

## Biogas generation potential of starch- and polylactide-based biodegradable plastics

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### Summary

Plastic materials decompose with an extremely slow rate and many decades are required for their complete degradation. Lately, commercial plastics have been partially replaced by biodegradable additives. Polylactic acid (PLA) and starch-based biopolymers are indicative alternatives employed to replace a 50-100 % of the mass of conventional plastic materials. In this work, a conventional and two different biodegradable commercial bags were subjected to single-stage mesophilic anaerobic digestion for 100 days to investigate their degradation performance and examine their biogas and methane production potential. LDPE-based plastic (LDPE-50) decomposed only negligibly producing  $0.0785 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$  of methane after 100 days of digestion whereas PLA-based bioplastic (PLAS-31) showed a better degradation performance ( $0.1782 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ). A methane production of  $0.1941 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$  was attained from a second type of PLA-based biodegradable bag (PLAS-13) indicating that bioplastics under specific anaerobic digestion conditions could provide a significant amount of biogas. The degradable organic material in bioplastics was the principal factor defining their conversion to biogas and methane. Anaerobic digestion had a minimal impact on the surface of LDPE-50, while the most significant modification of surface was seen for PLAS-13 where clean polymeric structures emerged after digestion due to a removal of a significant fraction of organics. PLAS-31 showed a great potential to further degrade even after the end of the 100 days of anaerobic digestion.

**Key words:** anaerobic digestion, BMP tests, bioplastics, LDPE, polylactic acid, biodegradation

### Introduction

Nowadays, the generated global amount of wastes continuously rises, and therefore it is more than imperative to implement measures that will mitigate the waste volume<sup>1</sup>. Bioplastics is a wide family of bio-decomposable materials that could assist towards this direction. Bioplastics can be divided into three classes depending on the origin and the biodegradability characteristics: (i) biodegradable with bio-origin, (ii) biodegradable with fossil-origin and (iii) non-biodegradable with bio-origin<sup>2</sup>. Polylactic acid (PLA), starch, cellulose pulp, polyhydroxyalkanoates (PHAs) are examples of biopolymers that have been used for the production of bioplastics, such as bags, dishes, straws, etc<sup>3</sup>. Several countries e.g. Italy established legislation according to which aerobic and anaerobic biological plants are obliged to accept and treat degradable bioplastics<sup>4</sup>. Although currently biodegradable plastics hold a relatively limited share in plastics market they have attracted a considerable attention for substituting conventional plastic materials<sup>5</sup>. A lot of different bioplastics have been formulated, some of which degrade fast presenting a short life-cycle which makes them acceptable for the environment<sup>1</sup>.

Because of the great interest for biodegradable plastics a number of standard methods have been established to evaluate their composition and set the conditions for their use. For instance, European standard EN 13432<sup>6</sup> defines the criteria that must be fulfilled and a bioplastic be used as a packaging material. Standard method 14995 specifies the properties of a biodegradable bag, i.e. (i) decompose by 90 %wt. under carbon dioxide atmosphere within a period of 6 months, (ii) a 90 %wt. of bag must decay

to a particle size less than 2 mm after a period of 3 months when the material is mixed with other organics, (iii) the material should not impede a composting process, and (iv) heavy metals contained in the final compost must fall within specific standard limits<sup>7</sup>. According to another standard method (EN 14046) the biodegradability of a material is determined in composting trial conducted under controlled temperature and humidity conditions for a period of 45 days. The final products of the process must be composed of CO<sub>2</sub>, H<sub>2</sub>O, mineral salts and a newly formed biomass with minimal environmental risk<sup>3</sup>.

Biodegradability depends on a number of factors with crystallinity being a primary one<sup>5</sup>. Theoretically, the amorphous parts are more easily degradable than the crystalline areas. The ordered structure of crystalline regions impedes intrusion of microorganisms. In contrast, a loose packed structure in amorphous parts makes the specific regions more flexible and easily accessible to microorganisms<sup>8</sup>. Chemical structure is another factor influencing the biodegradation of bioplastics. In principle, biodegradation is performed with a concurrent contribution of biotic and abiotic factors. Generally, abiotic factors such as temperature, water and sunlight lead to an initial scission of chemical bonds in the polymer producing shorter oligomers that can pass through the cell walls of microorganisms. Degradation of short units is then completed by biotic agents such as aerobic or anaerobic microorganisms<sup>2</sup>.

