the use of DESs to removal of VOCs from biogas streams (Słupek et al., 2020).

In order to control the biogas purification process, mainly gas chromatography technique (GC) with selective and universal detectors is used. However, the use of GC in "off-line" or "in-line" mode results in a long delay in the results obtained, which prevents immediate correction of the fermentation broth composition, which does not allow improvement the efficiency of biogas production. Therefore, the "on-line" control system is necessary. This possibility is provided by the use of electronic noses.

Electronic noses, which are analogues of the sense of smell, allow them to be used in many fields of science and industry, such as: medical diagnostics, environmental protection, food and chemical industry or criminology. Electronic noses allow complete analysis of the gas mixture composition, without the need to separate and identify its individual components. Compared to other techniques used to analyze gas mixtures such as gas chromatography, electronic noses have additional advantages: shorter analysis time and lower price of the device. They enable independent operation in the on-line mode (Szulczyński et al., 2018).

The paper presents application of simple electronic nose for the control of odorous volatile organic compounds i.e. cyclohexane, 1-butanol, toluene, dimethyl disulphide and propionaldehyde removal from model biogas stream composed of methane and carbon dioxide. For biogas purification, hexadecane, ionic and non-ionic deep eutectic solvents composed of natural non-toxic components i.e. camphor, guaiacol, urea, choline chloride were used as new absorbents.

2. Experimental

2.1 Synthesis od DESs

DESs were synthesized by mixing two components choline chloride (ChCl) with urea (U) in 1:2 molar ratio and Camphor (C) with Guaiacol (Gu) in 1:1 molar ratio, at 70°C for 30 min using magnetic stirrer until homogeneous liquid were received. In the studies, reagents i.e. choline chloride (ChCl) (purity ≥ 99%), ±camphor (C) (purity ≥ 95%), urea (U) (purity ≥ 98%), guaiacol (purity ≥ 98%) (Sigma-Aldrich, USA) were used. The liquid DESs forms were obtained due to the formation of hydrogen bonds between -NH groups in U and chlorine anion in ChCl (Figure 1A) and between the -OH group in guaiacol and =O group in camphor (Figure 1B).

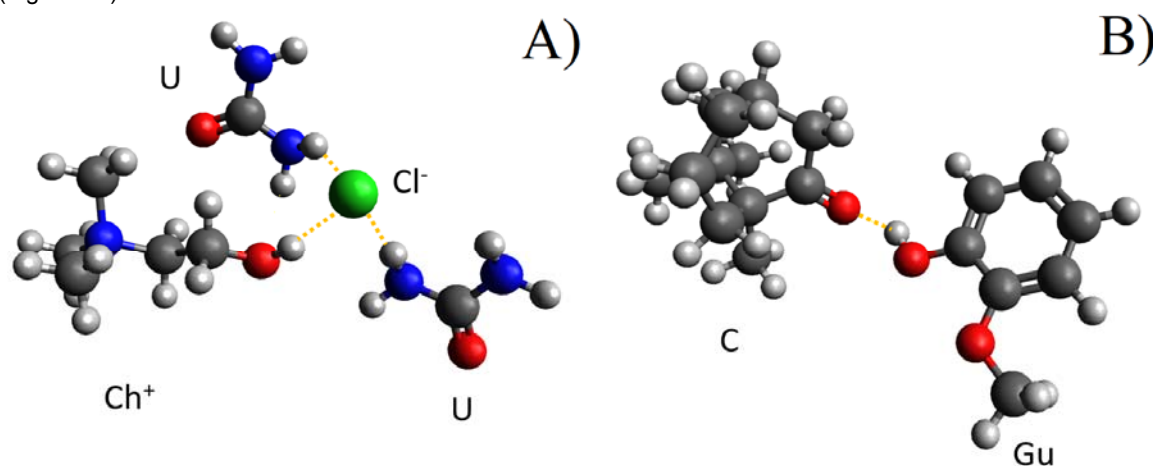


Figure 1: Molecular structures of DESs A) ChCl:U (1:2), and B) C:Gu (1:1)

2.2 Electronic nose development

In the presented study two models of chemical sensors were chosen for electronic nose application. They are commercially available metal oxide semiconductor sensors (MOS) manufactured by Figaro: TGS2600 and TGS2611. The selection of presented sensors models was caused by their high sensitivity values for volatile organic compounds, low cost, long life time and ease in signal processing.

