METHANE PRODUCTION POTENTIAL FROM VARIETY OF UNPRINTED PAPERS

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Abstract. Politicians in Latvia have decided to decrease support for biogas production. The new renewable biomass resources should be investigated to provide inexpensive and cost-effective methane production. Every year a lot of paper waste goes to landfills. Paper waste has a low density and the cost of transporting wastes to the landfill is high. In the past paper waste was used to produce new paper, but now there is no any paper mill in Latvia. There are some publications on the use of paper for biogas production. The purpose of the study is assessment of the methane volume obtainable from various unprinted papers in the anaerobic fermentation process. Investigation was provided in 16 bioreactors operated in batch mode at 38 ºC. Paper waste was filled into 14 bioreactors and inoculum only was filled into two bioreactors for control. The yields of methane 0.506 $l \cdot g^{-1}_{DOM}$ after 41 days of anaerobic digestion of office paper, 0.386 $l \cdot g^{-1}_{DOM}$ of toilet paper, 0.375 $l \cdot g^{-1}_{DOM}$ of packaging paper and 0.388 $l \cdot g^{-1}_{DOM}$ of cardboard were obtained. The study demonstrates that paper waste is a good raw material for the production of methane.

Key words: methane, office paper, toilet paper, packaging paper, cardboard.

Introduction

Support for biogas production is reduced by some legislative acts in Latvia, e.g. the owners of the areas cultivating maize for biogas plants are excluded from the range of duty-free tax receivers on diesel for maize biomass growing. New renewable biomass resources should be investigated to replace usage of maize biomass and to provide inexpensive and cost effective biomethane production.

Paper wastes are major organic components in municipal solid waste suitable for biogas production. 163 kg of paper wastes per inhabitant were produced in Latvia every year. Every year a lot of paper waste goes to landfills. Paper waste has a low density and the cost of passing it to the landfill in Latvia is high. In the past paper waste was used to produce new paper, but now there is no running paper mill in Latvia.

Nigerian scientists did an AD experiment for 30 days at temperature 27-35 ºC, using three 25 l plastic vessels filled in with 17 Lof substrate composed of: poultry droppings with inoculate (fresh cattle rumen content) in the bio-digester A; co-digestion ofpoultry droppings, inoculate with untreated corn cob and waste papers in the bio-digester B; co-digestion of poultry droppings, inoculate with pre-treated corn cob and waste paper in the bio-digester C; pre-treatment of corn cob and waste papers include mechanical grinding and thermal boiling at 100 ºC for an hour. "The results showed that poultry droppings alone in the bio-digester A gave a cumulative average biogas volume of 3452 cm^3 (115 $cm^3 \cdot day^{-1}$) and poultry droppings plus untreated co-substrates in the bio-digester B gave a cumulative average biogas volume of 4811 cm^3 (160.3 $cm^3 \cdot day^{-1}$), while poultry droppings plus treated co-substrates in the bio-digester C gave a cumulative average biogas volume of 6454 cm^3 (215.1 $cm^3 \cdot day^{-1}$)" [1].

Another research was provided on lignocellulosic materials, paper and paper board (PPB) that are processed for their fabrication. "This study evaluated correlations of methane yields and Monod and Gompertz kinetic parameters with structural carbohydrates, lignin, and ash concentration of five types of PPBs. All components were used as single and combined independent variables in linear regressions to predict the methane yield, maximum specific methanogenic activity (SMAmax), saturation constant (Ks), and the lag phase (λ). The results showed the methane yields ranging from 69.2 ± 8.61 to 97.2 ± 2.29 % of PPB substrates provided. The overall findings of this study are: (i) combinations of structural carbohydrates, lignin and ash used as ratios of degradable to either non degradable or slowly degradable fractions predict AD kinetic parameters of PPB materials better than singleindependent variables; and (ii) other components added during their fabrication may also influence both the methane yield and kinetic parameters" [2].

Another Nigerian scientists' study aimed to find the biogas production potential of paper waste alone (PW-A) and paper waste blend : cow dung (PW:CD) in the ratio 1:1 was provided into two 50L biodigesters in the ratio of 3:1 of water to waste under 45 day retention period at the temperature 26-43 ºC. "The physicochemical parameters of the wastes were determined including microbial analysis.

The results obtained showed that PW had a cumulative gas yield of 6.23 ± 0.07dm^3·kg^{-1} of slurry with the flash point on the 2nd day even though gas production reduced drastically, while the flammability discontinued and resumed after 14 days. Blending increased the cumulative gas yield to 9.34 ± 0.11 dm^3·kg^{-1}, slurry representing more than 50 % increase. The onset of gas flammability took place on the 6th day and was sustained throughout the retention period" [3].

