

# ADM1-based modeling of anaerobic codigestion of maize silage and cattle manure – a feedstock characterisation for model implementation (part I)

Ewa Klimiuk, Zygmunt Mariusz Gusiatin, Katarzyna Bułkowska\*, Tomasz Pokój,  
Sabina Rynkowska

University of Warmia and Mazury in Olsztyn, Poland  
Faculty of Environmental Sciences  
Department of Environmental Biotechnology

\*Corresponding author's e-mail: katarzyna.bulkowska@uwm.edu.pl

**Keywords:** cattle manure, maize silage, anaerobic digestion, ADM1 modeling.

**Abstract:** This paper presents the results of fractionation of particulate and soluble organic matter in a mixture of maize silage and cattle manure (49:51% volatile solids) that was used as a feedstock for anaerobic digestion. The extended Weender's analysis was adapted to measure raw protein, raw lipids, fraction of carbohydrates (including starch, cellulose, hemicelluloses) and lignin. The content of individual fractions in composite,  $X_c$  (as kg COD kg<sup>-1</sup> COD) was: 0.111 proteins, 0.048 lipids, 0.500 carbohydrates and 0.341 inerts. The biodegradability of  $X_c$  was 68%. Based on material balance, the carbon concentration in  $X_c$  was 0.0326 kmol C kg<sup>-1</sup> COD, whereas nitrogen concentration 0.0018 kmol N kg<sup>-1</sup> COD. The estimated pH of the feedstock based on acid-base equilibrium corresponded to the actual value (pH 7.14).

## Introduction

The technology of anaerobic digestion is being intensely developed, because it allows for simultaneous stabilization of biowaste and production of biogas as a renewable energy source. However, it is a complex multi-step process and shows a tendency to deteriorate, especially when the composition of feedstock or operational conditions for processes are improperly chosen. In addition, empirical identification of the factors affecting the performance and stability of an anaerobic digester requires long-term experiments at pilot or technical scale. For that reason, much attention has focused on the development of simulation techniques using mathematical models. Recently, the most promising is the Anaerobic Digestion Model No. 1 (ADM1), proposed in 1997 by the International Water Association's (IWA) Task Group on Mathematical Modelling (Batstone et al. 2002). Primarily, the ADM1 was intended for modeling biogas production from sewage sludge. At present, due to the rapid development of biogas plants operating with agricultural waste and biomass from energy crops as a feedstock, there is a much effort to use the ADM1 to simulate the production of agricultural biogas.

There are two key issues to be resolved: 1) properly defined feedstock composition in relation to the model state input variables, and 2) calibration (estimation of the model's sensitive parameters). Determination of substrate composition is complicated by the fact that agricultural waste and biomass from energy crops are rich in fiber materials, consisting of

several main components, such as cellulose, hemicellulose and lignin. As a consequence, many methodologies have been developed for substrate fractionation, including elemental analysis and anaerobic respirometry (Girault et al. 2010). In addition, the results of the simulation depend strongly on proper calibration of kinetic parameters (Koch et al. 2010).

Until now, studies on the use of the ADM1 model to simulate agricultural biogas production are not numerous. Some investigations have been conducted in batch reactors using monosubstrates such as cattle manure (Myint et al. 2007), pig slurry (Girault et al. 2012) or sweet sorghum extract (Antonopoulou et al. 2012). Wichern et al. (2009) and Koch et al. (2010) have used the ADM1 for the dynamic simulation of biochemical processes in the fermentation of grass silage. The ADM1 has also been adapted for waste digested with different co-substrates such as cattle manure with renewable energy crops (corn silage, crop groats, soy pellet, hay) in a 3.5 m<sup>3</sup> pilot-scale biogas reactor (Lübken et al. 2007). In order to obtain the database necessary to design and operate biogas plants, there is a great need to continue this type of research.

In Poland, waste conversion into biogas is being intensively developed. However, experience in the design of anaerobic digestion and biogas plants is generally low. For these reasons, the development of this technology can be significantly accelerated by simulating the process with models. In this context, the ADM1 can be a useful tool to assist operation and control of full-scale anaerobic digesters. The present study describes the ADM1 model, including

the fractionation and preparation of substrate in the form of maize silage and cattle manure mixture, as examples of typical substrates in agricultural biogas plants.

The paper is divided into two parts. Part I presents how fractions of proteins, lipids, carbohydrates and inerts in maize silage and cattle manure mixture were estimated experimentally. Next, carbon and nitrogen were balance-checked using stoichiometric coefficients. Finally, the matrix of steady-state influent variables for the ADM1 was prepared. Part II shows how the ADM1 was calibrated with experimental data from the anaerobic digestion of a mixture of maize silage and cattle manure in a lab-scale reactor and verified.

## Theoretical background – ADM1 description

### Biochemical processes in the ADM1

A scheme of anaerobic digestion including individual fractions of the substrate, intermediate metabolites and final products ( $\text{CH}_4$ ,  $\text{CO}_2$ ) is given in Figure 1. In the ADM1, it was assumed that substrates pose a complex material termed as composite ( $X_c$ ). The model includes the following processes: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. Disintegration can include an array of processes such as lysis, non-enzymatic decay, phase separation and physical breakdown. Hydrolysis belongs to extracellular processes. Disintegration with hydrolysis leads to the breakdown and solubilization of  $X_c$ . As a result of enzymatic hydrolysis, particulate carbohydrates, proteins and lipids are transformed to monosaccharides, amino acids and long-chain fatty acids.

