Agrochemical value of the liquid phase of wastes from fermenters during biogas production

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ABSTRACT

We tested the procedure of combined phytomass utilization Integrated Generation of Solid Fuel and Biogas from Biomass (IFBB) proposed for ensiled grass matter from the aspect of suitability of its use for a typical substrate of new Czech biogas stations, a mixture of cattle slurry, maize silage and grass haylage. The agrochemical value of the liquid phase from a biofermenter was also evaluated. We concluded that this procedure is suitable for the tested substrate and improves the agrochemical value of a fugate from biogas production. By chlorine transfer to the liquid phase, it enables to use the solid phase as a material for production of solid biofuels with a reduced threat of the generation of polychlorinated dioxins and dibenzofurans during combustion. However, the concentration of mineral nutrients in the liquid phase during IFBB procedure is extremely low after anaerobic digestion as a result of dilution with water, and so its volume value is negligible.

Keywords: anaerobic digestion; wastes; fertilizing value; separation; utilization; IFBB procedure; mineral fertilizers

Digestate, the waste from fermenters during biogas production, is composed of solid phase and liquid phase (fugate). We have demonstrated that the solid phase of the digestate is not an organic fertilizer because its organic matter is very stable and so it cannot be a relatively expeditious source of energy for the soil microedaphon (Kolář et al. 2008). Neither is it a mineral fertilizer because available nutrients of the original raw material and also nutrients released from it during anaerobic digestion passed to the liquid phase – fugate. The digestate, and naturally the fugate, have a low content of dry matter (fugate 0.8–3% by weight) (Gujer and Zehnder 1983) and this is the reason why analytical data on the ones to tens of weight % of available nutrients given in dry matter foster an erroneous opinion in practice that these wastes are excellent fertilizers. In fact, fugates are mostly highly diluted solutions in which the content of nutrients that are represented at the highest amount, mineral nitrogen, is only 0.04–0.4% by weight.

The surplus of water during fertilization with this waste increases the elution of this nutrient in pervious soils while in less pervious soils the balance between water and air in the soil is impaired with all negative consequences.

It would be ideal to realize biogas production from the liquid phase only – it would enable to introduce high performance UASB (Upflow Anaerobic Sludge Blanket) fermenters and to achieve large savings of technological volumes; however, the concentration of substances in the liquid phase should have to increase. The solid phase of substrates, which cannot be applied as an organic fertilizer after the fermentation process, would be used as biomass for the production of solid biofuels in the form of pellets or briquettes. Yet, it would be necessary to reduce its chlorine content to avoid the generation of noxious dioxins and dibenzofurans during the burning of biofuel pellets or briquettes at low burning temperatures of household boilers and other low-capacity heating units. Wachendorf et al. (2007, 2009) were interested in this idea and tried to solve this problem in a complex way by the hot-water extraction of the raw material (at temperatures of 5, 60 and 80°C) followed by separation of the solid and liquid phase by means of mechanical dehydration when a screw press was used. This procedure is designated by the abbreviation IFBB (Integrated Generation of Solid Fuel and Biogas from Biomass). These researchers were also successful in reaching the

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transfer ratio of crude fibre from original material (grass silage) to liquid phase of only 0.18, which is desirable for biogas production; for more easily available organic matters influencing biogas production, e.g. nitrogen-free extract, the ratio is 0.31. The transfer of potassium, magnesium and phosphorus to the liquid phase ranged from 0.52 to 0.85 of the amount in fresh matter, calcium transformation was lower, at the transfer ratio 0.44–0.48 (Wachendorf et al. 2009). Transformation to the liquid phase was highest in chlorine, 0.86 of the amount in original fresh matter, already at a low temperature (5°C). The transfer of mineral nitrogen to the liquid phase before the process of anaerobic digestion is very low because there is a minute amount of mineral N in plant biomass and the major part of organic matter nitrogen is bound to low-soluble proteins of the cell walls. Nitrogen from these structures toughened up by lignin and polysaccharides is released just in the process of anaerobic digestion. As the IFBB process also comprises transfer of organic nitrogen compounds (crude protein – nitrogen of acid detergent fibre ADF) to the liquid phase, approximately at a ratio of 0.40, the liquid phase, subjected to anaerobic digestion, is enriched with mineral nitrogen.

