

Conversion technology of anaerobic digestates from biogas plants to fertilizer formulation

<u>**Mateusz Samoraj**^{a,b}</u>, Krzysztof Trzaska^a, Dawid Skrzypczak^a, Katarzyna Chojnacka^a

^aDepartment of Advanced Material Technologies, Wrocław University of Science and Technology, Smoluchowskiego 25, 50-372 Wrocław, Poland

^bEKOPLON Sp. z o.o. sp. k., Grabki Duże 82, 28-225 Szydłów, Poland



Introduction

- The fertilizer industry is currently facing a crisis due to the availability and price of raw materials.
- Population growth rate exceeds grain yield by three times, crop area remains the same. The global crisis has made the situation much worse, millions of people are at risk of starvation.
- Waste materials are invaluable alternative source of nutrients. A promising raw material is the digestate from biogas production
- Today, the main goal is to improve the efficiency of fertilizer ingredients while reducing the environmental impact of their use.



Biomethane plants - future and challenges

Currently, in Poland there are 126 registered agricultural biogas plants with a total production capacity of **600 million m³/year**.

Even though the number of biogas plants has decreased since last year, their total capacity has **increased by 13%** (from 532 million m³/year to 600

million m³/year).

68%

32%

Agricultural biogas producers with fertilizer registration

Agricultural biogas producers without fertilizer registration



Figure 1. Number of biogas plants in Poland (source: Register of Agricultural Biogas Producers, KOWR)

Figure 1. Participation of agricultural biogas producers with fertilizer registration in 2019. mateu



Raw material selection





Composition of anaerobic digestates

Table 1. Composition of anaerobic digestates -macronutrients, micronutrients and toxic elements.

Matoriala	Macronutrients										
waterials	C [%]	N [%]	P ₂ O ₅ [%]	K ₂ O [%]	CaO [%]	MgO [%]	Na ₂ O [%]	SO ₃ [%]			
SUGAR BEET DIGESTATE	1.53 ±0.15	0.486 _0.049	0.0298 ±0.0045	0.0157 ±0.0023	0.0182 ±0.0027	0.0216 ±0.0032	0.0172 ±0.0026	0.0325 ±0.0049			
PLANT AND FOOD DIGESTATE	2.61 ±0.26	$\begin{array}{c} 0.808 \\ \pm 0.081 \end{array}$	0.577 ±0.087	0.303 ±0.046	0.352 ±0.053	0.417 ±0.063	0.334 ±0.050	0.629 ±0.094			

Micronutrients								Toxic elements					
Waterials	B [mg/kg]	Co [mg/kg]	Cu [mg/kg]	Mn [mg/kg]	Mo [mg/kg]	Zn [mg/kg]	Cd [mg/kg]	Cr [mg/kg]	Pb [mg/kg]	Ni [mg/kg]	As [mg/kg]	Hg [mg/k <mark>g]</mark>	
SUGAR BEET DIGESTATE	10.9 ±1.6	0.967 ±0.145	3.20 ±0.48	15.5 ±2.3	4.24 ±0.64	7.66 ±1.15	0.427 ±0.064	1.36 ±0.20	4.14 ±0.62	8.24 ±1.24	18.6 ±2.8	0.0230 ±0.0035	
PLANT AND FOOD DIGESTATE	3.34 ±0.50	0.125 ±0.019	2.41 ±0.36	13.2 ±2.0	3.00 ±0.45	16.8 ±2.5	0.477 ±0.072	1.65 ±0.25	<lod< th=""><th>6.73 ±1.01</th><th><lod< th=""><th>0.0480 ±0.0072</th></lod<></th></lod<>	6.73 ±1.01	<lod< th=""><th>0.0480 ±0.0072</th></lod<>	0.0480 ±0.0072	



Selection of hydrolysis conditions

Table 2. Composition of anaerobic digestates divided into macronutrients and micronutrients

