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Possibilities of anaerobic treatment of crude glycerol from biodiesel production

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Abstract

Work was focused on possibilities of biogas production from a crude glycerol. This material is by-product of biodiesel production. In the work results of crude glycerol treatment in the laboratory mixed reactor and in the laboratory UASB reactors are described. Results from long-term co-digestion of maize silage and crude glycerol in full scale anaerobic reactor at biogas plant are also discussed. From this work resulted that the operation of mesophillic anaerobic degradation of crude glycerol as the only organic substrate is feasible; the process operation is very sensible to organic over-loading of reactor. The laboratory anaerobic mixed reactor achieved stable operation at the organic loading rate of 4 kg/m$^3$.d (COD) with ca 980 ml of biogas production per ml of dosed glycerol. The laboratory UASB reactor inoculated with granular sludge achieved stable operation at the organic loading rate of 6.5 kg/m$^3$.d with ca 840 ml of biogas production per ml of dosed glycerol. Inoculation of the UASB reactor with suspended biomass showed that this type sludge is not suitable for this purpose because of sludge flotation during reactor operation. Long term processing of crude glycerol in the full scale biogas plant for anaerobic treatment of maize silage showed that crude glycerol is suitable co-substrate. Evaluated specific production of biogas from crude glycerol was about 0.89 m$^3$ per 1 kg of crude glycerol added. Dose of crude glycerol which represents only 5.2 % of overall dose to biogas plant produces almost 15 % of overall biogas production. Use of this co-substrate has significant influence on positive economical balance of biogas plant.

Key words: anaerobic digestion, biogas plant, crude glycerol, UASB reactor

1. Introduction

The biodiesel is an ecological alternative of the fuel based on methyl esters of long chain fatty acids (LFCAs) designated for diesel vehicles. The biodiesel is produced by the process of trans-esterification of vegetable oils, animal fats [1, 2], or often from wastes fats [3]. In Slovak Republic is the biodiesel most frequently produced from the rape seed oil with a base catalyst and a methanol [4]. Production of the biodiesel rapidly increases in the world and also in the SR. The EU has defined a program of replacement of 5.75 % from the consumption of the liquid fuels with biofuels to 2010.

In process of the biodiesel production is formed a heavier separate liquid phase, so called glycerol phase (g-phase). The portion of the g-phase represents approximately 16 – 18 % of the weight of the input of the oil/fat and its composition is not stabilized. It is influenced by several factors, especially by the acidity number of the input oil. It contains 50 – 60 % of the glycerol, 12 – 16 % of the alkalies especially in the form of alkali soaps and hydroxides, 15 - 18 % of methyl esters, 8 – 12 % of the methanol, 2 –3 % of the water and further components. After treatment of the g-phase with strong mineral acids the crude glycerol with the glycerol content of 78 – 82 % is obtained [5].
Annual production of the oil is approximately 2.4 mil. tons in Slovnaft refinery and replacement of 5.75 % by biodiesel fuel represents need for about 140 000 tons of the biodiesel. This amount of the biodiesel forms a production of 20 000 tons of the g-phase which do not has more wide use on our market. The same situation is in foreign countries. The crude glycerol is used in a pharmaceutics, a cosmetic and in a food industry. Requirement for these uses represents only a small part of the g-phase production. One of possibilities of its use is the anaerobic treatment. During an anaerobic digestion is produced biogas, which can be used for a production of energy. There is not sufficient information about the anaerobic treatment of the g-phase in the literature. Information about the anaerobic degradation of pure glycerol was found only. Part of this information refers to a glycerol as an intermediate product of anaerobic degradation of fats [6, 7]. Lipids are hydrolysed to glycerol and free LCFAs as the first step in anaerobic conditions. The glycerol is converted by acidogenesis to acetate, while the LCFAs are converted to acetate (or propionate in the case of odd-number carbon LCFAs) and hydrogen through the β-oxidation pathway (syntrophic acetogenesis) [8]. An anaerobic degradation of glycerol as direct substrate was described in several works. Result of the anaerobic production was other product as a biogas in these works. (e.g. 1,3-propanediol). Furthermore, there were a pure cultures of microorganisms used. [9, 10, 11, 12, 13]. Similar information about the anaerobic degradation of the g-phase by pure culture of microorganisms is described in the literature. Most frequent product of this degradation is 1,3-propanediol [14,15, and 16]. Anaerobic treatment of crude glycerol from biodiesel production is described in the work of Yazdani and Gonzalez [17]. Interesting energy content (16.3 MJ/kg [18]) in the g-phase gives an assumption of high biogas production. This paper deals with the anaerobic treatment g-phase in order to produce biogas. The suitable use of glycerol as a source for anaerobic treatment confirms a work [19], where glycerol as degradation products of milk fats was studied. General physiological activity of anaerobic microorganisms measured as ATP concentration increased under anaerobic degradation of glycerol to two times compared to initial ATP concentration. The initial ATP concentration in the biomass was $4.2 \times 10^{-8}$ mol/l. Feeding with glycerol increased the level of ATP to $10.3 \times 10^{-8}$ mol/l while feeding with milk fat and oleic acid reduced the ATP level to $2-3 \times 10^{-8}$ mol/l.