During acidogenesis soluble sugars and long-chain volatile fatty acids are oxidized and amino acids are degraded

to products such as acetate, propionate and butyrate. The acids are further converted to acetate and molecular hydrogen (acetogenesis). Finally, methane can be produced in two ways: cleavage of acetate to methane by acetoclastic methanogens and/or reduction of carbon dioxide by molecular hydrogen to produce methane with hydrogenotrophic methanogens. All extracellular processes were assumed to be the first order reactions, which are empirical functions reflecting the cumulative effects of multi-step processes. The kinetics of cellular processes is described by the uptake of substrate, and the growth and decay of microorganisms.

### Dynamic state variables

The ADM1 model is based on a system of ordinary differential equations for the vectors of state variables. It includes 24 state variables of liquid phase (with units of  $\text{kg COD m}^{-3}$ ,  $\text{kmol C m}^{-3}$  and  $\text{kg N m}^{-3}$ ) (Batstone et al. 2002). The list of selected particulate ( $X_i$ ) and soluble ( $S_i$ ) components depending of substrate type is presented in Table 1.

### Rate equation matrix

The ADM1 involves 19 equations describing biochemical process rates, 3 equations referring to gas-liquid transfer processes and an additional six acid-base kinetic processes. Kinetic rate equations and stoichiometry matrices for biochemical processes for soluble and particulate components, acid-base reactions and liquid-gas reactions are given by Batstone et al. (2002).

Six additional physicochemical processes concerning pH calculation include the acid/base equilibria of  $\text{CO}_2/\text{HCO}_3^-$ ,  $\text{NH}_4^+/\text{NH}_3$ , acetic acid/acetate, propionic acid/propionate, butyric

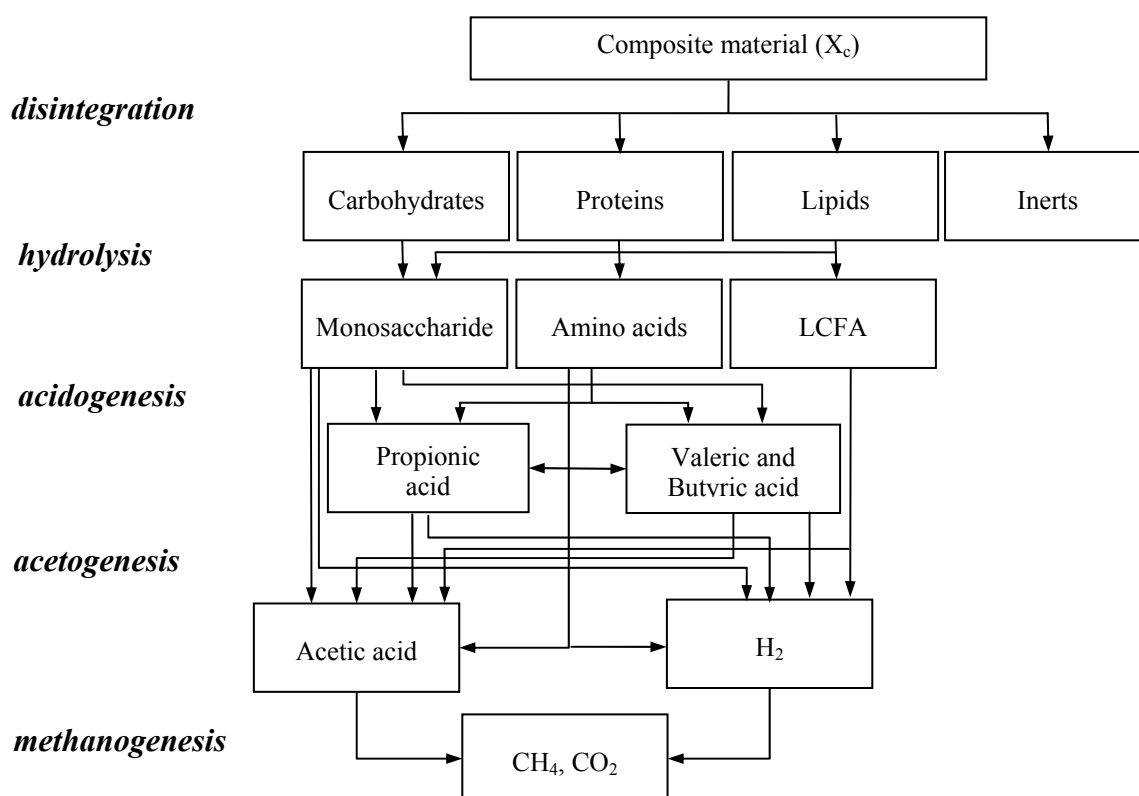


Fig. 1. COD flow chart for the main biochemical processes in anaerobic digestion used in the ADM1 (Batstone et al. 2002)