Currently, there is a substantial interest in the anaerobic digestion of bioplastics, although there are contrasting opinions about the degradation potential of those materials. According to an opinion, PLA-based bioplastics are characterized by a high degradation ability at anaerobic conditions whereas starch-based plastics by a moderate one<sup>8</sup>. Contrary to that, Battista et al.<sup>9</sup> who studied the methane generation capability of the same two bioplastic types reported that both materials remained almost unaffected by the anaerobic treatment even after 250 days, whereas methane yields were significantly low ranging between 0.1-0.2 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>. In another study, PLA-based bioplastics showed a very small decomposition while starch-based bioplastics an extremely high one approaching an 86 % of conversion even only after 23 days of anaerobic processing when they were co-digested with food waste in a thermophilic reactor<sup>10</sup>. Therefore, although degradation of bioplastics was examined in a number of studies there are great uncertainties about the degradability of the materials under anaerobic conditions especially for long digestion periods.

In the current work, a conventional plastic and two different biodegradable bags were subjected to mesophilic anaerobic digestion in long-term BMP tests. The aim was to examine the degradation of the materials designed to replace the conventional fossil-produced plastics and investigate their potential to produce biogas and methane. Another target was to compare the degradation of plastic bags composed of different biodegradable substances and identify any differences in their conversion over long treatment periods. The investigations were extended to the evaluation of the effect that anaerobic digestion had on the surface structure of the bioplastics.

## Experimental part

### *Substrates and inoculum*

Inoculum was a digestate obtained from the first stage of a mesophilic (40 °C) biogas plant (BPS Klokočov, Moravian-Silesian Region). Unit's feedstock composed of a mixture of beef slurry, straw, manure, grass, distillery waste, and small amounts of processed waste from paper industry. Digestate was homogenized under constant temperature (30 °C), shredded in a screw mill (2 mm openings) and used without any further treatment or filtration. Physicochemical parameters of inoculum and substrates are listed in Table 1.

Three types of bags were used as substrates for anaerobic tests. A first (referred to as LDPE-50) was a mixture containing low-density polyethylene (LDPE) and characterized by a thickness of 50 µm. A second (referred to as PLAS-31) and third (referred to as PLAS-13) were delivered with the indication that were prepared from polylactic acid with starch filling at different ratios. The thickness of PLAS-31 and PLAS-13 were measured at 31 and 13 µm, respectively. An IKA Tube Mill Control knife mill equipped with a disposable plastic head was used to reduce the size of samples in order to avoid any potential effect of the materials thickness on their anaerobic degradation. The milling process was

carried out cryogenically (liquid nitrogen to avoid potential melting of materials. Before the tests all samples were sieved and a powder with particles diameter lower than 1 mm was obtained. The three bags in powder form are shown in Figure 1.



**Figure 1 Milled and sieved biodegradable (a) LDPE-50, (b) PLAS-31, (c) PLAS-13**

### **Biochemical methane potential (BMP) tests**

The biogas and methane production potential of substrates were determined in mesophilic BMP tests. The tests were conducted in glass-bottle bioreactors (volume 1 L) equipped with glass-burettes acting as the gas collectors allowing the measurement of the generated biogas volume. The experiments were performed by following the ČSN EN ISO 11734<sup>11</sup> and VDI 4630<sup>12</sup> standard methods. An amount of 800 g of inoculum and 10 g of substrate were inserted in a glass bottle tightly closed with a burette to secure the anaerobic conditions. The degradation of inoculum was also examined by adding 800 g of inoculum alone in a distinct reactor. To increase the measurements accuracy each test was duplicated resulting in a total of eight reactors running in parallel. The reacting mixture was continuously stirred by using magnetic stirrers rotating with a frequency of 150 rpm. Reactors were placed in a water bath steadily operated at  $40 \pm 0.5$  °C whereas the gas burettes maintained at atmospheric temperature. The temperature of water bath was continuously inspected, whereas biogas volume, temperature and barometric pressure were continuously measured on a daily basis. Biogas composition was recorded once per day using a “Biogas5000” analyzer (Geotechnical Instruments Ltd.) equipped with dual infrared sensors for CH<sub>4</sub> (0-70%  $\pm$  0.5%) and CO<sub>2</sub> (0-60%  $\pm$  0.5%) and electrochemical sensors for O<sub>2</sub> (0-25%  $\pm$  1.0%), H<sub>2</sub> (0-2000 ppm  $\pm$  2.0%) and H<sub>2</sub>S (0-5000 ppm  $\pm$  2.0%). The presented biogas volume and composition results were calculated by subtracting the corresponding biogas volume and composition measured for the inoculum. More details about the BMP tests and the process followed can be found in an earlier study<sup>13</sup>.

The presented results are average values of two repetitions. The deviations between each two tests were statistically verified using the two-sample t-test analysis of Microsoft Excel. According to the analysis, statistical differences between two measurements were significant when the p-value was less than 0.05. The differences between the repeated tests were found insignificant in all cases.