A positive effect of glycerol as a co-fermentation substrate is supported by Amon et al. [20]. A 6% supplementation of glycerol to pig manure and maize silage resulted in a significant increase in CH₄ production from 569 to 679 litre CH₄/kg VSS.

In the work [21] was studied the improvement of the anaerobic treatment of potato processing wastewater in the UAS reactor by co-digestion with glycerol. In this work were for co-digestion used three types of glycerol tested – pure glycerol, crude glycerol and high conductivity glycerol. Specific production of biogas from crude glycerol was $770 \text{m}^3/\text{m}^3$.

From results of this work [21] concluded that glycerol is a feasible and economically interesting co-substrate to enhance anaerobic treatment of industrial wastewater.

Fountoulakis and Manios [22] studied possibilities of anaerobic co-digestion of crude glycerol from biodiesel production with organic fraction of municipal solid wastes and with mixture of olive mill wastewater and slaughterhouse wastewater. The supplementation of the feed with crude glycerol (1 % v/v) had a significant positive effect on biogas production. Crude glycerol, an easily storable residue of the biodiesel industry, is a feasible co-substrate to enhance methane production from domestic and industrial wastes.

This paper informs about our results on anaerobic digestion of crude glycerol from biodiesel production in laboratory and full-scale condition. Laboratory results were obtained from long-term operation of mixed reactor with suspended anaerobic biomass, UASB reactor with suspended resp. granulated biomass where crude glycerol as a single substrate was used. Use of crude glycerol as co-substrate at maize silage anaerobic treatment was studied in the laboratory and also in the full-scale condition.
2. Treatment of crude glycerol in the mixed laboratory anaerobic reactor with suspended sludge

Crude glycerol as an anaerobic substrate
Tests of anaerobic long-term degradation in the laboratory scale model were realised with the use of raw g-phase from the Slovak biodiesel producer. The average values of the primary characteristics of this material are shown in the Table 1.

Table 1 Selected characteristics of crude glycerol in the laboratory models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD</th>
<th>BOD₅</th>
<th>Total N</th>
<th>Total P</th>
<th>DIS</th>
<th>density</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured values</td>
<td>1 600 000</td>
<td>912 000</td>
<td>2 060</td>
<td>720</td>
<td>21 300</td>
<td>1052</td>
<td>10,4</td>
</tr>
<tr>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>kg/m³</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As it is evident from the Table 1 the very high organic content (COD, BOD₅) represents very good conditions for efficient biogas production. The ratio rate of BOD₅: COD has a value of 0.57 which is very favourable for anaerobic conditions. From this value the very good anaerobic degradation of g-phase can be expected. On the basis of the rate it can be expected that concentrations of nutrients N and P are not sufficient in the tested g-phase and it will be probably necessary to add them to anaerobic process. On the other hand the very high content of DIS and relatively high pH-value are parameters that can affect anaerobic process.