The presented studies used qualitative analysis methods to assess the effectiveness of biogas deodorization. Points corresponding to relevant biogas samples projection onto a two-dimensional plane created by the values of the sensors used. The tests were carried out for pure biogas (methane and carbon dioxide mixture), as well as before and after the absorption process. This approach allows you to quickly analyze the performance of the biogas purification process.

2.3 Gas chromatography analysis

In order to be able to perform the analysis reliably, it was necessary to determine the exact concentrations of odorous substances in the biogas stream. For this purpose, gas chromatography combined with flame ionization detector (GC-FID) was used. In presented research Varian CP-3800 gas chromatograph was used equipped with DB-WAX column 30 m x 0.53 mm x 1 μm . The method parameters are presented in Table 1.

Table 1: Gas chromatography method parameters.

Parameter	Value
Carrier gas	Nitrogen
Column flow	1.5 $\text{cm}^3 \text{min}^{-1}$
Split ratio	1
Oven temperature	100°C (isothermal)
Sample volume	0.5 cm^3

The calibration for concentration determination of every odorous volatile organic compound were performed. An example chromatogram for a sample of contaminated biogas is shown in the Figure 2.

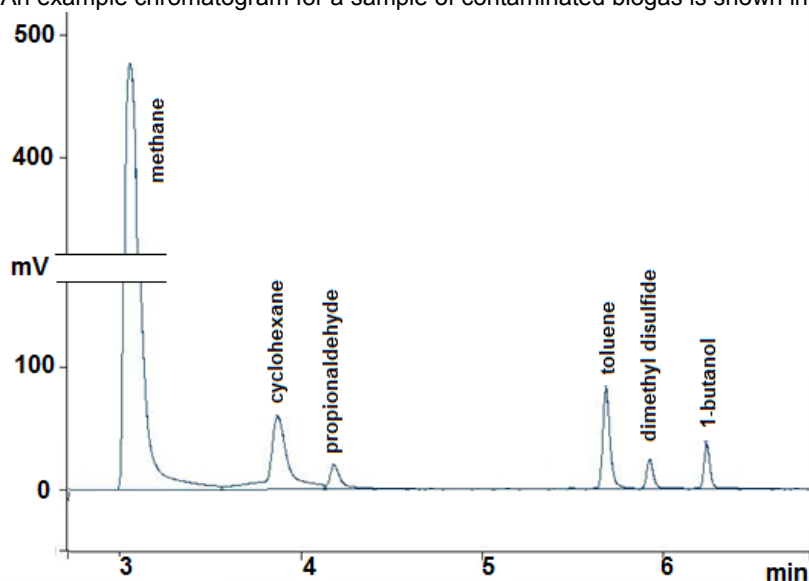


Figure 2: An example of chromatogram of impure biogas sample.

2.4 Experimental setup

The tests were carried out for three absorbents: hexadecane and two deep eutectic solvents: C:Gu (1:1), ChCl:U (1:2). The model impure biogas were prepared in Tedlar bags. the composition of the model gas was as follows: 75% methane and 25% carbon dioxide. The contaminants concentrations were equal to 16 ppm. The composition of the tested mixtures is presented in Table 2. The experimental setup is presented in Figure 3.

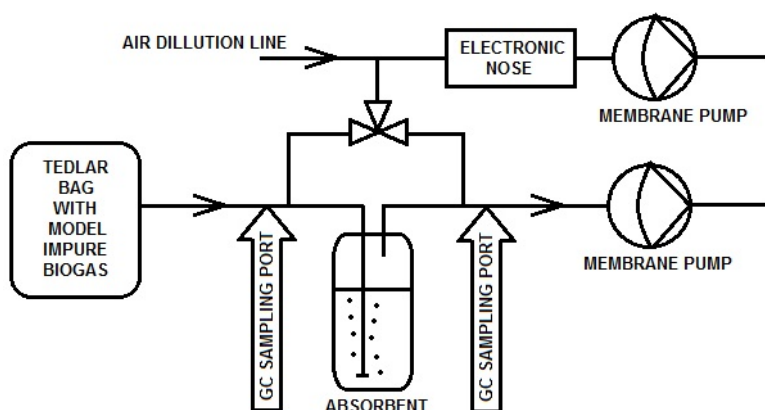


Figure 3: The schematic of the experimental setup.