				Macro		Micronutrients								
Sample					[%]			[mg/kg]						
	С	Ν	P_2O_5	K ₂ O	CaO	MgO	Na ₂ O	SO3	В	Со	Cu	Mn	Мо	Zn
Acid hydrolyzate	1.60±0.16	0.703 ±0.070	2.45±0.37	1.29±0.19	1.49±0.22	1.77±0.27	1.42±0.21	2.67±0.40	7.24±1.09	1.04±0.16	1.47±0.22	9.85±1.48	<2.50	11.2±1.7
Alkaline hydrolysate	2.33±0.23	0.508±0.051	0.518±0.078	0.273±0.041	0.317±0.047	0.375±0.056	0.300±0.045	0.566±0.085	2.09±0.31	0.442±0.066	3.22±0.48	11.7±1.8	<2.50	19.0±2.9

Table 3. Concentration of amino acids in the hydrolysate after acid and alkaline hydrolysis [mg/L]

Amino Acids	Alanine	Arginine	Aspartate	Aspartic acid	Cysteine	Glutamic acid	Glycine	Histidine	Leucine	Lysine	Methionine	Phenylalanine	Proline	Serine	Threonine	Tyrosine	Valine	TOTAL
	Ala	Arg	Asn	Asp	Cys-Cys	Glu	Gly	His	Leu	Lys	Met	Phe	Pro	Ser	Thr	Tyr	Val	1
A <mark>cid</mark> hydrolyzate	1819 ±55	11.0 ±0.3	8.00 ±0.24	10.6 ±0.3	15.0 ±0.5	7.28 ±0.22	19.2 ±0.6	12.6 ±0.4	7.24 ±0.22	-	38.3 ±1.1	9.13 ±0.27	9.47 ±0.28	5.91 ±0.18	4.09 ±0.12	1.12 ±0.03	3.54 ±0.11	1981
Alkaline hydrolysate	18.2 ±0.5	9.01 ±0.27	9.72 ±0.29	10.9 ±0.3	13.3 ±0.4	12.7 ±0.4	9.86 ±0.30	13.1 ±0.4	20.9 ±0.6	14.3 ±0.4	8.98 ±0.27	12.1 ±0.4	8.17 ±0.25	_	5.84 ±0.18	9.33 ±0.28	9.85 ±0.30	186

± - measurement error resulting from the method



Comparison of granulation methods





Comparison of nitrogen balances



Figure 4. Nitrogen (N) Balance for the Standard Production Process of Fertilizer (A) and Granulation with Slow Ash Addition (B) per 1 kg of Formulations, Accounting for 15% Measurement Error



Microbiological analysis

Table 4. Microbiological Characteristics of Digestate, Hydrolyzed Digestate, and Fertilizer in Colony-Forming Units per mL for Digestate and Hydrolyzed Digestate, and per g for Granular Fertilizer (TNM, the total number of microorganisms; TNY, the total number of yeasts; TNF, the total number of moulds; ND, not detected)

Sample	TNM TNY		TNF	<i>Salmonella</i> sp. [in 25 g]	Escherichia coli	Coliforms	
DIGESTATE (per ml)	3.7 x 10 ⁵	<10	$4.0 \ge 10^1$	ND	<10	7.1 x 10 ⁴	
HYDROLYZED DIGESTATE (per ml)	<10	<10	<10	ND	<10	<10	
GRANULAR FERTILIZER (per g)	GRANULAR FERTILIZER (per g) 7.9 x 10 ³		<10	ND	<10	<50	



Selection of mineral nitrogen source



10



Comparison of nitrogen balances



Figure 6. Nitrogen balance of the preparation of 1kg of granular fertilizer

Figure 7. Nitrogen balance of the preparation of 1kg granular fertilizer with ammonium nitrate



Comparison of nitrogen balances





Balance of macronutrients



Figure 9. Balance of Macronutrients (NPK) in Urea Enriched Fertilizer Production Process per 1 Ton of Formulation, with 15% Measurement Uncertainty According to ISO 17025 Quality Management System



Granules fraction



Figure 10. Comparison of 3 granule fractions. 0.75mm-1mm fraction (A.) 1mm-2mm fraction (B.) 2mm-4mm fraction (C.)



