

1 **Key issues in modeling and optimization of lignocellulosic biomass fermentative**  
2 **conversion to gaseous biofuels**

3 Karolina Kucharska<sup>a,\*</sup>, Iwona Hołowacz<sup>a</sup>, Donata Konopacka-Łyskawa<sup>a</sup>, Piotr Rybarczyk<sup>a</sup>,  
4 Marian Kamiński<sup>a</sup>

5 <sup>a</sup>Gdańsk University of Technology, Faculty of Chemistry, Department of Chemical and  
6 Process Engineering, 80-233 Gdańsk, Narutowicza 11/12 street, Poland

7 \*Corresponding author: [karkucha@pg.gda.pl](mailto:karkucha@pg.gda.pl)

8 **Abstract**

9 The industrial-scale production of lignocellulosic-based biofuels from biomass is expected to  
10 benefit society and the environment. The main pathways of residues processing include  
11 advanced hydrolysis and fermentation, pyrolysis, gasification, chemical synthesis and  
12 biological processes. The products of such treatment are second generation biofuels. The  
13 degree of fermentation of organic substances depends primarily on their composition and  
14 chemical structure. Optimization of fermentation conditions leads to better understanding of  
15 occurring processes. Therefore, an overview of recent developments in fermentation modeling  
16 is necessary to establish process parameters enabling high yields of biofuels production.  
17 Among process parameters affecting the yield and rate of biogas and biohydrogen, pH of the  
18 pulp, temperature, composition, biomass pre-treatment and digestion time are to be  
19 considered. The technology of anaerobic co-digestion has been intensively developed as a  
20 valuable solution for the disposal of organic wastes and sewage sludge. Modeling of biogas  
21 production from lignocellulosic biomass has been intensively investigated and is well  
22 described by adapted ADM1 model. Modeling of fermentative hydrogen production lacks a  
23 kinetic model incorporating process parameters with the view of pretreatment and  
24 fermentation. This paper presents the state-of-the-art on the problems related to  
25 lignocellulosic biomass pre-treatment and discusses the mechanisms of lignocellulosics  
26 conversion to gaseous biofuels.

27 **Keywords:** *lignocellulosic biomass, biomass conversion, biogas, biohydrogen, kinetic*  
28 *models, empirical models*

29

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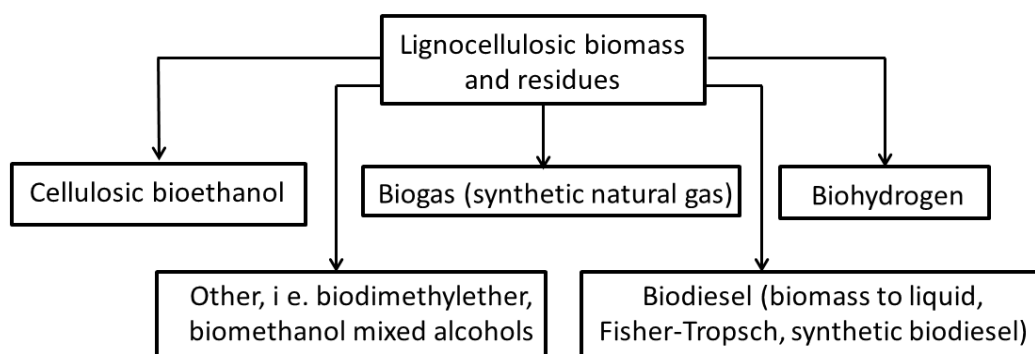
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## 56 1. Introduction

57

58 Large amounts of the biomass-originating energy come from processing of lignocellulosic  
59 biomass. Fuels generated from biomass include liquid and gaseous biofuels. Lignocellulosic  
60 materials consist of cellulose, hemicellulose, lignin and extractives. Cellulose and  
61 hemicellulose are a very good carbon source and may be potentially used in different  
62 biological processes after the pre-treatment step. This kind of biomass is typically inedible  
63 plant material, including crops of wood, grass, and agro-forest residues. Conversion of  
64 various types of biomass to useful products i.e. fuels has recently been an important topic  
65 both for scientific and industrial research.