**Table 1.** The dynamic state variables for particulate and soluble components for different substrates in the ADM1

Components ( $X_i$ )		Unit	Activated sludge (Ramirez et al. 2009)	Activated sludge (Girault et al. 2010)	Sludge (Boubaker and Ridha 2008)	Activated sludge (Souza et al. 2013)	Cow manure* (Lyseng et al. 2012)	Cow manure (Zhou et al. 2011)	Corn silage (Zhou et al. 2011)	Grass silage (Zhou et al. 2011)
Symbol	Description									
$X_c$	Composite	kg COD m <sup>-3</sup>	2.89	–	–	12.1	0.32	10.04	36.5	93.4
$X_{ch}$	Carbohydrates	kg COD m <sup>-3</sup>	0.1	20.7	0.5	4.84	0.32	29.6	209.9	194.4
$X_{pr}$	Proteins	kg COD m <sup>-3</sup>	0.1	20.7	0.45	15.7	0.97	7.07	22.2	48.5
$X_{li}$	Lipids	kg COD m <sup>-3</sup>	0.1	13.3	0.3	3.63	0.65	5.87	18.68	25.4
$X_i$	Particulate inerts	kg COD m <sup>-3</sup>	12.0	34.8	19	12.1	30.1	46.5	78.5	136.6
$S_{su}$	Monosaccharides	kg COD m <sup>-3</sup>	0.01	18.2	0.005	0.18	2.05	13.38	–	–
$S_{aa}$	Amino acids	kg COD m <sup>-3</sup>	0.01	18.2	0.004	0.59	4.23	3.34	–	–
$S_{fa}$	Long-chain fatty acids (LCFA)	kg COD m <sup>-3</sup>	0.00	18.2	0.02	0.13	2.87	–	–	–
$S_{va}$	Valeric acid	kg COD m <sup>-3</sup>	0.079	–	0.01	0	–	–	–	–
$S_{pro}$	Propionic acid	kg COD m <sup>-3</sup>	0.707	–	0.01	0	–	–	–	–
$S_{bu}$	Butyric acid	kg COD m <sup>-3</sup>	0.144	–	0.01	0	–	–	–	–
$S_{ac}$	Acetic acid	kg COD m <sup>-3</sup>	0.321	–	0.01	0	–	–	–	–
$S_i$	Soluble inerts	kg COD m <sup>-3</sup>	0.00	–	0.65	0.90	4.51	7.06	9.51	13.09

\* – in liquid form

acid/butyrate and valeric acid/valerate. All these substances are made up of acid-base pairs (e.g.  $S_{va, total} = S_{va^-} + S_{hva^+}$ ).

The charge balance can be expressed as:

$$\sum S_{cat^+} - \sum S_{an^-} = 0 \quad (1)$$

where:  $\sum S_{cat^+}$  – the total concentration of cationic equivalents,  $\sum S_{an^-}$  – the total concentration of anionic equivalents.

## Material and methods

### Substrates

As substrate for the experiments on biogas production maize silage and cattle manure were obtained from a farm in Komorowo (Kujawsko-Pomorskie Region of Poland).

### Feedstock

The feedstock was prepared by mixing maize silage and cattle manure at a ratio of 49:51 (% VS). The mixture was diluted with water to obtain a concentration of total solids (TS) in the influent of 113.5 g kg<sup>-1</sup> TS, and of volatile solids of 93.5 g kg<sup>-1</sup> VS. The elemental composition of the feedstock, as analyzed by a FLASH 2000 (Thermo Scientific, USA), was C<sub>14.2</sub>H<sub>22</sub>O<sub>8.7</sub>N.

### Fractionation of the particulate and/or soluble organic matter in the feedstock

#### Particulate organic matter composition

The concentration of the following particulate organic compounds in the feedstock were determined: raw protein (RP); raw lipid (RL); raw fibre (RF); nitrogen free extracts (NfE); neutral detergent fibre (NDF); acid detergent fibre (ADF) and acid detergent lignin (ADL). The sum of RF and NfE was classified as carbohydrates, which were further divided into starch (RF + NfE – NDF), hemicelluloses (NDF – ADF), cellulose (ADF – ADL).

The organic matter in the feedstock was fractionated on the basis of an extended Weender analysis with the Van Soest's method (PN-EN ISO 13906:2009).

#### Soluble organic matter

The soluble organic matter in the feedstock was characterized according to the concentration of monosaccharides, amino acids and volatile fatty acids (VFAs).

Water soluble carbohydrates were determined by the anthrone method (Daniels et al. 1994). The value for the concentration of amino acids and VFAs from lipids ( $S_{fa'in}$ ) was

used according to Rosén and Jeppsson (2006) and amounted to 0.001 kg COD m<sup>-3</sup>. The concentrations of individual VFAs (i.e. valeric, butyric, propionic and acetic) were measured using a gas chromatograph (GC, Varian 3800, Australia) by the method given by Gilroyed et al. (2010).

### Chemical oxygen demand (COD) for organic fractions in the feedstock

The ADM1 is COD-based as a common base unit in substrate characterization. In order to express the concentration (as COD) of all fractions in the feedstock, theoretical oxygen demand (ThOD) was calculated. It is possible to make the calculation calculate based on the elemental formula of the feedstock and individual organic fractions. The following equations are recommended to be used (Koch et al. 2010):

$$C_a H_b O_c N_d + \left( \frac{4a - b - 2c + 3d}{4} \right) H_2O \rightarrow \quad (2)$$

$$\left( \frac{4a + b - 2c - 3d}{8} \right) CH_4 + \left( \frac{4a - b + 2c + 3d}{8} \right) CO_2 + dNH_3$$

$$ThOD = \frac{16(2a + 0.5(b - 3d) - c)}{12a + b + 16c + 14d} \text{ (kgO}_2 \cdot \text{kg}^{-1} \text{C}_a \text{H}_b \text{O}_c \text{N}_d \text{)} \quad (3)$$

The elemental formulas, molar mass and ThODs for the feedstock and individual particulate organic fractions are given in Table 2.