Reactor configuration and operation
Laboratory anaerobic scale model with effective volume of 4 litres was situated in the room with the stable temperature of 37 °C; therefore it worked under mesophilic conditions. Crude glycerol was once a day dosed into the anaerobic reactor through the filler hole. The content of reactor was sporadically (more times per day) stirred. The produced biogas was lead through the bubbler filled with water that served as indicator of biogas production. The amount of produced biogas was measured by wet laboratory gas meter. Long-term investigation of the g-phase treatment was realised in the laboratory scale model with the scheme shown in Figure 1.

Figure 1 Scheme of the laboratory scale model of anaerobic treatment of crude glycerol.
During the experiment, basic technological parameters in reactor – temperature, pH, COD, sludge concentration (SS), organic portion of sludge (VSS), volatile fatty acids (VFA), \( \text{NH}_4^- \), \( \text{PO}_4^{3-} \), dissolved inorganic salts (DIS) and production of biogas and its composition were regularly monitored.

**Start-up of the anaerobic laboratory reactor**
The anaerobic reactor was filled with two litres of anaerobic digested sludge from municipal WWTP Bratislava. The sludge concentration was 20.6 g/l; organic portion in sludge was 49.6 \%. Tap water was added to the reactor to reach 4-litre volume. The sludge concentration during the start-time of the reactor was 10.3 g/l. The long term operation of the laboratory model consisted of daily dosing of crude glycerol into the reactor and monitoring the biogas production and sludge and sludge water quality in the reactor.

**Long term operation of the anaerobic laboratory reactor**
The initial dose of g-phase was 4 ml per day which represents hydraulic load of reactor 1.0 ml/l.d. The range of doses during the long-term operation varied between 1 ml/l.d and 5 ml/l.d and was controlled depending on technological reactor conditions (concentration on VFA, COD, actually biogas production, etc.). The course of crude glycerol doses during the reactor operation is described in Figure 2. Volumetric loads correspond to the g-phase dosing and represent values from 1.6 kg/m\(^3\).d up to maximal value of 8.0 kg/m\(^3\).d.

![Crude glycerol dosing course during long-term anaerobic operation of reactor](#)

The biogas production corresponds to individual doses of crude glycerol, or with individual volume loadings respectively, and is illustrated in Figure 3. As it is evident from Figure 3, the biogas production increased with increasing crude glycerol dose into anaerobic reactor. The average daily biogas production during the start-up of process was 2.75 l/d for crude glycerol dose of 1 ml/l.d and after 69 days of operation for dose of 3.5 ml/l.d was the average production about 12.3 l/d. The specific biogas production per 1 ml of dose increased from 688 ml/ml during the start-up period up to 880 ml/ml for dose of 3.5 ml/l.d.
Increased amounts of specific biogas production can be explained by gradual adaptation of the anaerobic biomass to the given substrate and improved homogenization of the reactor content caused by increased biogas production. The biogas production was equivalent to the amount of 3.1 m$^3$ per 1 m$^3$ of the reactor at organic loading rate of 5.6 kg/m$^3$.d (COD). Till the 70th day of operation the anaerobic reactor had very good parameters from the point of view of biogas production as well as other monitored parameters. The development of COD concentrations (average 560 mg/l), VFA (average 156 mg/l) and pH (average 7.1) ranged in standard values and didn’t show any problem. On the other hand, the increase of crude glycerol dose during the first three months of operation was relatively high (see Figure 2). First of all the adaptation time between dose changes was short and increase of dose between 2.0 and 3.5-5.0 ml/l was very rapid. That was probably the main reason for the total failure of anaerobic reactor after the 70th operation day.