Like Wachendorf et al. (2009), we proceeded in the same way applying the IFBB system for the parallel production of biogas and solid biofuels from crops grown on arable land. The IFBB technological procedure is based on a high degree of cell wall maceration as a result of the axial pressure and abrasion induced with a screw press. Reulein et al. (2007) used this procedure for dehydration of various field crops; it is also known from technologies of processing of rapeseed, sugar beet, leguminous crops for production of protein concentrates (Telek and Graham 1983, Rass 2001) and in biorefineries for the extraction of lactic acid and amino acids (Mandl et al. 2006).

The objective of our study was to test the IFBB procedure on the current mixed substrate used by newly established biogas stations in the Czech Republic, i.e. a mixture of cattle slurry, maize silage and grass haylage at an extraction temperature of 60°C, to control the whole process by changes in the chemical degradability of the mixture on the basis of acid hydrolysis according to Rovira and Vallejo (2002), and to evaluate the original and enriched fugate according to IFBB as mineral fertilizer.

MATERIAL AND METHODS

The basic substrate contained 37.5% by weight of cattle slurry and 62.5% by weight of solid substrates, i.e. a mixture of chopped maize silage and grass haylage of particle size max. 40 mm (82.5% of silage and 17.5% of haylage). In total, the substrate accounted for 19.3% of dry matter. This substrate at 15°C is designated as A. A portion of this substrate was mixed with water at a weight ratio 1:5, put into a thermostat with a propeller stirrer at 15°C and intensively stirred for 15 min. Analogically, the other portion was also mixed with water at a substrate to water ratio = 1:5 and put into a thermostat at a temperature of 60°C with 15-min intensive stirring. The sample of the substrate with water 15°C was designated as B, the sample with water 60°C was designated as C. The liquid phase from substrate A was separated by centrifugation while the liquid phases from substrates B and C were separated in a laboratory screw press for pressing of fruits and vegetables. The separated liquid phases of substrates A, B and C were diluted with water to obtain a unit volume and the analytical results were recalculated to a transfer ratio in the liquid phase in relation to the content of particular nutrients in dry matter of the original substrate mixture.

The experiments conducted in an experimental unit of anaerobic digestion and in an equipment for IFBB enabled to determine the content of mineral nutrients in substrate A after 42-day anaerobic digestion in mesophilic conditions (40°C), in the liquid phase of substrate A after anaerobic digestion, and in the liquid phase of substrates B and C after recalculation to the dry matter content and concentration corresponding to substrate A, also after the process of anaerobic digestion under the same conditions (42 days, 40°C).

The above recalculations enable to clearly show the advantages of the IFBB process in nutrient transfer from solid to liquid phase when substrate A and 5 times diluted substrates B and C are compared; however, they may unfortunately evoke a distorted idea about the real concentration of nutrients in liquid phases. It is to recall that IFBB increases the mass flow and transfer to the liquid phase but with regard to the 5-fold dilution the nutrient concentration in liquid waste for fertilization continues to decrease.

The solid phases of substrates A, B and C after anaerobic digestion were subjected to determination of organic matter hydrolyzability in sulphur acid solutions according to Rovira and Vallejo (2000, 2002) as modified by Shirata and Yokozawa (2006); we already used this method to evaluate the degradability of a substrate composed of pig slurry and sludge from a municipal waste water treatment plant (Kolář et al. 2008).

Mathematical and statistical evaluation of analytical results including the calculation of the mean reliability interval was done by the Lord's test and other methods for several-element sets based on the range R of parallel determinations (Eckschlager et al. 1980).

RESULTS AND DISCUSSION

Table 1 suggests that the IFBB procedure proposed for grass haylage is applicable to the typical substrate of Czech biogas stations, i.e. to a mixture of cattle slurry, maize silage and grass haylage. In agreement with Wachendorf et al. (2009) the observed transfer ratios are markedly higher at 60°C compared to 15°C of hydrothermal conditions but the value of transfer ratios to the liquid phase is generally lower in our experiments. We ascribe this fact to the properties of the material and also to the achieved axial force of the used press that was apparently lower even though the same perforation size of the conical part of the press (1.5 mm) and slope of the body (1:7.5) were used.