66 The industrial-scale production of lignocellulosic-derived biofuels from plant biomass is  
67 expected to benefit society and the environment in numerous ways. The development of  
68 technologies for biomass processing focuses mainly on biorafination processes. Biogas and  
69 biohydrogen are the most important gaseous biofuels while the most popular liquid biofuels  
70 are bioethanol, biomethanol, biodiesel, bio-based methyl or ethyl tert-butyl ether and pure  
71 vegetable oil [1]. The main pathways of lignocellulosic biomass and residues processing are  
72 advanced hydrolysis and fermentation, pyrolysis, gasification, chemical synthesis and  
73 biological processes. The main products are second generation biofuels, as given in Figure 1.



74

75 Fig. 1. Overview of biofuels from lignocellulosic biomass and residues

76 Biomass conversion through fermentation processes is crucial because it allows for  
77 production of various groups of substances under relatively mild conditions. The degree of  
78 fermentation of organic substances depends primarily on their composition and chemical  
79 structure. Because of arising food versus fuel debate, only feedstocks for biofuels production  
80 that do not compete with the food request should be considered. Therefore, agricultural and  
81 forestry residues and wastes seem to be the most interesting sources of biomass, as their  
82 exploitation leads to energy recovery.

83 High hydrolysis ratio is needed for efficient utilization of monosugars present in  
84 lignocellulosic structures. During the hydrolysis, besides free sugars, also inhibitors (i.e.  
85 lignin derivatives) affecting further conversion processes are formed. From a biochemical  
86 point of view, organic substances present in the hydrolyzed solution can be divided into  
87 several groups of substances: simple and complex carbohydrates, proteins, lipids and  
88 heteropolymers. The potential of biogas and biohydrogen production from lignocellulosic

89 biomass may be enormous when sustainability is concerned. The efficiency of fermentation  
90 leading to biofuels, related with the type of pretreatment is widely discussed. The major  
91 problems related to biofuels production from lignocellulosic biomass lie basically in the  
92 conversion ratio of polymeric compounds into fermentable sugars such as hexoses and  
93 pentoses. This kind of processing must involve pretreatment steps such as physical, chemical  
94 and physicochemical pretreatment, biological or enzymatic treatment, fermentation and  
95 purification [2,3]. The recalcitrance of lignocellulosic materials requires pretreatment to  
96 facilitate enzymatic action [4]. To maximize the fermentation of hexoses and pentoses and to  
97 minimize the presence of inhibitors during fermentation processes for cellulosic biofuels,  
98 application of microbial metabolism in the degradation and saccharification of the plant cell  
99 wall is considered [5].

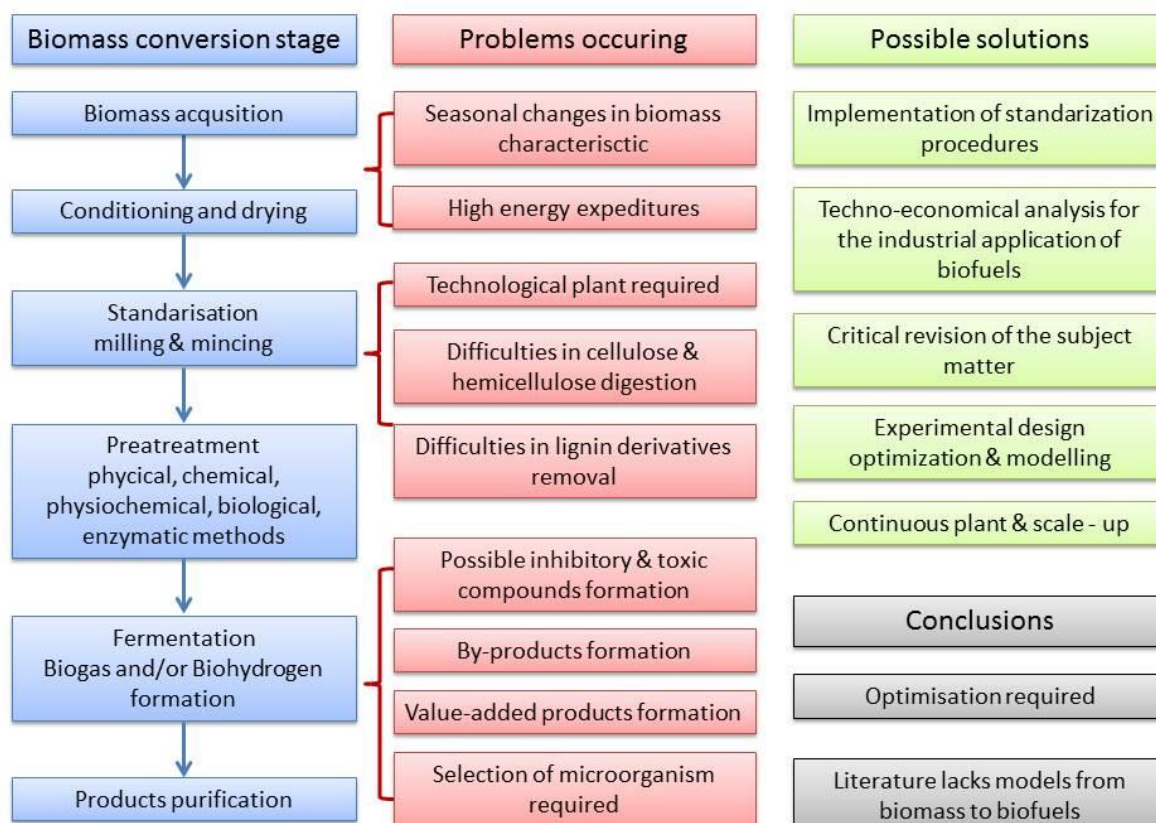
100 Biohydrogen and biogas from hydrolysates of lignocellulosic biomass can be produced via  
101 anaerobic fermentation. Different microorganisms are able to convert the cellulose and  
102 hemicellulose fraction of agricultural residues. Due to the presence of inhibitory compounds  
103 from lignin derivatives, there is no clearly defined and efficient method for lignin  
104 bioconversion without detoxification. Therefore, it is crucial to define and consider an  
105 influence of the presence of different by-products on the fermentation process. Optimization  
106 of fermentation may lead to a more complete understanding of occurring processes.  
107 Anaerobic digestion is a multi-step process carried out by highly differentiated  
108 microorganisms. The process requires strictly anaerobic conditions enabling the  
109 transformation of organic matter into carbon dioxide and methane or biohydrogen. Different  
110 types of microbial populations have specific optimal working conditions and are inhibited by  
111 various process parameters such as pH, temperature, alkalinity, concentration of free  
112 ammonia, hydrogen, sodium, potassium, volatile fatty acids (VFA) or heavy metals. An  
113 overview of recent developments in fermentation modeling is necessary to define process  
114 parameters ensuring high yields of biofuels production.