In order to obtain concentration of individual organic fractions in kg m<sup>-3</sup>, the concentration of each component (as %TS) was multiplied by concentration of total solids in the feedstock (113.5 g kg<sup>-1</sup>) and feedstock density ( $\rho = 1.0 \text{ kg m}^{-3}$ ). To obtain concentrations in kg COD m<sup>-3</sup>, the concentration of composite and individual organic fractions i.e. proteins, lipids, carbohydrates and lignin (kg m<sup>-3</sup>) was multiplied by ThOD of each compounds.

### Estimation of biodegradable organic matter ( $D_{VS}$ )

The degradable organic matter was estimated by the following equation (Koch et al. 2009):

$$D_{VS} = 1 - \frac{VS_D \cdot (1 - VS_F)}{VS_F \cdot (1 - VS_D)} \quad (\%) \quad (4)$$

where:  $VS_F$  – the loss on ignition of feedstock (%TS),  $VS_D$  – the loss on ignition of digestate (%TS).

**Table 2.** Elemental formulas, molar mass and ThOD values for feedstock and organic fractions

Component	Elemental formula	Molar mass (g mol <sup>-1</sup> )	ThOD (kg O <sub>2</sub> kg <sup>-1</sup> VS)	References
Feedstock	C <sub>14.2</sub> H <sub>22</sub> O <sub>8.7</sub> N	345	1.354	present study
Protein	C <sub>5</sub> H <sub>7</sub> O <sub>2</sub> N	113	1.42	Koch et. al. (2010)
Lipids	C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>	884	2.90	
Carbohydrates	(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>	162n	1.19	
Lignin	C <sub>10.92</sub> H <sub>14.24</sub> O <sub>5.76</sub>	237.44	1.56	

In this study, the  $D_{VS}$  amounted to:

$$D_{VS} = 1 - \frac{0.603 \cdot (1 - 0.826)}{0.826 \cdot (1 - 0.603)} = 68\%$$

### Other indicators in the matrix of ADM1

The other indicators include concentration of bicarbonates, ammonium and cations (sum of K, Mg, Ca, Na). Bicarbonates were calculated on the basis of total alkalinity measured by titration to pH 4.3 with normalized 0.1 M HCl using a Schott titroline system. The concentration of ammonium was determined according to standard methods (APHA 1992); cations were measured by atomic absorption spectrometry (Varian, 187 AA28OFS).

## Results and discussion

### Characterization of main components in the feedstock

The concentration of organics (as VS) in the feedstock and of raw protein, raw fat, carbohydrates (starch, cellulose, hemicelluloses) and lignin in the composite are given in Table 3.

In the literature, most data of chemical composition concern single substrates, i.e. plant biomass and manure. Lübken et al. (2007) found that in manure  $X_{pr}$  was 16.9% TS, whereas for  $X_{li}$  and  $X_{ch}$  5.3% TS and 57.7% TS, respectively. For comparison, the values obtained by Biernacki et al. (2013) for liquid cattle manure were: 14.1% TS (for  $X_{pr}$ ), 3.25% TS (for  $X_{li}$ ) and 64.8% TS (for  $X_{ch}$ ). Wichern et al. (2009) obtained 15.1% TS of proteins, 1.5% TS of lipids and 73.7% TS of carbohydrates in grass silage. Similar content of protein (17.1% TS), lipids (3.0% TS) and carbohydrates (71.1% TS) in the composite for grass silage were demonstrated by Koch et al. (2009). For maize silage  $X_{pr}$ ,  $X_{li}$  and  $X_{ch}$  were 10.3; 5.1 and 77.9% TS, respectively (Biernacki et al. 2013).

### Estimation of the content of individual fractions in composite

According to Koch et al. (2010) the content of biodegradable carbohydrates are the sum of fully degradable starch and degradable part of cellulose and hemicelluloses. As completely biodegradable compounds are proteins and lipids. The inerts

are the sum of non-degradable part of cellulose, hemicelluloses and lignin. The degradable part of cellulose and hemicelluloses was estimated based on degradation coefficient ( $d$ ) at known level of biodegradable organic matter ( $D_{VS}$ ). For that purpose the following equation was used (Koch et al. 2010):

$$d = \frac{NDF - VS(1 - D_{VS})}{(NDF - ADL)} \quad (5)$$

where: NDF – concentration of neutral detergent fibre, (kg COD kg<sup>-1</sup>) ADL – concentration of acid detergent lignin (kg COD kg<sup>-1</sup>).

In the study, it was assumed that the composite ( $X_c$ ) is the sum of four fractions: proteins ( $f_{pr_{Xc}}$ ), lipids ( $f_{li_{Xc}}$ ), carbohydrates ( $f_{ch_{Xc}}$ ) and inerts ( $f_{Xl_{Xc}}$ ) in relation to VS of the feedstock (expressed as COD), with the exception of soluble inerts ( $S_l$ ):

$$X_c = \sum (X_{pr}, X_{li}, X_{ch}, X_l) - S_l \quad (6)$$

assuming that:

$$f_{pr_{Xc}} + f_{li_{Xc}} + f_{ch_{Xc}} + f_{Xl_{Xc}} = 1 \quad (7)$$

The fractions of proteins ( $f_{pr_{Xc}}$ ), lipids ( $f_{li_{Xc}}$ ), carbohydrates ( $f_{ch_{Xc}}$ ) and inerts ( $f_{Xl_{Xc}}$ ) were calculated using the equations given below:

$$f_{pr_{Xc}} = \frac{RP}{X_c} = \frac{13.11}{118.11} = 0.111 \text{ (kgCOD kg}^{-1}\text{COD)} \quad (8)$$

$$f_{li_{Xc}} = \frac{RL}{X_c} = \frac{5.64}{118.11} = 0.048 \text{ (kgCOD kg}^{-1}\text{COD)} \quad (9)$$

$$f_{ch_{Xc}} = \frac{(RF + NfE - NDF) + (NDF - ADL) \cdot d}{X_c} = \frac{29.61 + 62.6 \cdot 0.470}{118.11} = 0.500 \text{ (kgCOD kg}^{-1}\text{COD)} \quad (10)$$