The results in Table 1 illustrate that the separation of liquid and solid phase of the substrate that was not subjected to anaerobic digestion by means of centrifugation only is rather imperfect from the aspect of the mass flow of components. The IFBB system (water dilution, intensive stirring at a temperature of 60°C and subsequent separation of the liquid and solid phase with a screw press) increases the transfer of organic and mineral substances into the liquid phase by about 15–20%, and it is also true of saccharidic nitrogen-free extract and organic nitrogen compounds. This fact documents that the liquid phase has a higher amount of active, well-degradable organic material for anaerobic digestion, and so it is possible to expect not only the higher production of biogas but also more mineral nitrogen in the liquid after anaerobic digestion.

The high mass flow of alkaline metals and chlorine into the liquid phase, and on the contrary, the low transfer of calcium, confirm the opinion of German researchers (Wachendorf et al. 2009) that the IFBB procedure largely increases the quality of biomass solid phase as a material for production of solid fuels: the production of polychlorinated dioxins and dibenzofurans is reduced, waste gases are less corrosive and the temperature of ash fusion is higher.

Nitrogen compounds of the substrate dry matter account for 16.3%, i.e. these nitrogen organic compounds contain 2.6% of nitrogen in dry matter (Table 1). The content of mineral nitrogen in the substrate before anaerobic digestion was 1%. If the digestate contains 2.26% of mineral nitrogen in the same dry matter after anaerobic digestion, it is to state that during anaerobic digestion about a

Table 1. Dry matter content in the fresh mass of used materials and their chemical composition in % dry matter. Transfer ratio of mass flow to liquid phase from the fresh mass of the substrate not diluted with water at 15°C (A), diluted with water at 1:5 at 15°C (B) and diluted with water at 1:5 at 60°C (C). Liquid phase A was separated by centrifugation, liquid phases B and C with a screw press

	Cattle slurry	Maize silage	Grass haylage	Substrate	Transfer ratio to liquid phase A	B	C
Dry matter	6.4	28.9	18.7	19.3	0.06 ± 0.01	0.18 ± 0.04	0.20 ± 0.03
N-matters (N × 6.25)	25.6	11.5	7.4	16.3	0.05 ± 0.01	0.20 ± 0.04	0.26 ± 0.05
Digestible nitrogencompounds	–	6.2	3.8	7.3	–	–	–
Nitrogen-free extract	–	52.8	48.6	49.9	0.30 ± 0.03	0.45 ± 0.05	0.48 ± 0.05
Crude fibre	–	25.7	29.8	18.0	0.01 ± 0.00	0.10 ± 0.00	0.10 ± 0.00
Fat	–	4.8	1.5	2.8	–	–	–
Organic matters	76.4	94.8	87.3	87.0	–	–	–
Mineral N (N-NH_4^+, NO_3^-)	2.4	< 0.1	> 0.1	1.0	0.74 ± 0.05	0.89 ± 0.06	0.95 ± 0.06
P	1.3	0.2	0.3	0.6	0.40 ± 0.05	0.52 ± 0.07	0.65 ± 0.08
K	5.3	1.4	1.7	2.9	0.57 ± 0.04	0.60 ± 0.04	0.79 ± 0.05
Ca	1.3	0.4	0.6	0.8	0.31 ± 0.06	0.38 ± 0.08	0.46 ± 0.08
Mg	0.5	0.2	0.3	0.3	0.38 ± 0.07	0.43 ± 0.08	0.55 ± 0.07
Na	0.1	< 0.1	<< 0.1	< 0.1	0.70 ± 0.08	0.77 ± 0.04	0.80 ± 0.08
Cl	0.3	0.2	0.2	0.2	0.77 ± 0.06	0.85 ± 0.05	0.85 ± 0.06

Table 2. Contents of mineral nutrients after anaerobic digestion (42 days, 40°C) in digestate (substrate A), in its liquid phase and in fermented liquids from IFBB in % dry matter by weight

	Substrate A	Liquid phase of substrate A	Liquid phase of substrate after recalculation to dry matter content and concentration of substrate A	
			B	C
N	3.28	2.43	2.92	3.11
P	0.87	0.35	0.45	0.56
K	4.20	2.39	2.52	3.32
Ca	1.16	0.25	0.30	0.36
Mg	0.43	0.11	0.13	0.16

Statistical evaluation of this recalculation table is in original data in Table 3

half of organic nitrogen mineralized and enriched the original 1% content of the substrate before the fermentation process. Yet, the dry matter content decreased in the course of fermentation, and therefore the concentration of all nutrients in digestate apparently increased contrary to the original substrate. In our experiment the concentration of substrate dry matter decreased from 19.3 to 13.3% by weight during anaerobic digestion. The content of mineral nitrogen amounting to 3.28% at this dry matter content corresponds to 2.26% of min. N at the original dry matter content of 19.3% by weight (Table 2). The contents of the nutrients P, K, Ca and Mg in digestate dry matter after anaerobic digestion (Table 2) are apparently substantially higher than before fermentation. However, anaerobic digestion did not actually bring about any increase in the content of these nutrients, and the increased concentrations completely correspond to a reduction in dry matter content, 19.3:13.3 = 1.45.