The increase of dose to the value of 5.0 ml/l resulted into sharp decrease of biogas production (see Figure 3) simultaneously followed by sudden increase of COD and VFA concentration (see Figure 4). As shown in Figures 4 the rapid increase of COD (as for 5500 mg/l), VFA concentration (as for 1720 mg/l) lead to inhibition of methanogenic processes in reactor. The values of pH decreased to the value of 6.0. Neither pH regulated by NaHCO$_3$ to the value of 7 improved the situation. The anaerobic reactor negotiated the shocked change nearly three weeks. During the first four weeks after failure the lowest substrate doses (1 ml/l) were added into the reactor. The COD concentration gradually decreased below 1000 mg/l, as VFA concentration (Figure 4).

At the dose of crude glycerol 3.5 ml per litre of the reactor the COD concentration increased above 2000 mg/l, the VFA concentration also increased and biogas production decreased. After 6-day interruption of crude glycerol dosing the volumetric load reached the value of 4 kg/m$^3$.d and this value of the volumetric load was remained. The reactor showed stable operation with specific biogas production of 979 ml per 1 ml of crude glycerol during 65 days at this organic load value.
The average specific biogas production during the whole anaerobic reactor operation was 906 ml per 1 ml of crude glycerol. After calculation to standard conditions (temperature 0 °C, atmospheric pressure 101 325 Pa) the specific biogas production was 798 Nm$^3$ per 1 m$^3$ of g-phase. The average values of the biogas composition during the long-term operation of reactor ranged in the standard values: methane (61.1%), carbon dioxide (38.6%), hydrogen and hydrogen sulphide were not present.

![Figure 4 COD and VFA concentration during long-term operation of reactor](image)

Figure 4 COD and VFA concentration during long-term operation of reactor

### 3. Treatment of crude glycerol in the UASB reactor

**Reactor configuration and operation**

Crude glycerol was processed in laboratory UASB reactors with volume 3.7 litres (Figure 5), which contained suspended or granulated biomass. The reactor operated at temperature in mesophilic range (37°C). In this case the same glycerol as in mixed reactor was used (Table 1). Low doses of crude glycerol could not generate enough hydraulic load. Therefore, recirculation was installed in the laboratory model. For external recirculation of the output from UASB reactor was installed a tank with active volume 300 ml, to which the substrate was dosed one to three-times a day. At maximum dose of 15 ml the Glycerol was twenty-times diluted. Hydraulic retention time of recirculation flow in the UASB reactor was 24 hrs (suspended sludge) and 8 hrs (granulated sludge), respectively.

For inoculation of first UASB reactor was used sludge from municipal WWTP of Devinska Nova Ves (70.83 g of sludge, volatile suspended solids – VSS, 54 %). For inoculation of the second UASB reactor was used mixture of anaerobic granulated sludges from IC reactor for wastewater treatment of stillage from ethanol production form corn and from paper mill. The total amount of granulated sludge was 181.45 g.

During the experiment, basic technological parameters in reactor – temperature, pH, COD, sludge concentration (SS), organic portion of sludge (VSS), volatile fatty acids (VFA), NH$_4$-N, PO$_4$-P, dissolved inorganic salts (DIS) and production of biogas and its composition were regularly monitored.
During start-up of UASB reactor with suspended biomass the amount of Glycerol was 3 ml, which corresponds to organic loading rate 1.297 kg/m³.d (COD). Gradual increasing of the dose is shown on the Figure 6, the same as cumulative production of biogas. The increase of biogas production was in proportion to the higher dosage. Even if there were not any problems during the operation of the reactor on the monitored parameters (COD, VFA concentration), the sludge had in some periods a tendency to flotate. Grease like parts of crude glycerol was sorbed on flocs of suspended sludge and was coming to surface. In case of the flotation, recirculation was interrupted and sludge was mechanically mixed.

