Process control of biogas purification using electronic nose and gas chromatography

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ABSTRACT

Nowadays, biogas produced from landfills and wastewater treatment plants or lignocellulosic biomas 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. 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 guaiacol in 1:1 molar ratio. For process efficiency monitoring the electronic nose was used. The obtained results were compared with gas chromatography analysis.

Synthesis of DESs

DESs wre 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.

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 gruop in camphor (Figure 1B).

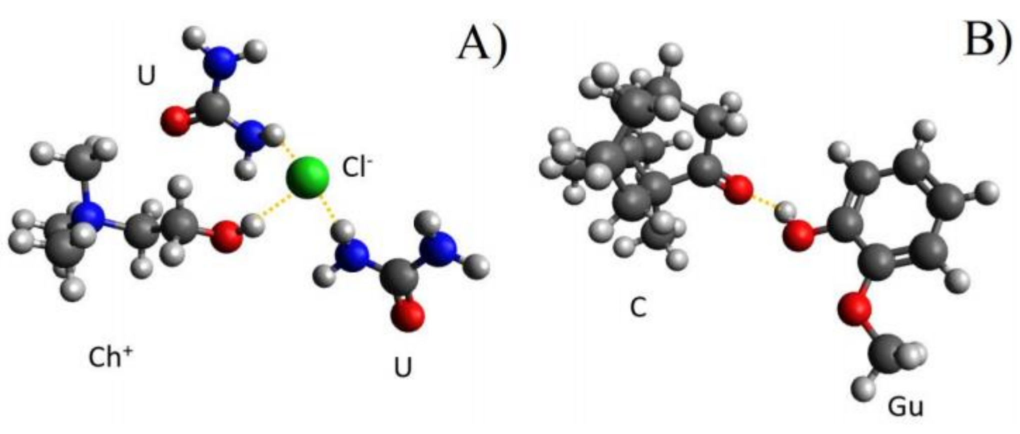

Fig 1. Molecular structures of DESs A) ChCl (1:2), and B) C:Gu (1:1)

Electronic nose development

Two models of chemical sensors were chosen for electronic nose application. They are commercialy 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

Fig 2. MOS type sensor)

Gas chromatography analysis

In order 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 presened research Varian CP-3800 gas chromatograph was used equipped with DB-WAX column 30 mx0.53 mm x 1 µm.

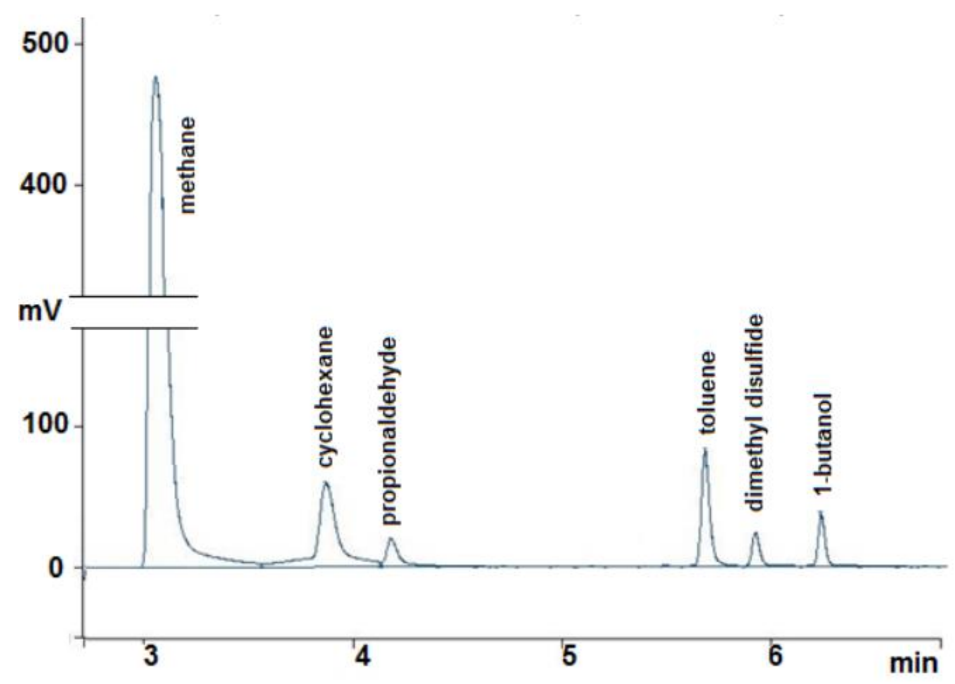

Figure 3. An example of chromatogram of impure biogas sample

Experimantal setup

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.