It is not a new fact, but Table 2 shows how this mineral nitrogen is transferred to the liquid phase of substrates B and C compared to substrate A. Obviously, the liquid phase of substrate B has a higher amount of mineral nitrogen than that of substrate A, and so the effects of the screw press, which – already before anaerobic digestion – enriched the liquid substrate B with colloid sols of nitrogen organic compounds from the crushed cell walls of the plant material that provided further mineral nitrogen during fermentation, were significantly positive at the same temperature. It was still more evident in the liquid phase of substrate C while a conclusion can be drawn that a higher temperature contributes to higher extraction of insoluble or partly soluble nitrogen organic compounds from which further mineral nitrogen is released after subsequent fermentation.

Table 3 documents the original, i.e. before the recalculation, concentrations of mineral nutrients in the liquid phase of substrates A, B and C. These results indicate that liquid phase A can be considered as a highly diluted mineral fertilizer. Even though the IFBB process increases the concentration of nutrients (nitrogen) in the liquid phase before and after fermentation (liquid phase B and C), the dilution is very high. The recommended dilution with water, used by Wachendorf et al. (2009) as well as in our experiments, produces liquid wastes diluted after anaerobic digestion to such an extent that they are practically hardly utilizable as a solution of mineral nutrients. Fugates are still rather problematic as mineral fertilizers, especially for applications in humid years and to soils with low microbial activity; consequently they slow immobilization of mineral nitrogen,

Table 3. Contents of mineral nutrients after anaerobic digestion (42 days, 40°C) in the liquid phase of digestate A and in the liquid phases B and C with the application of IFBB in % by weight of solutions that should be used for mineral fertilization

	Liquid phase		
	A	B	C
N	0.32 ± 0.03	0.09 ± 0.01	0.10 ± 0.01
P	0.05 ± 0.00	0.01 ± 0.00	0.02 ± 0.10
K	0.31 ± 0.04	0.08 ± 0.01	0.11 ± 0.15
Ca	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Mg	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

Sample size $n = 4$, reliability interval of the mean for a significance level $\alpha = 0.05$

Table 4. Proportions of the three pools of carbon in the solid phase of substrate A before anaerobic digestion (A_1), after anaerobic digestion (A_2) and in the solid phase of substrate A_1 after IFBB procedure before anaerobic digestion at 15°C (B) and at 60°C (C) as determined by the acid hydrolysis approach of Rovira and Vallejo (2002). Sample size n = 4, reliability interval of the mean for a significance level α = 0.05

Solid phase of substrate	Proportion		
	LP I	LP II	RP
A_1	43 ± 8	41 ± 7	16 ± 2
A_2	22 ± 4	20 ± 3	58 ± 8
B	39 ± 6	44 ± 6	17 ± 3
C	31 ± 6	47 ± 8	16 ± 2

Description of fractions according to the method of Rovira and Vallejo 2002: LP I (labile pool I) – the reserve of very labile, easily hydrolyzable organic matters expressed as % of the total amount of organic matter in a sample; LP II (labile pool II) – the reserve of medium labile, less easily hydrolyzable organic matters in %; RP – (recalcitrant pool) – the reserve of hydrolysis-resistant, very hardly degradable organic matters in %

and naturally they are hardly applicable to pervious soils.

Table 4 shows the results of hydrolytic experiments with solid phases of substrates A, B and C. They confirm a fact previously observed in work with substrate consisting of a mixture of pig slurry and primary sludge from a municipal waste water treatment plant, that the solid phases of wastes from anaerobic digestion cannot be efficient as mineral fertilizers because of their very low degradability (Kolář et al. 2008). The IFBB process, which enriches the liquid phases with organic, easily degradable substances and improves biogas yields during the anaerobic degradation of only liquid phases, further depletes the solid phases of substrates of these substances and impairs their quality as organic fertilizers, even though it is not the case of an increase in the resistant component but only in worse hydrolyzable labile pool II (LP II).

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