The contaminated biogas flows through a vial filled with absorption liquid. At the inlet and outlet of the vial the gas samples were collected and analyzed using electronic nose and gas chromatography throughout the whole process. The recorded sensor signals were saved on the computer using the Simex SIAi-8 analog-to-digital converter. Analyzed sample was sucked by the pump and flowed through the e-nose system to the measurement chamber at a constant flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$. Due to high methane concentrations, the sample is diluted with air before entering the measuring chamber. The oxygen is necessary for the correct operation of sensors installed in the chamber. The electronic nose operated in stop-flow mode: the sample flow time through the chamber was 60 seconds, while the stop time was 30 seconds.

The sensors signal values recorded for a sample after absorption were transferred to the two-dimensional space. The purification efficiency (PE) were calculated using the formula:

$$PE_{e-nose} = \frac{a}{b} \cdot 100\% \quad (1)$$

Where: a – geometrical distance between point representing process sample and point representing impure biogas sample, b - geometrical distance between representing pure and impure biogas sample (Figure 4).

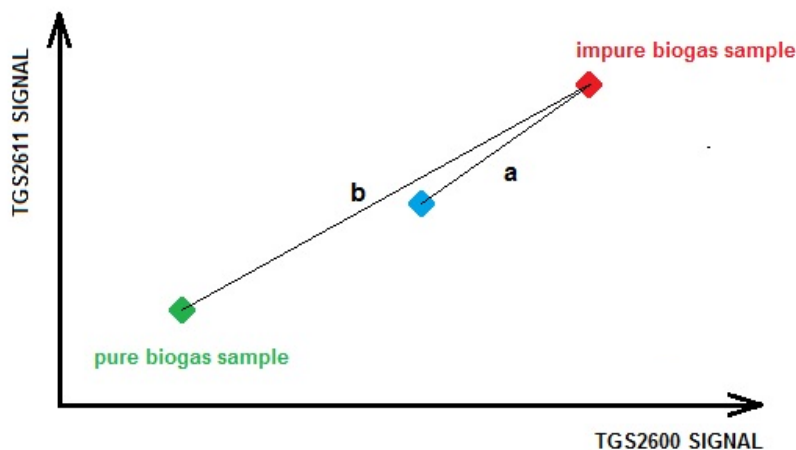


Figure 4: Purification efficiency determination using electronic nose (geometrical representation).

Every process sample were analyzed using gas chromatography. In this case, The purification efficiency were calculated using the formula:

$$PE_{GC} = \left(1 - \frac{\sum A_i}{\sum A_i^0}\right) \cdot 100\% \quad (2)$$

where: $\sum A_i$ – the sum of peaks area determined for all compounds in the process sample, $\sum A_i^0$ - the sum of peaks area determined for all compounds in the impure biogas sample.



3. Results and discussion

Model impure biogas mixtures composition and purification efficiency of its absorption process (using electronic nose and gas chromatography) in three absorbents is presented in the Table 2. Graphical representation of purification efficiency determined using electronic nose for three absorbents is presented in Figure 5.