### **Analyses**

The pH of samples was determined potentiometrically using a WTW 340i pH-meter with SenTix 410 sensor<sup>14</sup>. Total solids (TS) content was measured by drying approximately 10 g of material at 105°C under oxygen atmosphere to constant weight (weight change <2.0 %wt) in a KERN DLB 160 3A moisture analyser with halogen lamp<sup>15</sup>. A thermogravimetric analyser (LECO TGA 701) was used for the determination of volatile solids (VS). The process included heating of sample at 550 °C in O<sub>2</sub> atmosphere to constant weight according to EN 15935:2012<sup>16</sup>. The accuracy in the determination of TS and VS was ensured by repeating each measurement for five times. Samples density was assessed in a Thermo Fisher Scientific Pycnomatic ATC semi-automatic gas pycnometer operated with helium at 50 kPa following the standard methods of EN 12154:2014 and ASTM D5373-16<sup>17,18</sup>. Elemental composition (CHNSO) was determined in a LECO Truspec CHN 628+ S628 elemental analyser according to the EN18753:2017 standard method<sup>19</sup>.

A scanning electron microscope (SEM) (Tescan Vega) with Tungsten cathode and energy-dispersive X-ray spectroscopy (EDS) was used for the examination of microstructure of bags. Micrographs were obtained using a secondary electron (SE) and backscattered electron (BSE) mode with an acceleration voltage of 30 KeV. Samples before imaging were gold sputtered in order to ensure adequate electron conductivity. For a more accurate characterization of the materials the thickness of bags was also determined using the obtained micrograms.