**Table 3.** Concentrations of individual components in the feedstock (standard deviation is given in parenthesis)

Symbol	Component	Values		
		%TS	kg m <sup>-3</sup>	kg COD m <sup>-3</sup>
$X_{COD}$	VS in feedstock	82.6	93.5 (±8.88)	126.6
$X_{pr}$	Protein	8.18	9.3 (±0.46)	13.11
$X_{li}$	Lipids	1.72	1.9 (±0.095)	5.64
$X_{ch}$	Starch	21.98	24.9 (±3.56)	29.61
	Cellulose	36.57	41.4 (±6.19)	49.26
	Hemicellulose	9.9	11.2 (±1.62)	13.34
$X_l$	Lignin	4.05	4.6 (±0.42)	7.15
$S_l$	Soluble inerts	–	–	8.49

$$f_{X_{l,Xc}} = \frac{ADL + ((NDF - ADL) \cdot (1 - d))}{X_c} = \frac{7.15 + 62.6 \cdot 0.530}{118.11} = 0.341 (\text{kgCOD kg}^{-1}\text{COD}) \quad (11)$$

The calculated values of organic fractions were presented in Table 4 and compared with data obtained by other authors.

By comparison of the values found in the literature with data from our study, it can be concluded that different substrates used for biogas production were characterized with variable participation of individual organic fractions. Grass silage contained more proteins than both the maize silage, the cattle manure and maize silage mixture. However, unmixed maize silage contained mainly carbohydrates, while the content of inerts was the lowest.

#### Estimation of carbon and nitrogen content in inerts

The carbon content of the product arising from disintegration of composite was examined according to the equation:

$$C_{X_c} = f_{C_{Xl}} \times X_l + f_{C_{Xpr}} \times X_{pr} + f_{C_{Xch}} \times X_{ch} + f_{C_{Xli}} \times X_{li} \quad (12)$$

The carbon content in composite ( $C_{X_c}$ ), proteins ( $C_{X_{pr}}$ ), lipids ( $C_{X_{li}}$ ) and carbohydrates ( $C_{X_{ch}}$ ) was calculated using the data in Tables 2 and 3 showing an elemental formulas and organic fractions in the feedstock. Taking into account the feedstock composition ( $C_{14.2}H_{22}O_{8.7}N$ ) it follows that  $X_c$  is equivalent to  $0.0304 \text{ kmol C kg}^{-1} \text{ COD}$ . For proteins, lipids and carbohydrates the carbon contents were 0.03; 0.022 and  $0.0313 \text{ kmol C kg}^{-1} \text{ COD}$ , respectively. The carbon content in inerts ( $C_{X_l}$ ) was calculated as a difference  $C_{X_c} - C_{X_{pr}} - C_{X_{li}} - C_{X_{ch}}$  and amounted to  $0.007 \text{ kmol C kg}^{-1} \text{ COD}$ . For comparison, the carbon content in composite for manure amounted to  $0.028 \text{ kmol C kg}^{-1} \text{ COD}$ ,  $0.03 \text{ kmol C kg}^{-1} \text{ COD}$  in proteins,  $0.022 \text{ kmol C kg}^{-1} \text{ COD}$  in lipids and  $0.0313 \text{ kmol C kg}^{-1} \text{ COD}$  in carbohydrates. In particulate inerts,  $C_{X_l}$  was  $0.03 \text{ kmol C kg}^{-1} \text{ COD}$  (Schön 2009). Wett et al. (2006) determined that for agricultural waste the carbon content in composite ( $C_{X_c}$ ) was  $0.028 \text{ kmol C kg}^{-1} \text{ COD}$ .

The content of nitrogen includes ammonium release from disintegration products of composite materials, according to equation:

$$N_{X_c} = f_{N_{Xl}} \times X_l + f_{N_{Xpr}} \times X_{pr} + f_{N_{Xch}} \times X_{ch} + f_{N_{Xli}} \times X_{li} \quad (13)$$

Because carbohydrates and lipids contain no nitrogen, the nitrogen content can be simplified to the form:

$$N_{X_c} = f_{N_{Xl}} \times X_l + f_{N_{Xpr}} \times X_{pr} \quad (14)$$

In the present study, the nitrogen content in composite material, determined based on elementary analysis of the feedstock, was equal to  $0.00175 \text{ kmol N kg}^{-1} \text{ COD}$  ( $N_{X_c}$ ). For proteins, the nitrogen concentration was taken from literature and amounted to 6.25% (Batstone et al. 2003). On this basis, the nitrogen content in proteins ( $N_{X_{pr}}$ ) was  $0.00352 \text{ kmol N kg}^{-1} \text{ COD}$ . The nitrogen content in inerts ( $N_{X_l}$ ) calculated from the difference between  $N_{X_c}$  and  $N_{X_{pr}}$ , amounted to  $0.005 \text{ kmol N kg}^{-1} \text{ COD}$ . Schön et al. (2009) evaluated the nitrogen content in composite ( $N_{X_c}$ ) as  $0.0026 \text{ kmol N kg}^{-1} \text{ COD}$ , in aminoacids and proteins as  $0.00715 \text{ kmol N kg}^{-1} \text{ COD}$ , whereas in particulate inerts as  $0.0014 \text{ kmol N kg}^{-1} \text{ COD}$ . Comparable value of the nitrogen content in composite was obtained by Wett et al. (2006) for agricultural waste.