115 Anaerobic digestion of lignocellulosic biomass towards biogas production has been well  
116 described. The results of recently published studies show that the substrate characterization is  
117 ultimately the most influential model input on methane yield prediction. The development of  
118 methods for feedstock characterization and accurate calculations of kinetic factors to provide  
119 the required model inputs are still the supreme challenges. Lignocellulosic biomass may also  
120 be used for biogas production, either exclusively or mixed with other organic materials so as  
121 to obtain a feedstock with a convenient ratio of carbon to nitrogen. Among different process  
122 parameters affecting the yield and rate of biogas generation, the pH of the pulp, temperature,  
123 substrate composition, biomass pre-treatment method and digestion time seem to be the most  
124 important. The lack in the literature of the kinetic model incorporating important parameters  
125 affecting fermentative hydrogen production suggest that modeling of a bioprocess should be a  
126 representation of the sum of biological, chemical and physical processes occurring in the  
127 bioreactor. Modeling of hydrogen production from complex organic substrates by dark  
128 fermentation requires the knowledge of other bioprocesses i.e. hydrolysis or acid genesis.  
129 However, modeling of conversion towards biohydrogen is still developed.

130 It is assumed the future energy economy will be based on renewable sources. Biomass-based  
131 fermentative technology utilizing microorganisms capable of conversion of waste to valuable  
132 acids and alcohols with liberation of biogas or biohydrogen is tested for different types of  
133 biomass and process parameters. The possibility of predicting the fermentation process  
134 leading to biofuel production may allow saving time and increasing the efficiency of  
135 resources utilization, scaling up and the design of the system including appropriate



136 operational factors. Possible problems occurring during biomass conversion stage are pointed  
 137 in Figure 2. Probable solutions and conclusions for the purposes of this review have been  
 138 mentioned.



139  
 140 Fig. 2. Problems occurring and potential solutions encountered during the conversion of  
 141 lignocellulosic biomass.

142 **Techno-economic aspects of gaseous biofuel production**

143 The industrial application of a given solution for the production of gaseous biofuels requires a  
 144 comprehensive analysis of its costs. To select the optimal production method, biogas or bio-  
 145 hydrogen yield and energy requirements, ease of production as well as different production  
 146 costs including capital costs, operating costs, variable and fixed expenses, and replacement  
 147 costs should be taken into account [6–9]. Nevertheless, the commercialization of the proposed  
 148 solution depends on a large extent on the prices of fossil fuels as well as legal rules and policy  
 149 on biofuels established in a given country [8,9].