## Results and discussion

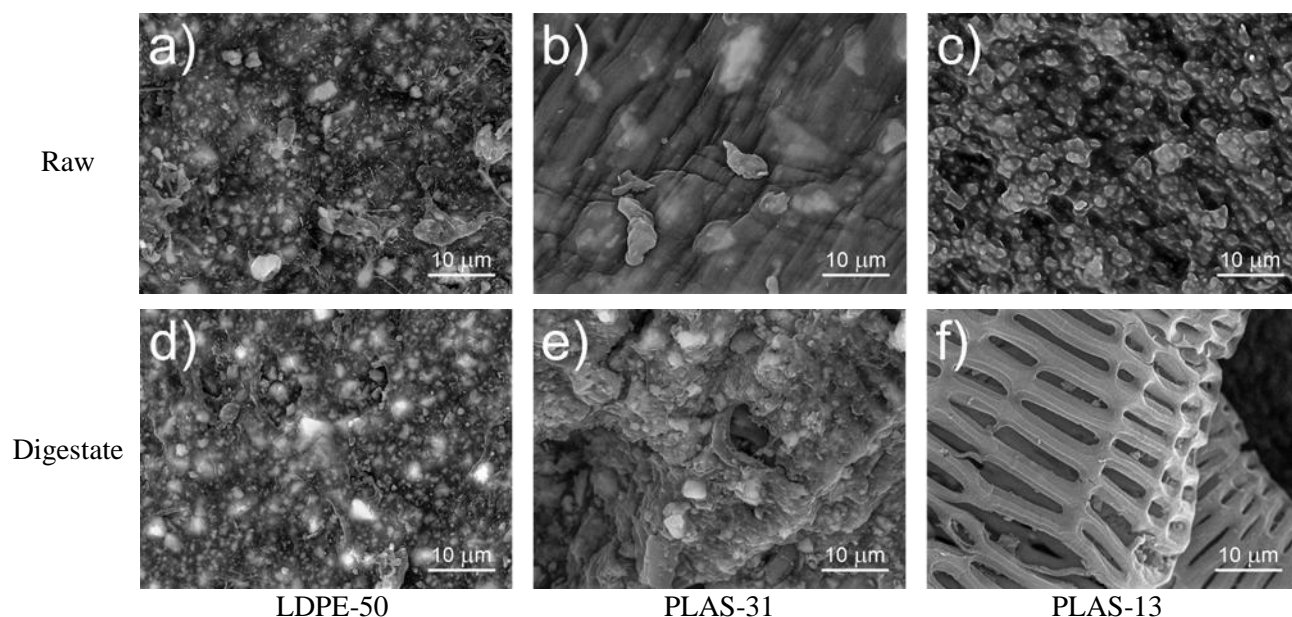
### Plastic bags characterisation

Physicochemical characteristics of plastic samples such as pH, TS, VS, density and elemental content are presented in Table 1. Total solids (TS) content of LDPE-50 (99.35 %wt) and PLAS-31 (99.52 %wt) were noticeably close, whereas the proportion in PLAS-13 (96.97 %wt) deviated from those values only by a 2 %wt. On the other hand, the volatile solids (VS) content of PLAS-31 (95.08 %wt<sub>TS</sub>) and PLAS-13 (99.41 %wt<sub>TS</sub>) were similar, whilst the VS concentration in LDPE-50 was significantly lower (78 %wt<sub>TS</sub>). VS content of the two bioplastics agree well with the values appearing in the literature for similar biodegradable polymers, which in all cases are higher than 95 %wt<sub>TS</sub><sup>20</sup>. PLAS-31 and PLAS-13 showed also similar elemental composition containing mainly carbon (55.23-56.07 %wt<sub>TS</sub>) and a fairly high amount of hydrogen of 6-7 %wt<sub>TS</sub>. In contrast, the carbon content of LDPE-50 was merely at 44.37 %wt<sub>TS</sub> and the hydrogen at 4.74 %wt<sub>TS</sub>. According to these results PLAS-31 and PLAS-13 would likely be more efficient substrates than LDPE-50 in an anaerobic digestion reactor. The opposite however can be predicted from the pH values measured for the three bags. In particular, LDPE-50 presented a pH of 7.47, which is far inside the alkaline range, whereas the pH of PLAS-31 and PLAS-13 was much lower and inside the acidic range (4.89 and 4.73, respectively). Anaerobic digestion process is favoured by alkaline environment while inhibited by acidic conditions<sup>21</sup>. With respect to the pH, therefore, LDPE-50 would likely constitute a more competent substrate in an anaerobic digestion system. Biodegradable plastic bags contain a great amount of carbon and small or negligible proportions of nitrogen<sup>22</sup>, therefore the C:N ratio was remarkably high. The C:N ratio of a substrate influences the anaerobic digestion performance of the material<sup>23</sup>. A C:N ratio between 20 and 30 favours the stability of digestion and ensures an adequate supply of nutrients for microbial cell growth. The significantly high C:N ratio found here indicates that co-digestion of bioplastics and a proteinaceous substrate would be a favourable option for the valorisation of bioplastics in biogas production<sup>24</sup>.

From Table 1, LDPE-50 showed the highest density (1480 kg m<sub>TS</sub><sup>-3</sup>) among the bioplastics, followed by PLAS-13 (1321 kg m<sub>TS</sub><sup>-3</sup>), whereas PLAS-31 presented the lowest density value (1250 kg m<sub>TS</sub><sup>-3</sup>). Similar density characteristics could not be seen in the SEM images (Figure 2). In this case, PLAS-31 appeared to have a dense structure consisting of parallel layers of slab-type formations leaving only small fractures among them. On the opposite, the most "open" structure appeared for PLAS-13, whereas the surface of LDPE-50 was seen to consist of small pores and voids forming a surface that was far from dense. Nevertheless, SEM images were taken by focusing on specific and substantially small areas on material's surface, and thereby cannot be exclusively considered for the evaluation of the density of a material.

**Table 1: Physicochemical characteristics of inoculum and plastics**

Material	pH	TS	VS	ρ	C	H	N	S	O
	-	wt%	%wt <sub>TS</sub>	kg m <sub>TS</sub> <sup>-3</sup>	%wt <sub>TS</sub>				
Inoculum	8.20	7.36	63.0	1054	34.54	4.57	3.06	0.19	21.01
LDPE-50	7.47	99.35	77.64	1480	44.37	4.74	0.009	0.04	29.55
PLAS-31	4.89	99.52	95.08	1250	56.07	6.31	0.16	0.04	32.69
PLAS-13	4.73	96.97	99.41	1321	55.23	6.98	0.18	0.07	36.92



**Figure 2: SEM images of the plastic bags before (a, b, c) and after anaerobic digestion (d, e, f)**

### Anaerobic digestion results

Table 2 presents total amounts of biogas and methane (volumetric basis) produced from the mesophilic anaerobic digestion of bioplastics. A relative generation factor describing biogas and methane yields from a bioplastic as proportion of yields from inoculum (baseline) was also shown. PLAS-13 showed the most significant biogas release after 100 days of digestion and LDPE-50 the lowest. Biogas and methane production from PLAS-13 was by 59 % and 46 % higher than that attained by LDPE-50. Similarly, biogas and methane generated from PLAS-31 were by 43 and 39 % greater than those of LDPE-50. However, LDPE-50 showed an appreciable methane release of 0.00324 m<sup>3</sup> which was by 23 % higher than that of inoculum. This suggests that even the LDPE-based material exhibited a relatively small potential to be converted during the anaerobic digestion process.