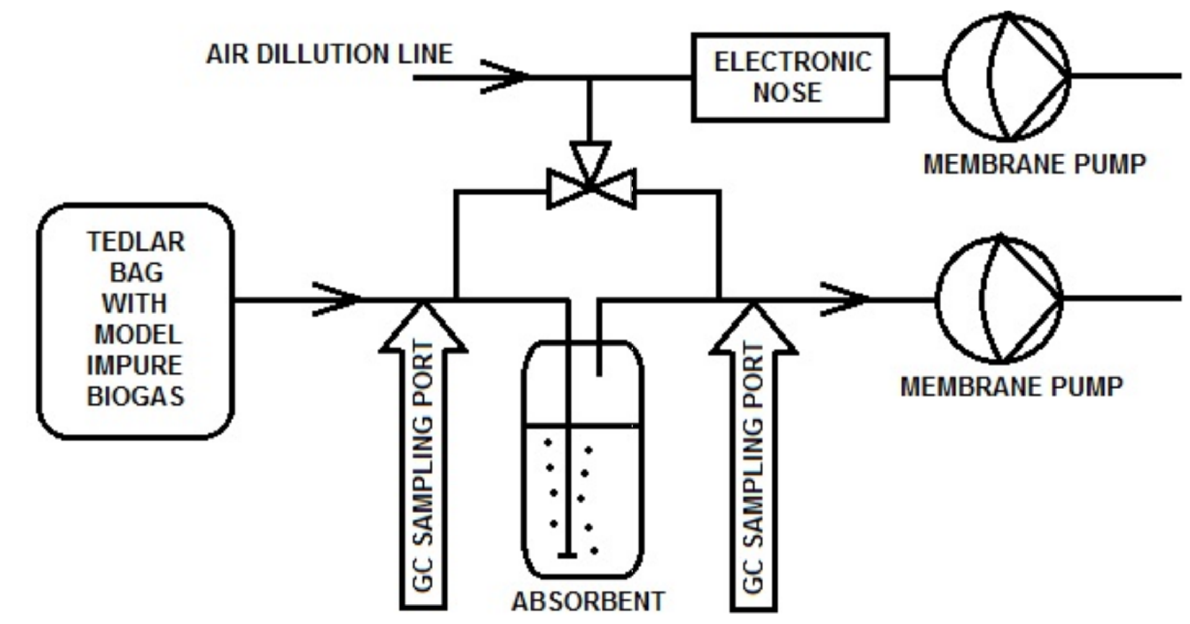

Figure 4. The schematic of experimental setup

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

$$PE_{e-nose} = \frac{a}{b} \cdot 100\%$$

where: a – gemetrical distance between point representing process sample and point representing impure biogas sample, b – geometrical distance between point representing pure and impure biogas sample