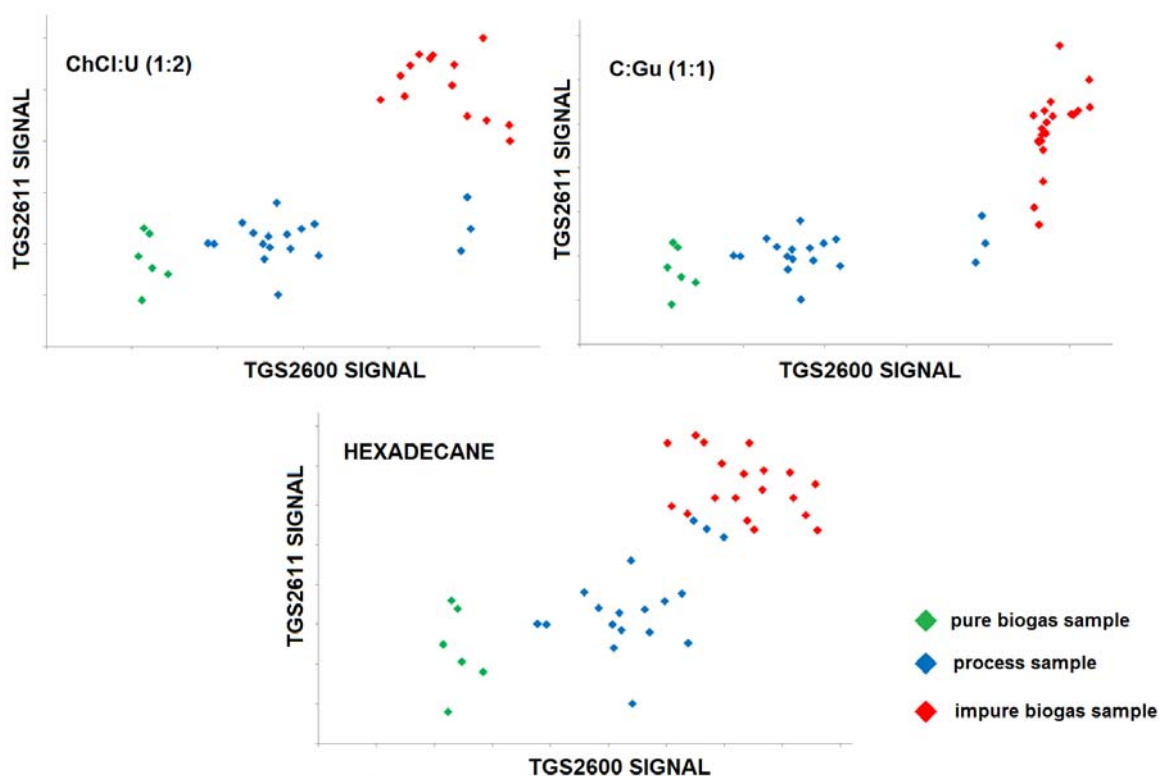


Figure 5: Results of purification efficiency determination using electronic nose (graphical representation).

Table 2: Tested mixtures composition and their purification efficiency in absorption process.

Mixture number	Concentration in the mixture [ppm]					hexadecane		C:Gu (1:1)		ChCl:U (1:2)	
	cyclohexane	DMDS	toluene	1-butanol	propionaldehyde	PE _{enose}	PE _{GC}	PE _{enose}	PE _{GC}	PE _{enose}	PE _{GC}
1	16	0	0	0	0	43.3	42.4	66.9	67.6	58.0	55.1
2	16	0	0	0	0	40.8	44.0	64.7	58.9	55.3	53.6
3	16	0	0	0	0	27.4	29.6	56.6	48.7	44.9	40.4
4	0	16	0	0	0	25.1	49.1	43.4	65.4	26.3	58.3
5	0	16	0	0	0	27.9	47.9	39.2	69.9	30.9	60.3
6	0	16	0	0	0	25.9	44.5	37.5	57.3	28.8	51.7
7	0	0	16	0	0	71.7	65.2	83.3	72.5	78.8	74.1
8	0	0	16	0	0	74.6	67.8	85.0	89.3	81.0	72.9
9	0	0	16	0	0	60.0	61.8	76.2	75.5	69.9	68.5
10	0	0	0	16	0	39.0	33.9	63.8	61.9	54.1	52.4
11	0	0	0	16	0	35.0	33.3	61.0	69.6	50.6	56.7
12	0	0	0	16	0	30.2	29.3	57.8	51.4	46.5	41.8
13	0	0	0	0	16	50.6	51.6	70.8	70.1	63.0	66.8
14	0	0	0	0	16	50.0	44.5	70.6	77.6	62.6	55.7
15	0	0	0	0	16	48.6	52.0	69.6	68.2	61.4	52.2
16	16	16	16	16	16	20.5	20.1	29.1	31.4	5.3	4.9
17	16	16	16	16	16	19.5	20.1	25.8	26.1	8.8	8.1
18	16	16	16	16	16	18.3	20.4	21.9	24.2	7.9	8.8