**Table 2: Biogas and methane production after 100 days of digestion (in m<sup>3</sup>)**

Reactor	Material	Biogas		Relative generation	Methane		Relative generation
		m <sup>3</sup>			m <sup>3</sup>		
				%			%
1	Inoculum	0.00365	0.00374	100	0.00256	0.00263	100
2		0.00382			0.00270		
3	LDPE-50	0.00447	0.00460	123	0.00314	0.00324	123
4		0.00472			0.00334		
5	PLAS-31	0.00619	0.00620	166	0.00425	0.00425	162
6		0.00620			0.00426		
7	PLAS-13	0.00692	0.00679	182	0.00452	0.00443	169
8		0.00667			0.00435		

Table 3 provides biogas and methane production results for the anaerobic digestion of the three bags on a VS-basis. PLAS-13 released the greatest biogas amount (0.3182 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>) during digestion followed by PLAS-31 with 0.2599 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup> and LDPE-50 with 0.1113 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>. The same trend was also observed for the production of methane. In particular, methane yields after 100 days of digestion from PLAS-13 were 0.1941 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>, the maximum amount achieved from the anaerobic digestion tests. On the other hand, cumulative methane yields from the decomposition of LDPE-50 were the lowest

(0.0785 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>). Methane release from PLAS-31 (0.1782 m<sup>3</sup> kg<sub>VS</sub><sup>-1</sup>) was lower than the yields from PLAS-13 and much higher than those from LDPE-50. Considering the biogas and methane generation potential, therefore, the materials can be lined up in the order of PLAS-13>PLAS-31>LDPE-50, which is similar to the classification that can be received according to their TS and VS contents (Table 1). This observation suggests that the degradable organic fraction in polymers was likely principal factor defining the generation of gas. The proportional correlation between VS and methane generation was also plausible indicator of an absence of inhibition during the anaerobic digestion process. Table 3 presents methane partial pressures in biogas streams generated from anaerobic digestion of the three plastics. Although biogas and methane yields from PLAS-13 were the greatest, the partial pressure of methane in biogas was fairly low. In general, the proportion of methane in biogas released from the plastics followed an inverse rank than that of the total biogas yields, i.e. biogas yields from LDPE-50 contained the greatest proportion of methane (70.5 %vol.), trailed by the yields from PLAS-31 (68.5 %vol.), while biogas from PLAS-13 contained only a 61.0 %vol. of methane. Nevertheless, the total quantity of methane produced from each bioplastic was mostly defined by the amount of released biogas.

The extent of decomposition of each plastic was evaluated by computing a theoretical maximum gas production based on the elemental composition of the material. Theoretical calculations were based on a formula developed by Richards<sup>25</sup> and the results (VS-basis) are included in Table 3. "Anaerobic biodegradability (B<sub>d</sub>)" was used to characterize the biodegradation of materials<sup>26</sup>. This factor describes the actual conversion achieved by a substrate in a BMP assay as percentage of the maximum conversion that can be achieved according to the chemical composition of the substrate and can be expressed as:

$$\text{Anaerobic biodegradability (B}_d\text{)} = \frac{\text{Experimental conversion}}{\text{Theoretical conversion}} \times 100\% \quad (1)$$

In essence, B<sub>d</sub> represents the percentage of degradable constituents of a substrate decomposing within the time span of a BMP test. From Table 2, PLAS-13 contained the highest proportion of organics converted to biogas at the end of 100 days (30.4 %), while LDPE-50 the lowest (10.3 %). Likewise, PLAS-13 contained the highest percentage of organics converted to methane (32.9 %), LDPE-50 the lowest (13.6 %), whereas PLAS-31 an average amount (28.7 %). It should be emphasized that the theoretical calculation based on the elemental content of bioplastics and thereby computed biogas and methane encompassed hypothetical yields from conventional plastic fractions of bioplastic used as supporting materials in the production of bags that were evidently not degradable during anaerobic digestion. For a given plastic, therefore, theoretical gas yields would be overestimated and not precisely indicative for the real gas generation potential of the material. Hence, it is expected that the real degradability of each material would be higher than that shown in Table 3 based on the elemental composition of substrates. Nevertheless, B<sub>d</sub> factor constituted an excellent indicator for making comparisons on the conversion of the three plastic materials.

**Table 3: Theoretical and experimental cumulative biogas and methane yields (on VS-basis)**

Substrate	Biogas yields			CH <sub>4</sub>		CH <sub>4</sub> yields		
	Theory	Test	B <sub>d</sub>	Theory	Test	Theory	Test	B <sub>d</sub>
	m <sup>3</sup> kg <sub>VS</sub> <sup>-1</sup>		%	%vol.		m <sup>3</sup> kg <sub>VS</sub> <sup>-1</sup>		%
Inoculum	1.0340	<b>0.1007</b>	9.7	55.5	<b>70.2</b>	0.5736	<b>0.0707</b>	12.3
LDPE-50	1.0778	<b>0.1113</b>	10.3	53.5	<b>70.5</b>	0.5762	<b>0.0785</b>	13.6
PLAS-31	1.1123	<b>0.2599</b>	23.4	55.9	<b>68.5</b>	0.6212	<b>0.1782</b>	28.7
PLAS-13	1.0478	<b>0.3182</b>	30.4	56.3	<b>61.0</b>	0.5898	<b>0.1941</b>	32.9