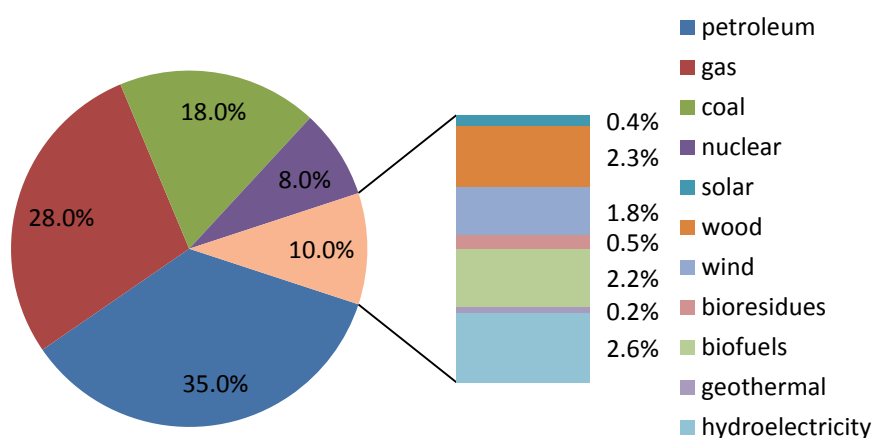
150 In the field of biogas production, technologies are currently successfully implemented. There  
 151 are many installations producing biogas by anaerobic digestion and the improvement can be  
 152 done on the basis of experience of existing plants [10–12]. The working installations for  
 153 anaerobic digestion are usually integrated with heat or energy generation that can be used on-  
 154 site and surplus can be an additional benefit to the total cost analysis [10,13]. Recently the  
 155 new inexpensive solutions have been proposed to utilize local waste and integrate waste  
 156 management with the energy generation [14,15]. Research is also carried out to optimize the  
 157 key steps of anaerobic digestion process to improve both economic and environmental  
 158 performance of AD plants [12].

159 In the case of biohydrogen production from lignocellulose biomass, high cost and low  
 160 hydrogen yields as well as relatively low operating fermentation broth concentration are still  
 161 major bottlenecks in the development of its production [7,16]. Even improving above  
 162 mentioned parameters, it is projected that the cost of bio-hydrogen obtained via dark  
 163 fermentation will still be too high to be economically viable. Therefore, integrated  
 164 technologies for bio-hydrogen production are proposed, taking into account the use of added-  
 165 value products and co-generation of energy [7,8] or combining solid state fermentation and  
 166 dark fermentation for hydrogen production [17,18]. Because bio-hydrogen technologies are  
 167 still at a laboratory scale, further and intense research is required to explore the potential,  
 168 feasibility, and extent of the possible improvements [7].

169 This review is focused on the description of the key challenges in modeling and optimization  
 170 of lignocellulosic biomass conversion processes. The main objective is to develop a  
 171 framework and methodology presenting a holistic influence of a particular stage of the  
 172 bioconversion process on the overall system performance and efficiency.

## 173 2. Characteristics of lignocellulosic materials

174 Biofuels are obtained from different types of biomass including plant-derived materials like  
 175 wood, food crops, grassy and woody plants as well as residues from agriculture and forestry,  
 176 oil-rich algae and organic components of municipal and industrial wastes [19]. An interesting  
 177 group of substrates for production of second-generation biofuels is lignocellulosic biomass.  
 178 The interest is mainly due to the vast abundance of the renewable lignocellulosic substrates,  
 179 being a non-food feedstock, utilization of which reduces the volumes of residues burned in  
 180 the field and consequently limits the environmental pollution [20,21]. Lignocellulosic  
 181 substrates for biofuels come mainly from residues of sawmills, forestry, paper industry and  
 182 agriculture i.e. straw, corncobs, parts of sugar beets and sunflowers [22,23]. It is known that  
 183 biofuels generated from lignocelluloses constitute globally about 7.5% of total energy used  
 184 worldwide. Lignocellulosic materials from agriculture as well as forest-management are the  
 185 largest sources of C-5 and C-6 sugars with a high potential for the production of biofuels and  
 186 other useful products [23]. In Figure 3 the present energy consumption is presented. The  
 187 structure of energy consumption in the field of bioresidues is specified.