Analyzing the obtained results the value of the purification efficiency determined by means of electronic nose and gas chromatography should note that the results obtained from the electronic nose do not differ significantly from the values determined by the reference method (gas chromatography). Only for dimethyl disulfide, the electronic nose significantly deviates from the reference values. This is due to the very low sensitivity values for dimethyl disulfide of both sensors used for this substance. For this reason, the disulfide signals are much lower and the PE estimation error is higher. Presented results show that deep eutectic solvent - Camphor (C) with Guaiacol (Gu) in 1:1 molar ratio has the highest values of purification efficiency for purification model biogas of single volatile organic compounds and their mixture.

4. Conclusions

The research presents application of simple electronic nose for the process performance control of odorous volatile organic compounds i.e. cyclohexane, 1-butanol, toluene, dimethyl disulfide and propionaldehyde removal from model biogas stream composed of methane and carbon dioxide. The results obtained using an electronic nose are slightly different from the results obtained using gas chromatography. This shows that electronic noses can be successfully use to monitor the biogas purification process by absorption. They are significantly cheaper than chromatographs, they enable much shorter time of single analysis and easy possibility of automation. As part of the research, the usefulness of deep eutectic solvents (DES) as a green alternative to ionic liquids for biogas purification, due to their environmental-friendly composition, simple synthesis, low cost, and biodegradability has also been demonstrated. The study shows that the deep eutectic solvent consisting of Camphor (C) with Guaiacol (Gu) in 1:1 molar ratio proved to be the best choice for biogas purification from cyclohexane, dimethyl disulfide, 1-butanol, propionaldehyde and toluene.

Acknowledgments

The investigations were financially supported by the Grant "Determination of the mechanism of improved biofiltration efficiency of air contaminated with hydrophobic compound vapors as a result of the addition of hydrophilic compound vapors" No. UMO-2019/35/N/ST8/04314 from the National Science Centre (Poland).

References

- Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V., 2003, Novel Solvent Properties of Choline Chloride/Urea Mixtures, *Chemical Communications*, 0, 70–71.
- Allegue L.B., Hinge J., 2014, Biogas upgrading Evaluation of methods for H₂S removal, Danish Technological Institute, 31.
- Andrés C., Guardia A., Couvert A., Wolbert D., Le S., Soutrel I., Nunes G., 2019, Odor concentration (OC) prediction based on odor activity values (OAVs) during composting of solid wastes and digestates, *Atmospheric Environment*, 201, 1–12.
- Aissaoui T., AlNashef I.M., Benguerba Y., 2016, Dehydration of natural gas using choline chloride based deep eutectic solvents: COSMO-RS prediction, *Journal of Natural Gas Science and Engineering*, 30, 571–577.
- Makoś P., Przyjazny A., Boczkaj G., 2018, Hydrophobic deep eutectic solvents as "green" extraction media for polycyclic aromatic hydrocarbons in aqueous samples, *Journal of Chromatography A*, 1570.
- Słupek E., Makoś P., Gębicki J., 2020, Deodorization of model biogas by means of novel non- ionic deep eutectic solvent. *Archives of Environmental Protection*, 46, 41–46.
- Sun Q., Li H., Yan J., Liu L., Yu Z., Yu X., 2015, Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation, *Renewable and Sustainable Energy Reviews*, 51, 521–532.
- Szulczyński B., Namieśnik J., Gębicki J., 2018, Analysis of Odour Interactions in Model Gas Mixtures using Electronic Nose and Fuzzy Logic, *Chemical Engineering Transactions*, 68, 259-264.
- Xin R., Qi S., Zeng C., Khan F.I., Yang B., Wang Y., 2017, A functional natural deep eutectic solvent based on trehalose: Structural and physicochemical properties, *Food Chemistry*, 217, 560–567.