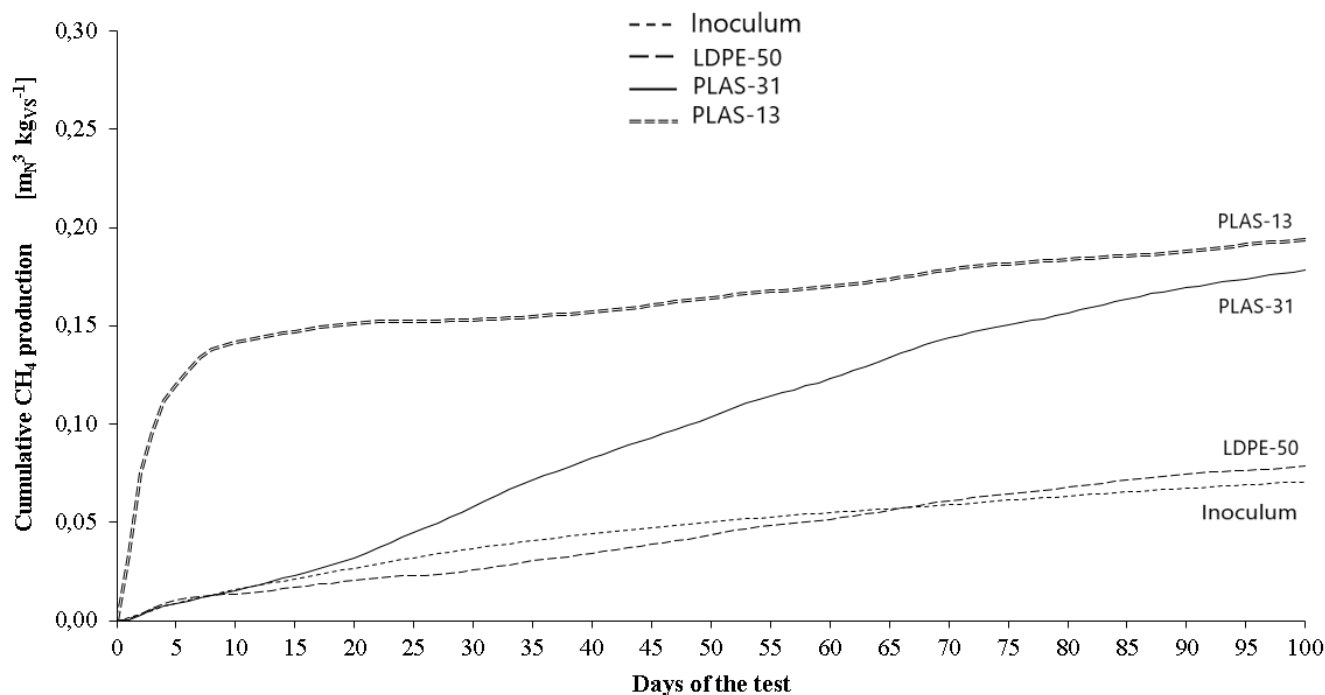
The superior methane generation performance of PLAS-13 is also obvious in Figure 3 where cumulative methane production from bioplastics (VS-basis) was plotted versus digestion time. For PLAS-13, methane release was intense in the very initial period of incubation and declined at significantly low values after a short period and until the end of assay. As a result, methane yields followed an inverse-L pattern consisting of a rapid gas production for the first 6-7 days and a long and almost asymptotic segment, wherein the gas generation rate was significantly low. It is interesting to note that a 78 % of the



total methane yields was produced in the first twenty days and a small amount of gas (approximately  $0.0427 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) was released during the rest of the digestion process. Methane generation was not nil at the end of the assay and hence a small amount of gas would be produced after 100 days of the BMP test. For PLAS-31, cumulative methane yields followed a linear shape denoting continuously increasing yields throughout the digestion process. The specific bioplastic showed a high potential for conversion even on the last incubation day and therefore its degradation would likely proceed for a longer period of time than 100 days. Gas release from PLAS-13 was comparable to that from LDPE-50 from the twelfth day onwards (Figure 3). This observation presumably suggests that the increasing methane production from PLAS-13 likely resulted from a slow decomposition of plastic structures in the polymeric material. It is also interesting to mention that inoculum adopted a methane production pattern that resembled to that of LDPE-50 during 100 days of incubation. Inoculum exhibited a slightly higher methane release than LDPE-50 for the first 70 days, however, degradation of the conventional plastic started being greater than that of inoculum in the following period and until the end of digestion. Hypothetically, at an incubation time over the 100 days the cumulative methane curve of digestion of LDPE-50 would presumably follow the same increasing trend and its deviation from the corresponding curve of inoculum would be progressively augmented.