Table 5. Amino acid content of different types of fertilizers and hydrolysates. The results are presented in mg/kg for solid products and mg/L for liquid products.

AMINO A	CIDS	ACID HYDROLYSATE Amino acid concentration (mg/L)	GRANULAR FERTILIZER Amino acid content (mg/kg)			
Alanine	Ala	1819±55	469±15			
Arginine	Arg	11.0±0.3	27.4±0.8			
Aspartate	Asn	8.00±0.24	21.8±0.7			
Aspartic acid	Asp	10.6±0.3	22.0±0.7			
Cysteine	Cys-Cys	15.0±0.5	48.6±0.8			
Glutamic acid	Glu	7.28±0.22	25.6±0.9			
Glycine	Gly	19.2±0.6	13.8±0.5			
Histidine	His	12.6±0.4	30.6±1.3			
Leucine	Leu	7.24±0.22	27.5±0.2			
Lysine	Lys	-	28.7±0.9			
Methionine	Met	38.3±1.1	61.1±1.7			
Phenylalanine	Phe	9.13±0.27	31.5±0.9			
Proline	Pro	9.47±0.28	18.8±0.7			
Serine	Ser	5.91±0.18	15.4±0.6			
Threonine	Thr	4.09±0.12	15.3±0.9			
Tyrosine	Tyr	1.12±0.03	1.46±0.04			
Valine	Val	3.54±0.11	-			
TOTA	L	1981	883			



Final formulation

Table 6. Elemental composition of macronutrients of fertilizer granulated with blood as a nitrogen source and modified granulating agent to peat with ash addition.

		Macronutrients									
Materials	C [%]	N [%]	P ₂ O ₅ [%]	K ₂ O [%]	CaO [%]	MgO [%]	SO ₃ [%]				
FINAL	38,3	8,57	3,40	2,02	1,99	0,471	6,44				
FORMULATION	±3,8	±0,86	±0,5 1	±0,30	±0,30	±0,071	±0,97				
REQUIREMENT OF EU 2019/1009 REGULATION	>7,5%	>2%									



Table 7. Elemental composition of micronutrients of fertilizer granulated with blood as a nitrogen source and modified granulating agent to peat with ash addition.

Figure 11. Proportions of raw materials (%m/m) in fertilizer granulated with blood as a nitrogen source and modified granulating agent to peat with ash addition.

						0	5 5	1		
	0	Micron	utrients		Toxic elements					
Materials	Cu [%]	Fe [%]	Mn [%]	Zn [%]	As [mg/kg]	Cd [mg/kg]	Cr (VI) [mg/kg]	Ni [mg/kg]	Pb [mg/kg]	
FINAL	0,376	0,343	0,0470	1,23	25 0+5 2	1 72±0 26	-0.500	6 07+1 04	-6.00	
FORMULATION	±0,056	±0,051	±0,0070	±0,18	55,0±5,2	1,75±0,20	<0,300	0,97±1,04	<0,00	
REQUIREMENT OF										
EU 2019/1009					40	<3	2	50	120	
REGULATION										



Next steps



Scale up to pilot plant

transfer of verified technology to pilot-scale



Tests on plants

utilitatian tests in field conditions



Biofortification

verification if increased doses of micronutrients in plants will allow for biofortification of animal products





This work was financed by European Union's Horizon2020 Research & Innovation Programme under grant agreement No 696356 and from the Executive Agency for Higher Education, Research, Development and Innovation Funding - UEFISCDI (Romania), the National Centre for Research and Development - NCBR (Poland), Agenda Estatal de Im/estigación - AEI (Spain), and the Ministry of Agriculture and Forestry- MMM (Finland).



Thank you for your attention!

Mateusz Samoraj, PhD

Department of Advanced Material Technologies, Wrocław University of Technology Smoluchowskiego 25, 50-372 Wrocław, Poland mail: mateusz.samoraj@pwr.edu.pl Tel. +48 71 320 3437