#### Acid-base equations

In anaerobic digestion systems, acid-base equilibrium reactions of VFAs, ammonium and the bicarbonate system are important. VFAs affect the alkalinity and pH of the system, which in turn can have inhibitory effects on the processes. Moreover, in ADM1, inorganic nitrogen (i.e. ammonium) is considered as it influences pH and limits biomass growth. Ammonium inhibition occurs mainly at high pH, which favors deprotonation of ammonium. The charge balance is as follows:

$$S_{\text{cat}^+} + S_{\text{nh}_4^+} + S_{\text{H}^+} - S_{\text{hco}_3^-} - S_{\text{ac}^-}/64 - S_{\text{pro}^-}/112 - S_{\text{bu}^-}/160 - S_{\text{va}^-}/208 - S_{\text{OH}^-} - S_{\text{an}^-} = 0 \quad (15)$$

The concentrations of ammonium, bicarbonates, cations and anions were measured experimentally. The concentration of dissociated forms of individual VFAs was calculated using the formula given by Batstone et al. (2002):

$$S_{\text{VFA}^-} = \frac{K_{a,\text{VFA}} S_{\text{VFA},\text{total}}}{K_{a,\text{CO}_2} + S_{\text{H}^+}} \quad (16)$$

where:  $K_{a,\text{VFA}}$ ,  $K_{a,\text{CO}_2}$  – the acid-base equilibrium coefficients,  $S_{\text{VFA},\text{total}}$  – total concentration of VFAs,  $S_{\text{H}^+}$  – concentration of hydrogen.

**Table 4.** Composite COD fractioning according to f-factor

Parameter	Koch et al. (2010)	Biernacki et al. (2013)		present study
	grass silage	grass silage	maize silage	mixture of cattle manure and maize silage
Protein from $X_c$ ( $f_{pr,Xc}$ )	0.187	0.21	0.11	0.111
Lipids from $X_c$ ( $f_{li,Xc}$ )	0.033	0.04	0.055	0.048
Carbohydrates from $X_c$ ( $f_{ch,Xc}$ )	0.401	0.54	0.695	0.500
Inerts from $X_c$ ( $f_{Xl,Xc}$ )	0.379	0.21	0.140	0.341
$d$	0.36	–	–	0.470
$D_{VS}$ (%)	60	79	86.4	68

The concentration of hydrogen can be calculated according to Batstone et al. (2002), using the following equation (17):

$$[S_{H^+}] = \frac{\Theta^2 + \sqrt{\Theta^2 + 4Kw}}{2} \quad (17)$$

where  $\Theta$  can be calculated as follows:

$$\Theta = S_{hco3-} + S_{ac-}/64 + S_{pro-}/112 + S_{bu-}/160 + S_{va-}/208 + S_{OH-} + S_{an-} - S_{cat+} - S_{nh4+} \quad (18)$$

Assuming that  $pH = -\log_{10}[S_{H^+}]$ , pH amounted to 7.14.

The values of steady-state influent variables for the ADM1 were tabulated in Table 5.

In the present study, among 33 steady-state influent variables for the ADM1, 15 variables were determined experimentally, whereas the rest was adopted from literature. Apart from 24 variables, indicated as in Batstone et al. (2002), additional 9 variables were added. They included particulate products arising from biomass decay ( $X_p$ ), cations ( $S_{cat}$ ), anions ( $S_{an}$ ), dissociated valerate ( $S_{va-}$ ), butyrate ( $S_{bu-}$ ), propionate ( $S_{pro-}$ ), acetate ( $S_{ac-}$ ), concentration of bicarbonate ( $S_{hco3}$ ) and ammonia ( $S_{nh3}$ ) necessary for estimation of acid-base equilibrium.

The authors using modeling of fermentation usually do not provide data of soluble components in substrate unlike particulate components. Comparison of the obtained results with literature data is difficult due to the fact that the values of different components depend on the manner how to create the matrix of steady-state input variables. According to Koch et al. (2010), the composite ( $X_c$ ) is a sum of all particulate