In an attempt to gain more information on the decomposition of the three polymers, plastic particles at the end of each assay were rinsed with distilled water and their surface area was examined using SEM analysis (Figure 2 (d-f)). Digestate derived from LDPE-50 possessed a very similar surface area to the pristine material which is likely related to its limited decomposition during anaerobic digestion. Polymeric structures seem to decompose slowly, as such the material would likely further degrade with a low rate in case of a prolonged process over 100 days. Surface area of PLAS-31 was more clearly influenced by digestion with the initial dense structure (Figure 2(b)) being replaced by a more open one containing voids and to some extent visible polymeric formations (Figure 2(e)) probably originating from the plastic substances used as substrate for the production of bioplastic. Plastic structures became visible probably due to a partial decomposition and removal of organic matter from the material. The remaining distinguishable organics constitute additional indication of a potential of the material to further degrade. PLAS-13 showed the most significant change of surface area. In this case, clean polymeric structures could be distinguished in Figure 2(f) that were likely related to the polymers used for the production of the bioplastic. As mentioned above, removal of soluble organic compounds from PLAS-13 was significant even by the first 6-7 days of incubation and thus any degradable components would probably be lost within 100 days of digestion. According to this assumption, methane release in most of the anaerobic digestion process based on a very slow degradation of the plastic fraction of PLAS-13 and could potentially proceed for a longer period than 100 days.

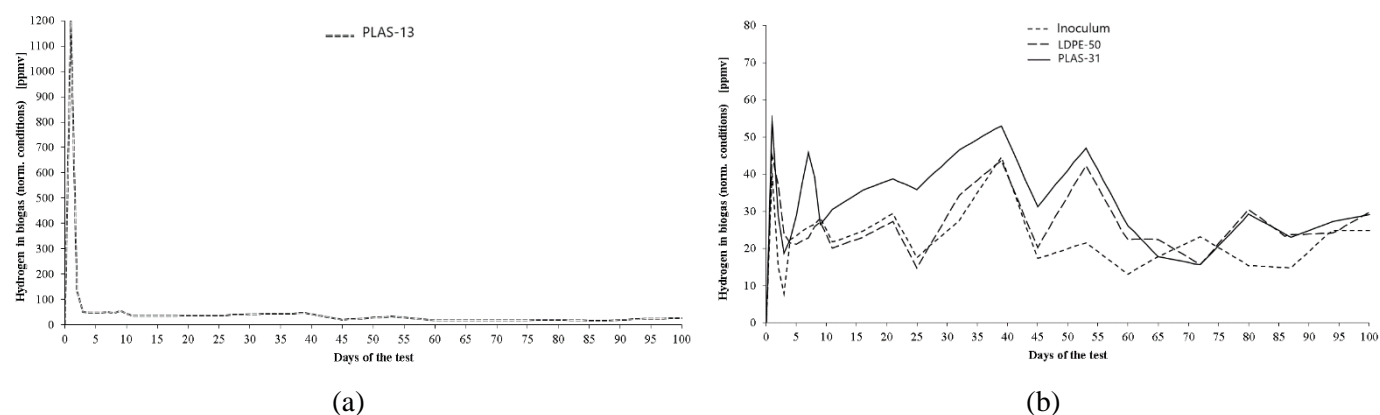
A main difference of the three polymers concerned the time of their decomposition. As discussed above, PLAS-13 decomposed mainly in the initial period of incubation (6-7 days) and then the plastic fraction degraded slowly until the end of the BMP assay. PLAS-31 converted with a stable rate throughout the digestion process and presents potential to continue decomposing with the same rate over a longer period of time than the 100 days, until the degradable part would be totally consumed by bacteria. LDPE-50 decomposed according to the same linear pattern with PLAS-31 but with a much lower rate, as such the time required for its degradation would be longer than both bioplastics. Consequently, even the conventional plastic bag showed a small decomposition under anaerobic conditions, however, the time required for its total conversion would be much longer compared to the bioplastic materials.