Swedish researchers studied anaerobic fermentation of paper tube residuals as substrate for biogas (methane) production with addition of both 2 % NaOH and 2 % H_2O_2. "Digestion of the pre-treated materials at these conditions yielded 493 N ml·g$^{-1}_{VS}$ methane, which was 107 % more than the untreated materials. In addition, the initial digestion rate was improved by 132 % compared to the untreated samples. The addition of NaOH was, besides the explosion effect, the most important factor to improve the biogas production" [4].

The effect of waste paper of different amount (0, 4, 8, 12 or 20 g) on biogas production from its co-digestion with fixed amount of cow dung 5 g and water hyacinth 5 g was studied at room temperature in five batch reactors for over 60 days period at the University of Port-Harcourt. "Waste paper addition was varied for a fixed amount of cow dung and water hyacinth until maximum biogas production was achieved. Biogas production was measured indirectly by the water displacement method. The production of biogas showed a parabolic relationship as the amount of waste paper (g) increased with a goodness of fit of 0.982. Maximum biogas volume of 1.11litres was observed at a waste paper amount of 17.5g, which corresponds to 10.0 % total solids of the biomass in 250mL solution" [5].

Municipal solid waste contains 20-40 % paper influencing its anaerobic digestion usually. Scientists from the Brazil University of the Sinos Valley provided experimental research on anaerobic co-digestion of the organic fraction of municipal solid waste (OFMSW) with fruit and vegetable waste (FVM) in mixing ratios 1:0, 1:1, 3:1 and 0:1 in bath AD process at temperature 35 °C. "The 1:3 mixing ratio of OFMSW:FVW (VS basis) showed the optimal performance, reaching the highest average cumulative biogas yield (433.9 N ml·g^{-1}VS), highest average methane yield (396.6 Nml·g$^{-1}_{VS}$) and the highest average VS removal rate (54.6 %)" [6].

The initial percentage of paper wastes in OFMSW, however, was not provided in this scientific article. Also, the investigations mentioned above do not include the data on biogas and methane production in the AD process of different types of paper wastes in the temperature range 36-40 °C used in most biogas cogeneration plants in Latvia.

The aim of this study is evaluation of the biogas and methane production potential from different types of paper biomass, as there are no previous investigations on the biogas and methane yield from paper biomass in Latvia.

Materials and methods

Before fermentation the raw materials (office paper, toilet paper, packaging paper and cardboard paper) samples were analysed for dry matter and organic matter content before the experiment. Data on the content of the organic matter were used for optimizing of the organic load of substrate.

The widely applied methods [6-8] were used for the AD process investigation. For this research in 16 experimental bioreactors with volume of 0.75 litres similar methods are used, as described in [6]. Two bioreactors for control were filled with 500.0 ± 0.2 g inoculums and the rest bioreactors were filled with mixtures of inoculums (500 g) and added paper biomass (10 ± 0.005 g), according to the experimental plan, Table 1.

"Dry organic matter (DOM) content was determined by weighting the initial biomass samples dried in the thermostat at 105 ºC and processed in the oven (type Nabertherm) to provide the aching process within a special heating cycle with the maximal cycle temperature 550 ºC.

All the components were carefully mixed together and filled in the bioreactors. All bioreactors were placed in a single heated camera at the same time before anaerobic digestion. Gases released from each bioreactor were collected in storage bags positioned outside of the heated camera.Gas volumes collected in storage bags were measured regularly using the flow meter (Ritter drum-type gas meter). The composition of gases, including oxygen, carbon dioxide, methane and hydrogen sulphide, was measured by help of the gas analyser (model GA 2000). The substrate pH value was measured before and after finishing off the AD process, using a pH meter (model PP-50) with accessories. Scales (type KFB 16KO2) was used for weighting (accuracy ± 0.2 g) of the total weight of substrates before and after the AD process.

Fermented cattle manure was utilized as inoculums, and it has very low organic matter content providing low biogas volumes released from pure inoculums (filled in control bioreactors R1 and R16), resulting in small biogas and methane volumes to be subtracted in calculations of true biogas and methane volumes from the added biomass. The AD process was provided until biogas release was finished. The experimental data were processed using appropriate statistical methods [7].

Results and discussion

The results of the investigation of sample substrates, including inoculums, before starting of the AD process are shown in Table 1.