Figure 5 Scheme of the laboratory UASB reactor for anaerobic treatment of crude glycerol

Figure 6 Crude glycerol dosing and cumulative production of biogas in UASB reactor with suspended biomass
Highest organic loading rate during operation of the UASB reactor with suspended biomass was 4.32 kg/m$^3$.d (COD) at dose of crude glycerol 10 ml. After increasing of glycerol dose to 10 ml (70th day of the reactor operation) concentration of COD rise to 2940 mg/l (before dose increasing it was to 1500 mg/l) and concentration of VFA was 860 mg/l. In this period strong flotation of sludge was observed and mixing of sludge didn’t support of sludge return to sludge bed. Because of systematic flotation of the suspended sludge, operation of the UASB reactor was interrupted.

During operation of UASB reactor with suspended sludge 494 ml of crude glycerol was processed and 358 l of biogas was produced. Average specific production of biogas was 0.725 l per 1 ml of glycerol. Despite of this fact we state that inoculation of UASB reactor with suspended sludge is not very suitable for processing of the crude glycerol, because of sludge flotation.

**Operation of UASB reactor with granulated biomass**

For prevention of sludge flotation, granulated sludge was used for inoculation of the second UASB reactor for crude glycerol processing.

Dosing of crude glycerol started at value 3 ml/d and gradually increased (Figure 7). Maximum dose was 15 ml/d. From dose 6 ml/d was dosing divided to two portions, at dose over 10 m/d to three portions during working time.

![Figure 7 Crude glycerol dosing and cumulative production of biogas in UASB reactor with granulated biomass](image)

Maximum organic loading rate was 6.486 kg/m$^3$.d. At this loading concentration of COD increased to 2560 mg/l and concentration of VFA to 585 mg/l, but operation of UASB reactor and biogas production was stable. Specific production of biogas increased with ascending dose of glycerol. Higher dose of glycerol means higher production of biogas, better mixing of the sludge bed in the UASB reactor and better contact the substrate with anaerobic microorganisms. Maximum specific production of biogas was at glycerol dose 15 ml/d – 0.840 l per 1 ml of crude glycerol.
4. Treatment of crude glycerol in the full scale biogas plant

Crude glycerol was treated in biogas plant which as the main substrate used maize silage. This biogas plant has been described in the work [23]. The technology of maize silage anaerobic treatment is obvious from Figure 8. Effective volume of a full scale anaerobic reactor was 2450 m$^3$. The reactor was mixed by two propeller mixers with horizontal axis of rotation. Fresh silage was dosed by a chain transporter into the reactor. Silage pits were situated close to the biogas station. Average moisture content of silage used for the biogas station start-up was about 75 %. Reactor was operated at 37 °C. Expected production of biogas was about 4200 m$^3$/d. Biogas was burnt in the cogeneration unit with electrical power output 276 kW and heat power output 479 kW. For the optimum operation of the cogeneration unit it is necessary to reach the biogas production about 170-180 m$^3$. Gasholder volume 80 m$^3$ was sufficient because production of biogas was stable. Biogas can be burnt also in biogas boiler with heat power output 470 kW. The boiler played its main role at the starting time of the reactor operation, when the reactor was heated by natural gas burning. On the other hand, the boiler can be used in the situations when cogeneration unit operation is interrupted or if excess biogas is produced.

For various technical reasons, are processed in biogas plants also other substrates. One of the main reasons is the stability of pH. Already shortly after the start-up of biogas plant has been observed a decrease of pH values, because maize silage as a single substrate has not sufficient buffer capacity. Therefore, they were dosed to the reactor substrates to increase of the alkalinity. Among them was stabilized sludge from wastewater treatment plant for the brewery in Hurbanovo, meat and bone meal or molasses stillage from ethanol production. Another reason for the dosage of other substrates has been the lack of maize silage.