**Figure 3: Cumulative CH<sub>4</sub> production during anaerobic digestion of polymeric materials**

Figure 4 displays the daily hydrogen release from the anaerobic digestion of plastics. Hydrogen yields were significantly high over the initial three days of incubation of PLAS-13 (Figure 4(a)), which was probably related to a significant amount of methane liberated from the specific substrate at the beginning (6-7 days) of digestion (Figure 3). The large hydrogen generation rate even by the first day confirms an enhanced content of easily soluble organic compounds in PLAS-13. In essence, the soluble components are hydrolysed immediately after the process initiation leading to an accumulation of higher volatile acids, lactate ethanol, propionate, and butyrate (referred to as electron sinks) which cannot be directly consumed by methanogens. At this point, an intervention of hydrogen producing acetogenic bacteria is required for sinks degradation. These bacteria convert the electron sinks to acetate, carbon dioxide and hydrogen before acetate and hydrogen consuming methanogenic bacteria start producing biogas<sup>27</sup>. The high amount of hydrogen during the first three days of digestion presumably enabled an immobilization of hydrogen consuming methanogenic microorganisms and led to a rapid methane release within the first eleven days of digestion (Figure 3). Thereafter, hydrogen yields declined and became comparable to those produced by the other two polymeric materials (Figure 4(b)). This change was also reflected on the cumulative methane generation curves where the rate of methane release from digestion of PLAS-13 reduced and became comparable to that of LDPE-50 and lower than that of PLAS-31. It is interesting to mention that the hydrogen production in the case of PLAS-31 was greater than that of the other two plastics from the twelfth day and until the end of digestion. This likely led to the great methane generation rate of the specific material (Figure 3), as described above.





**Figure 4: Daily  $H_2$  production during anaerobic digestion of (a) PLAS-13 and (b) LDPE-50 and PLAS-31**

## Conclusions

The anaerobic digestion of three types of commercial bags was examined under mesophilic conditions in long-term BMP tests. LDPE-50 decomposed only negligibly and methane produced from its digestion only slightly exceeded that of inoculum. PLA-based bioplastic (PLAS-31) showed a better degradation performance and the biogas produced from its anaerobic digestion approached a value of  $0.2599 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$  at the end of the 100 days of BMP test. The corresponding amount produced by PLAS-13 ( $0.3182 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ) was the highest among the examined biodegradable bags. The biodegradable organic content of bioplastics was the main factor defining the generation of biogas and methane. Surface of LDPE-50 only slightly changed with anaerobic digestion. The most significant modification of the surface was observed for PLAS-13 where clean polymeric structures appeared after digestion. PLAS-31 presented a higher capability to produce biogas for a period longer than 100 days.

## Acknowledgements

The work was supported by the Ministry of Education, Youth and Sports of the Czech Republic under the projects ERDF "Institute of Environmental Technology – Excellent Research" [No. CZ.02.1.01/0.0/0.0/16\_019/0000853], Large Research Infrastructure ENREGAT [No. LM2018098] and the Operational Programme Research, Development and Education [No. CZ.02.1.01/0.0/0.0/17\_049/0008419 COOPERATION].

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## Potenciál výroby bioplynu u biologicky rozložitelných plastů na bázi škrobu a polylaktidu

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### Souhrn

Plastové materiály se při ukládání v přírodě rozkládají extrémně pomalu a jejich úplná degradace trvá mnoho dekád. V poslední době jsou složky komerčních plastových materiálů alespoň částečně nahrazovány biologicky odbouratelnými přísadami. Kyselina polymléčná (PLA) a polymery na bázi škrobu jsou alternativy používané pro tento účel, aby nahradily 50-100% hmoty plastového materiálu. Příspěvek diskutuje výsledky produkce bioplynu a methanu vsádkovou jednostupňovou mezofilní anaerobní digesí z konvenčního a dvou rozdílných komerčních biodegradabilních pytlů po dobu 100 dní, aby se zjistila jejich degradační schopnost a prozkoumal se jejich potenciál produkce bioplynu a methanu po dlouhé období procesu vyhnívání. Plast na bázi LDPE (LDPE-50) se po 100 dnech digesce rozložil zanedbatelně za vzniku  $0.0785 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$  methanu, zatímco bioplast na pázi PLA (PLAS-31) vykázal lepší degradační schopnost ( $0.1782 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ ). Pro další biologicky odbouratelný pytel (PLAS-13) byla získána produkce methanu  $0.1941 \text{ m}^3 \text{ kg}_{\text{VS}}^{-1}$ , což naznačuje že za specifických podmínek by bioplasty mohly poskytnout poměrně zajímavé množství bioplynu. Rozložitelný organický materiál v bioplastech byl hlavním faktorem určujícím jejich přeměnu na bioplyn a methan. Anaerobní digesce měla minimální dopad na povrch LDPE-50, zatímco k nejvýraznější změně povrchu došlo u PLAS-13, kde po digesci vznikly čisté polymerní struktury v důsledku odstranění významné části organických látek. PLAS-31 vykazoval po 100 dnech potenciál pro další degradaci anaerobní digescí.

**Klíčová slova:** anaerobní digesce, BMP testy, bioplasty, LDPE, kyselina polymléčná, biodegradace