Table 1

Results of analyses of raw material samples before anaerobic digestion

Bio-reactors	Raw material	pH	TS, %	TS, g	ASH, %	DOM, %	DOM, g	Weight, g
R1; R16	IN	7.59	3.75	18.75	31.34	68.66	12.874	500
R2-R5	OP	-	92.64	9.264	11.95	88.05	8.156	10
R6-R8	TP	-	90.85	9.085	1.35	98.65	8.962	10
R9- R11	PP	-	92.2	9.220	14.34	85.66	7.898	10
R12-R15	C	-	91.5	9.150	13.86	86.14	7.882	10
R2-R5	10OP + 500IN	7.60	5.49	28.014	24.93	75.07	21.03	510
R6- R8	10TP + 500IN	7.59	5.46	27.835	21.93	78.07	21.836	510
R9-R11	10PP + 500IN	7.59	5.48	27.97	25.73	74.27	20.772	510
R12-R15	10C + 500IN	7.60	5.47	27.900	25.61	74.39	20.756	510

Note: IN – inoculum; OP – office paper*; TP* – toilet paper*; PP* – packaging paper*; C* – cardboard; A*SH – ashes; TS – total solids; DOM – dry organic matter (on raw substrate basis); R1-R16 – bioreactors.*

As shown in Table 1, all paper types have a high dry matter and organic dry matter content. The biggest organic dry matter content is in toilet paper, because it has very few impurities.

Almost completely fermented cattle manure was used as inoculum and it was fermented in the control bioreactors R1 and R16. Very low average methane yield 0.063 L was obtained from the control bioreactors, and it was less than 2.2 percent of the average yields from the other bioreactors with paper waste addition. Biogas and methane yields from the bioreactors R2-R15 with added paper biomass are shown in Table 2 and Fig. 1 with already subtracted average values of biogas and methane obtained from the control bioreactors R1 and R16 filled in with pure inoculum.As shown in Table 2, the best average methane content in the biogas and methane yield was obtained from the bioreactors filled in with office paper.Also, the average yield of biogas was significantly higher than that of other types of paper. This could be explained by the composition of office paper.

A good methane yield was extracted also from toilet paper. This can be explained by the fact that toilet paper contains a lot of organic matter and has small content of impurities.

Table 2

Production of biogas and methane

Bioreactor	Raw material	Biogas, l	Biogas, $l \cdot g^{-1}_{DOM}$	Methane, aver. %	Methane, l	Methane, $l \cdot g^{-1}_{DOM}$
R1 500g IN	500IN	0.5	0.039	17.80	0.089	0.007
R16 500g IN	500IN	0.2	0.016	18.50	0.037	0.003
Average: R1, R16	**500IN**	**0.35**	**0.028**	**18.15**	**0.063**	**0.005**

Table 2 (continued)

Bioreactor	Raw material	Biogas, l	Biogas, $l \cdot g^{-1}_{DOM}$	Methane, aver. %	Methane, l	Methane, $l \cdot g^{-1}_{DOM}$
R2	500IN + 10OP	6.55	0.803	55.79	3.653	0.448
R3	500IN + 10OP	7.45	0.913	53.08	3.955	0.485
R4	500IN + 10OP	8.05	0.987	55.35	4.456	0.546
R5	500IN + 10OP	8.65	1.061	51.99	4.497	0.551
Average: R2-R5 ± st.dev.	**500IN + 10OP**	**7.68 ± 0.90**	**0.941 ± 0.110**	**54.05 ± 1.82**	**4.140 ± 0.408**	**0.506 ± 0.050**
R6	500IN + 10TP	6.85	0.764	52.79	3.616	0.403
R7	500IN + 10TP	6.25	0.697	52.18	3.261	0.364
R8	500IN + 10TP	6.45	0.719	54.33	3.504	0.391
Average: R6-R8 ± st.dev.	**500IN + 10TP**	**0.52 ± 0.31**	**0.727 ± 0.034**	**53.10 ± 1.11**	**3.460 ± 0.181**	**0.386 ± 0.020**
R9	500IN + 10PP	5.65	0.715	49.68	2.807	0.355
R10	500IN + 10TP	5.75	0.728	54.61	3.140	0.397
R11	500IN + 10TP	5.55	0.702	53.14	2.949	0.373
Average: R9-R11 ± st.dev.	**500IN + 10TP**	**5.65 ± 0.10**	**0.715 ± 0.013**	**52.48 ± 2.53**	**2.965 ± 0.167**	**0.375 ± 0.021**
R12C	500IN + 10C	4.95	0.628	54.18	2.862	0.340
R13	500IN + 10C	6.15	0.780	52.82	3.253	0.412
R14	500IN + 10C	6.35	0.806	51.69	3.282	0.416
R15	500IN + 10C	5.75	0.729	53.04	3.050	0.387
Average: R12-R15 ± st.dev.	**500IN + 10C**	**5.80 ± 0.62**	**0.735 ± 0.079**	**52.93 ± 1.02**	**3.067 ± 0.196**	**0.388 ± 0.035**

Note: $l \cdot g^{-1}_{DOM}$– litres per 1 g dry organic matter added (added fresh biomass into inoculums).

Very good methane yields were obtained from all types of paper. The lowest yield on average was obtained from packaging paper. The amount of biogas extracted from office paper is slightly higher than reported by other [5] researchers.