**Table 5.** Steady-state influent variable values for the ADM1

No.	Variable	Unit	Influent	After disintegration	Manner of estimation
1	$S_{su}$	kg COD m <sup>-3</sup>	0.2400		experiment
2	$S_{aa}$	kg COD m <sup>-3</sup>	0.0011		default*
3	$S_{fa}$	kg COD m <sup>-3</sup>	0.0010		default
4	$S_{va}$	kg COD m <sup>-3</sup>	0.1680		experiment
5	$S_{bu}$	kg COD m <sup>-3</sup>	0.3900		experiment
6	$S_{pro}$	kg COD m <sup>-3</sup>	0.7454		experiment
7	$S_{ac}$	kg COD m <sup>-3</sup>	2.3467		experiment
8	$S_{h2}$	kg COD m <sup>-3</sup>	0.0000		default
9	$S_{ch4}$	kg COD m <sup>-3</sup>	0.0000		default
10	$S_{co2}$	kg COD m <sup>-3</sup>	0.0000		default
11	$S_{nh4}$	kmole N m <sup>-3</sup>	0.018571429		experiment
12	$S_l$	kg COD m <sup>-3</sup>	8.4900		experiment
13	$X_c$	kg COD m <sup>-3</sup>	118.1111		experiment
14	$X_{ch}$	kg COD m <sup>-3</sup>	0.0000	59.0555	experiment
15	$X_{pr}$	kg COD m <sup>-3</sup>	0.0000	13.1103	experiment
16	$X_{li}$	kg COD m <sup>-3</sup>	0.0000	5.6693	experiment
17	$X_{su}$	kg COD m <sup>-3</sup>	0.0855		default
18	$X_{aa}$	kg COD m <sup>-3</sup>	0.0637		default
19	$X_{fa}$	kg COD m <sup>-3</sup>	0.0670		default
20	$X_{c4}$	kg COD m <sup>-3</sup>	0.0280		default
21	$X_{pro}$	kg COD m <sup>-3</sup>	0.0135		default
22	$X_{ac}$	kg COD m <sup>-3</sup>	0.0900		default
23	$X_{h2}$	kg COD m <sup>-3</sup>	0.0430		default
24	$X_l$	kg COD m <sup>-3</sup>	0.0000	40.2759	experiment
25	$X_p$	kg COD m <sup>-3</sup>	0.0008		default
26	$S_{cat}$	kmole m <sup>-3</sup>	0.080000000		experiment
27	$S_{an}$	kmole m <sup>-3</sup>	0.020000000		experiment
28	$S_{va-}$	kg COD m <sup>-3</sup>	0.167069985		experiment
29	$S_{bu-}$	kg COD m <sup>-3</sup>	0.387963936		experiment
30	$S_{pro-}$	kg COD m <sup>-3</sup>	0.740940795		experiment
31	$S_{ac-}$	kg COD m <sup>-3</sup>	2.335989136		experiment
32	$S_{hco3}$	kmole C m <sup>-3</sup>	0.032300000		experiment
33	$S_{nh3}$	kmole N m <sup>-3</sup>	0.0004		default

\* The default values were adopted from Batstone et al. (2002) and Rosén and Jeppsson (2006)

components in input, whereas Rosén and Jeppsson (2006) define composite as an individual fraction, beyond particulate proteins, lipids and carbohydrates.

## Conclusions

1. The matrix in ADM1 contains 33 steady-state influent variables, therein 15 were estimated experimentally, whereas the other were taken as default from literature.
2. Degradation coefficient ( $d$ ) for the mixture of maize silage and cattle manure was 0.47. On this basis, inert fraction in composite ( $X_c$ ) was 0.341 kg COD kg<sup>-1</sup> COD; proteins 0.111 kg COD kg<sup>-1</sup> COD; lipids 0.048 kg COD kg<sup>-1</sup> COD and carbohydrates 0.5 kg COD kg<sup>-1</sup> COD.
3. The carbon and nitrogen contents in  $X_c$  were 0.0326 kmol C kg<sup>-1</sup> COD and 0.0018 kmol N kg<sup>-1</sup> COD, respectively; while in inert fraction – 0.007 kmol C kg<sup>-1</sup> COD and 0.005 kmol N kg<sup>-1</sup> COD.
4. The pH calculated from acid-base equilibrium amounted to 7.14 and was consistent with the experimental data (pH 7.12 ± 0.19).

## Acknowledgements

The authors acknowledge and are grateful for the financial support of the strategic program of the National (Polish) Centre for Research and Development (NCBiR): “Advanced Technologies for Energy Generation. Task 4: Elaboration of Integrated Technologies for the Production of Fuels and Energy from Biomass, Agricultural Waste and other Waste Materials” (Project No. SP/E/4/65786/10).