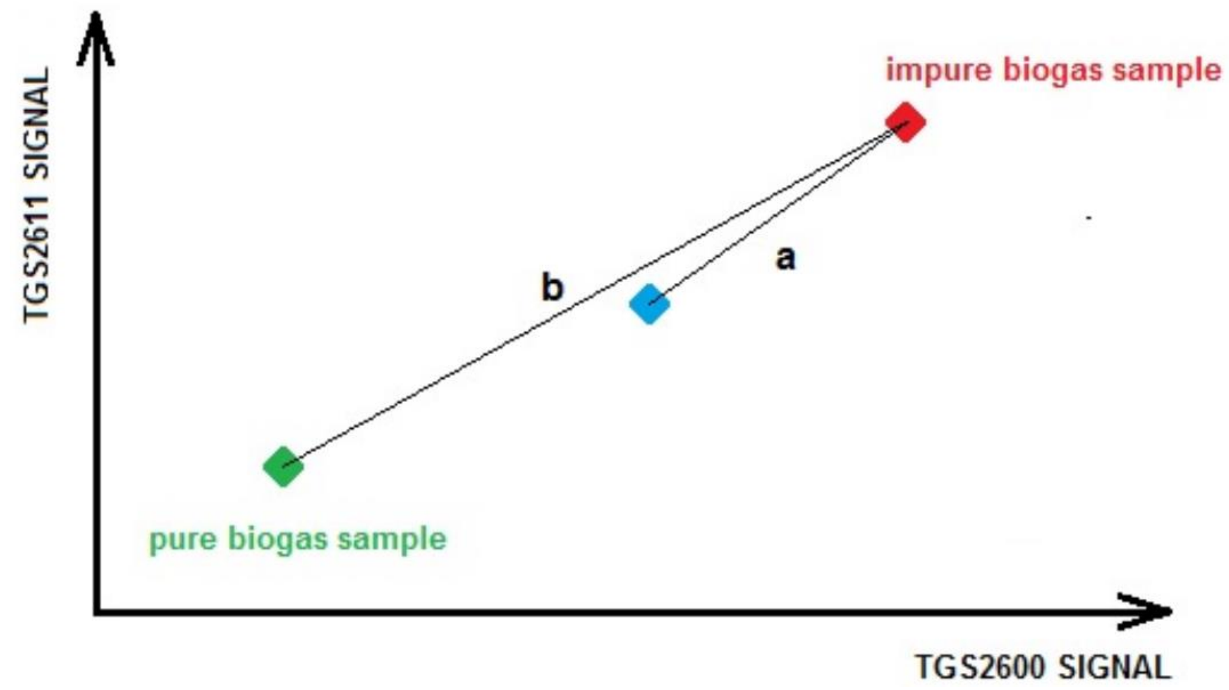

Figure 5. Purification efficiency determination using electronic nose (geometrical representation)

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

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

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

RESULTS

Graphical representation of purification efficiency determined using electronic nose for three absorbents is presented in Figure 6. The composition of the tested mixtures and the obtained results of purification efficiency are presented in the table.

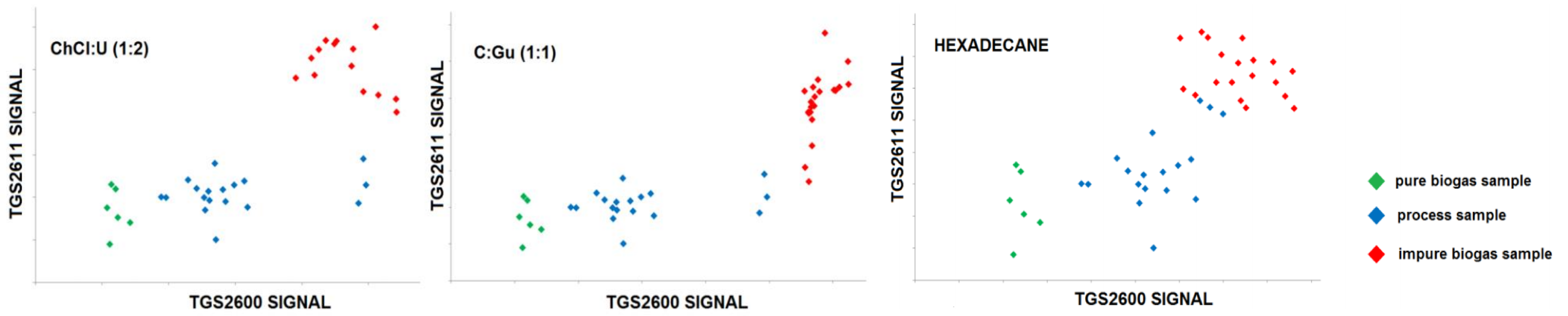

Figure 6. Results of purification efficiency determination using electronic nose (geometrical representation)

Mixture number	Concentration in the mixture [ppm] cyclohexane	DMDS	toluene	1-butanol	propionaldehyde	hexadecane PE_{enose}	hexadecane PE_{GC}	C:Gu (1:1) PE_{enose}	C:Gu (1:1) PE_{GC}	ChCl:U (1:2) PE_{enose}	ChCl:U (1:2) 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

SUMMARY

The results obtained using an electronic nose are slightly different from the results obtained using gas chromatography. This shows that electronic nose can be successfully use to monitor the biogas purification process by absorption. Only for dimethyl disulfide, the e-nose significantly deviates from the reference values. This is due to the very low sensitivity values for dimethyl disulfide of both sensors. Electronic nose are significantly cheaper than chromatographs, they enable much shorter time of single analysis and easy possibility of automation. As a part of a research, the usefulness of deep eutectic solvents (DES) as a green alternative to ionic liquids for biogas purification has also been demonstrated.