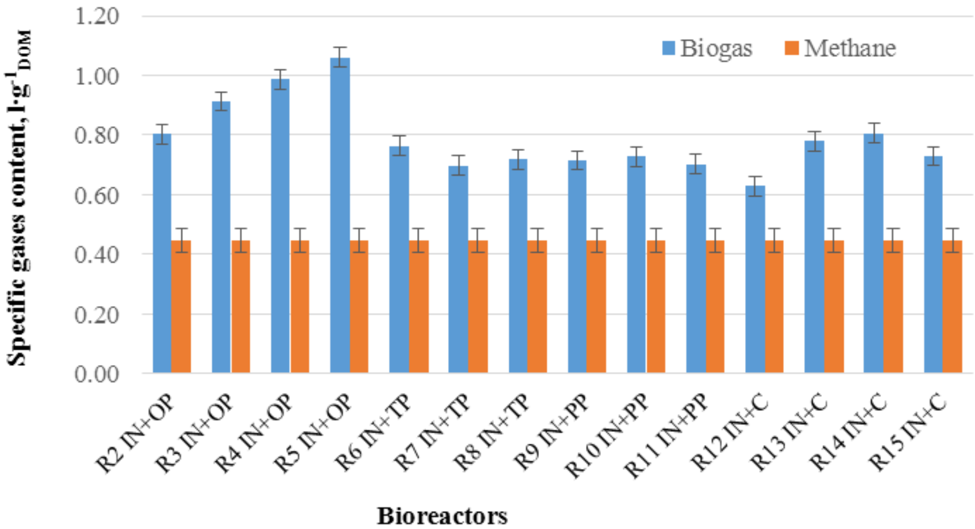

Fig. 1. **Specific biogas and methane output from each bioreactor:** IN – inoculum; OP – office paper; TP – toilet paper; PP – packaging paper; C – cardboard

The average methane contents from bioreactors loaded with different papers are shown in Figure 3. The highest average methane yield 0.506 $l \cdot g^{-1}_{DOM}$was obtained from the bioreactors R2-R5, where office paper was filled in. The obtained result is much higher compared to that, reported by the Indonesian researchers, methane yield 0.058 $l \cdot g^{-1}_{DOM}$ from cattle dung : newspapers at ratio 1 : 1 and methane yield 0.106 $l \cdot g^{-1}_{DOM}$ from the same substrate with BS4 enzyme addition during a 5-week period [10]. The results are not directly comparable, as fresh cow dung was used by the Indonesian researchers as inoculums, while cattle manure at finished fermentation stage was used in our experimental research.

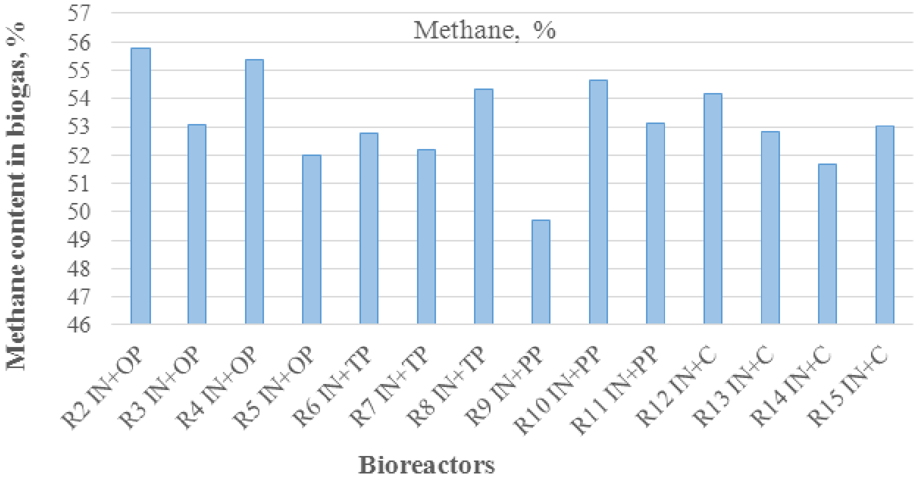

Fig. 2. **Average specific methane output and methane content in bioreactors with different paper wastes**: IN – inoculum; OP – office paper; TP – toilet paper; PP – packaging paper; C – cardboard

The higher methane content was obtained in biogas from office paper that was by 0.8-3.0 % higher compared to the other types of paper waste investigated. This evidence may be explained due to the similar type of carbohydrates contained in all paper waste**.**

Conclusions

1. All types of papers processed in anaerobic fermentation gave very good methane yields.
2. The methane volume obtained from office paper was by 31.1 % higher than released from toilet paper.
3. The methane yield obtained from office paper was by 34.9 % higher than obtained from packaging paper.
4. The methane yield obtained from cardboard was by 30.4 % lower compared to that from office paper.
5. Paper residues and paper waste are good raw materials for biogas producing and can be recommended for using in biogas plants.

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