Figure 8 Scheme of the biogas station in Hurbanovo

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For this reason, were used as substrates, corn residues from drying grain corn, mixture of oats and peas whether recently crude glycerol from biodiesel production. Course dosage of each substrate during operation biogas plants is shown in Figure 9. The Figure 10 indicated the production of biogas. Unstability of the biogas production was connected with already mentioned the lack of buffer capacity of maize silage and subsequent use of other substrates. The reasons for unstable operation were described in detail in work [24].

![Figure 9 Dosing of different substrates at biogas plant](image)

In accordance with the objective of this work, we will only deal with the most recent operation biogas plants of about 300 days, when the co-substrate of the maize silage processing was crude glycerol from biodiesel production. Selected characteristics of the crude glycerol are shown in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>COD</th>
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<th>DIS</th>
<th>density</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured values</td>
<td>1 870 000 mg/l</td>
<td>1 085 000 mg/l</td>
<td>1 690 mg/l</td>
<td>192 mg/l</td>
<td>5 150 mg/l</td>
<td>1080 kg/m³</td>
<td>9,03</td>
</tr>
</tbody>
</table>

To assess the specific biogas production from crude glycerol and its contribution to total production of biogas, we selected stable operation of biogas plants in the last 141 days, when it was in the anaerobic reactor dosing only maize silage and crude glycerol. In this period the average daily production of biogas was 4091.4 m³. The daily dose of silage dry matter was 5280.4 kg (used silage dry matter was 42.47 %) and daily dose of crude glycerol was 683.7 kg. To determine the specific biogas production from crude glycerol, we had needed to know the specific biogas production from maize silage. We used the value...
which was given in the work of Kalina [24] – 0.66 m$^3$ per 1 kg of silage dry matter. Using this value was calculated the average daily amount of biogas from maize silage for the observed period 3485 m$^3$ and the average daily amount of biogas from crude glycerol 606.4 m$^3$. Calculated specific biogas production per 1 kilogram of crude glycerol was 0.887 m$^3$. This value corresponded with values measured in laboratory conditions in a reactor with mixed suspended biomass and UASB reactor with granular biomass.

![Figure 10 Course of biogas production at biogas plant](image)

Portion of biogas from crude glycerol represents 14.82 % of total production, while the portion of the total dry matter added is 11.46 % and portion of the total weight of dosed raw materials only 5.21%.

At the electrical power output of cogeneration unit 300 kW is the daily share of electricity produced from crude glycerol 1067 kWh.

At the current price of 4.42 Sk per 1 kWh, this represents a daily profit of 4716, - Sk (156.55 €) and a saving of almost 15 % silage (1865 kg at a price around 60 € for 1 tonne).

5. CONCLUSIONS

On the basis of long-term operation of the laboratory scale model of anaerobic treatment of crude glycerol the following conclusions can be stated:
- The operation of mesophillic anaerobic degradation of crude glycerol as the only organic substrate is feasible; the process operation is very sensible to organic over-loading of reactor (extremely high COD); and process operation requires addition of small amounts of nutrients;
Crude glycerol represents the material with high content of organic substances that can be easily decomposed with the very high specific biogas production. The laboratory anaerobic mixed reactor achieved stable operation at the organic loading rate of 4 kg/m$^3$.d (COD) with ca 980 ml of biogas production per ml of dosed glycerol. The laboratory UASB reactor inoculated with granular sludge achieved stable operation at the organic loading rate of 6.5 kg/m$^3$.d with ca 840 ml of biogas production per ml of dosed glycerol.

Inoculation of the UASB reactor with suspended biomass showed that this type sludge is not suitable for this purpose because of sludge flotation during reactor operation. Long term processing of crude glycerol in the full scale biogas plant for anaerobic treatment of maize silage showed that crude glycerol is suitable co-substrate. Evaluated specific production of biogas from crude glycerol was about 0.89 m$^3$ per 1 kg of crude glycerol added. Dose of crude glycerol which represents only 5.2 % of overall dose to biogas plant produces almost 15 % of overall biogas production. Use of this co-substrate has significant influence on positive economical balance of biogas plant.

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