## References

- Antonopoulou, G., Gavala, H.N., Skiadas, I.V. & Lyberatos, G. (2012). ADM1-based modeling of methane production from acidified sweet sorghum extract in a two stage process, *Bioresource Technology*, 106, pp. 10–19.
- APHA (American Public Health Association) (1992). *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington 1992.
- Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H. & Vavilin, V.A. (2002). *Anaerobic digestion model No. 1. Scientific and Technical Report No. 13*, IWA Publishing, London 2002.
- Batstone, D.J., Pind, P.F. & Angelidaki, I. (2003). Kinetics of thermophilic anaerobic oxidation of straight and branched chain butyrate and valerate, *Biotechnology and Bioengineering*, 84, 2, pp. 195–204.
- Biernacki, P., Steinigeweg, S., Borchert, A. & Uhlenhut, F. (2013). Application of Anaerobic Digestion Model No. 1 for describing anaerobic digestion of grass, maize, green weed silage, and industrial glycerine, *Bioresource Technology*, 127, pp. 188–194.
- Boubaker, F. & Ridha, B.C. (2008). Modelling of the mesophilic anaerobic co-digestion of olive mill wastewater with olive mill solid waste using anaerobic digestion model No. 1 (ADM1), *Bioresource Technology*, 99, pp. 6565–6577.
- Daniels, L., Hanson, R.S. & Phillips, J.A. (1994). Metabolism. Chemical analysis, in: *Methods for General and Molecular Bacteriology*, Gerhardt P. & Wood W.A. (Eds.), American Society for Microbiology, Washington 1994.
- Gilroyed, B.H., Reuter, T., Chu, A., Hao, X., Xu, W. & McAllister, T.A. (2010). Anaerobic digestion of specified risk materials with cattle manure for biogas production, *Bioresource Technology*, 101, 15, pp. 5780–5785.
- Girault, R., Bridoux, G., Nauleau, F., Poullain, C., Buffet, J., Steyer, J.P., Sadowski, A.G. & Béline, F. (2012). A waste characterization procedure for ADM1 implementation based on degradation kinetics, *Water Research*, 46, 13, pp. 4099–4110.
- Girault, R., Steyer, J.P., Zaher, U., Sadowski, A.G., Nopens, I., Béline, F., Žak, A., Kujawski, O., Holm, N.C. & Roenner-Holm, S.G.E. (2010). Influent fractionation and parameter calibration for ADM1: Lab-scale and full-scale experiments. 2nd IWA/WEF Wastewater Treatment Modelling Seminar, WWTmod, Conference Proceedings, Québec, Canada, 28–30 March 2010, pp. 171–182.
- Koch, K., Lübken, M., Gehring, T., Wichern, M. & Horn, H. (2010). Biogas from grass silage – Measurements and modeling with ADM1, *Bioresource Technology*, 101, 21, pp. 8158–8165.
- Koch, K., Wichern, M., Lübken, M., Horn, H. (2009). Mono fermentation of grass silage by means of loop reactors, *Bioresource Technology*, 100, 23, pp. 5934–5940.
- Lübken, M., Wichern, M., Schlattmann, M., Gronauer, A. & Horn, H. (2007). Modelling the energy balance of an anaerobic digester fed with cattle manure and renewable energy crops, *Water Research*, 41, 18, pp. 4085–4096.
- Lyseng, B.C., Bergland, W., Botheju, D., Haugen, F. & Bakke, R. (2012). Biogas reactor modelling with ADM1, Telemark University College, Porsgrunn 2012.
- Myint, M., Nirmalakhandan, N. & Speece, R.E. (2007). Anaerobic fermentation of cattle manure: Modeling of hydrolysis and acidogenesis, *Water Research*, 41, 2, pp. 323–332.
- PN-EN ISO 13906:2009. Animal feeding stuffs – Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents.
- Ramirez, I., Mottet, A., Carrère, H., Déléris, S., Vedrenne, F. & Steyer, J.P. (2009). Modified ADM1 disintegration/hydrolysis structures for modeling batch thermophilic anaerobic digestion of thermally pretreated waste activated sludge, *Water Research*, 43, pp. 3479–3492.
- Rosén, C. & Jeppsson, U. (2006). Aspects on ADM1 implementation within the BSM2 framework. Tech. Report no. LUTEDX/(TEIE-7224)/1-35/(2006). Department of Industrial Electrical Engineering and Automation, Lund University, Lund, Sweden 2006.
- Schön, M. (2009). Numerical modelling of anaerobic digestion processes in agricultural biogas plants, Dissertation.
- Souza, T.S.O., Carvajal, A., Donoso-Bravo, A., Peña, M. & Fdz-Polanco, F. (2013). ADM1 calibration using BMP tests for modeling the effect of autohydrolysis pretreatment on the performance of continuous sludge digesters, *Water Research*, 47, pp. 3244–3254.
- Wett, B., Schoen, M., Phothilangka, P. Wackerle, F. & Insam, H. (2006). Model based design of an agricultural biogas plant – application of Anaerobic Digestion Model No. 1 for an improved chamber scheme. 7<sup>th</sup> International symposium on waste management problems in agro-industries, Amsterdam, 27–29 September, 2006.
- Wichern, M., Gehring, T., Fischer, K., Andrade, D., Lübken, M., Koch, K., Gronauer, A. & Horn, H. (2009). Monofermentation of grass silage under mesophilic conditions: Measurements and mathematical modeling with ADM1, *Bioresource Technology*, 100, 4, pp. 1675–1681.
- Zhou, H., Löffler, D. & Kranert M. (2011). Model-based predictions of anaerobic digestion of agricultural substrates for biogas production, *Bioresource Technology*, 102, pp. 10819–10828.



## Modelowanie kofermentacji kiszonki kukurydzy i obornika bydlęcego za pomocą ADM1 – charakterystyka wsadu surowcowego (część I)

**Streszczenie:** W pracy przedstawiono wyniki stężenia substancji chemicznych rozpuszczonych i nierozpuszczonych w mieszaninie kiszonki kukurydzy zwyczajnej i obornika bydlęcego (49:51% suchej masy organicznej), który wykorzystano jako substrat do wytwarzania biogazu. Do frakcjonowania nierozpuszczalnych związków organicznych, stanowiących kompozyt ( $X_c$ ), wykorzystano metodę Weender'a. Udział poszczególnych frakcji (jako ChZT) w kompozycie wyniósł: białka – 0,111, tłuszcze – 0,048, węglowodany – 0,500 oraz związki inertne – 0,341. Stężenie związków biodegradowalnych w kompozycie wyniosło 68%. Na podstawie bilansu materiałowego węgla i azotu obliczono, że stężenie węgla w kompozycie wynosi  $0,0326 \text{ kmol C kg}^{-1} \text{ ChZT}$ , zaś azotu  $0,0018 \text{ kmol N kg}^{-1} \text{ ChZT}$ . Odczyn (pH) wsadu surowcowego wyznaczony z równowagi kwasowo-zasadowej odpowiadał rzeczywistości, tj. 7,14.