189 Fig. 3. Present energy consumption concerning the source of energy [24,25]

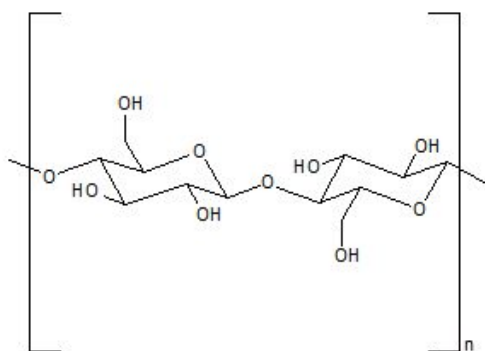
190 Lignocellulose is a main component of plants' cell walls and it is composed of cellulose  
191 (about 50%), hemicellulose (about 30%) and lignin (about 20%) [23,26]. Some examples of  
192 main constituents of selected lignocellulosic materials are presented in Table 1.

193 Table 1. Composition of selected lignocellulosic materials

Material	Chemical component				Reference
	Cellulose, %	Hemicellulose, %	Lignin, %	Ash, %	
Hazelnut	40.7	27.1	32.2	3.1	[27]
Sunflower seed	47.5	26.7	25.8	2.8	[27]
Algal biomass	7.1	16.3	1.5	1.8	[28]
Orange peels	13.6	6.1	2.1	1.5	[28]
Sugarcane bagasse	35.3	33.2	25.2	4.1	[29]
Siam weed	40.2	29.9	23.2	0.9	[29]
Shea tree	45.9	20.3	29.9	2.0	[29]
Grasses	25-40	25-50	10-30	>3.0	[30]
Rice straw	32.1	24.0	18.0	1.2	[30]
Sweet sorghum	45.0	27.0	21.1	1.8	[30]

194

195 Cellulose (Fig. 4.) is a crystalline biopolymer of  $\beta$ -D-glucopyranose monomeric units. The  
196 length of a cellulose molecule is determined by the number of glucan units. Hardwood  
197 hemicellulose is a branched polysaccharide that consists mainly of xylose and 4-O-  
198 methylglucuronic acid together with acetyl groups [31]. All types of cellulose micro fibrils are  
199 composed of linearly linked D-glucopyranose units, and only the degree of polymerization  
200 differs [32] and depends on the type of plants. Typically, it is estimated to be in the range  
201 from 2000 to 27000 glucan units.

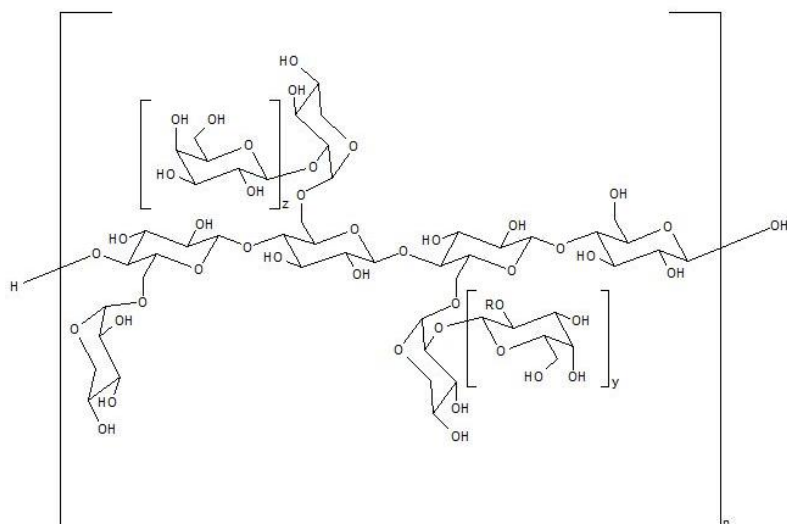


202

203 Fig. 4. Chemical structure of cellulose units.

204 Hemicelluloses (Fig. 5.) are amorphous, complex heteropolymers exhibiting a degree of  
205 polymerization lower than cellulose. The predominant hemicellulose component is xylan for  
206 hardwoods and mannan for softwoods. The content of hemicellulose in raw material is usually  
207 about 11 – 37% of the lignocellulosic dry weight. This fraction is easily hydrolyzed by acids.  
208 The products of hydrolysis include xylose, mannose, glucose, galactose, arabinose, and small  
209 amounts of rhamnose, glucuronic acid, methyl glucuronic acid, and galacturonic acid [32].



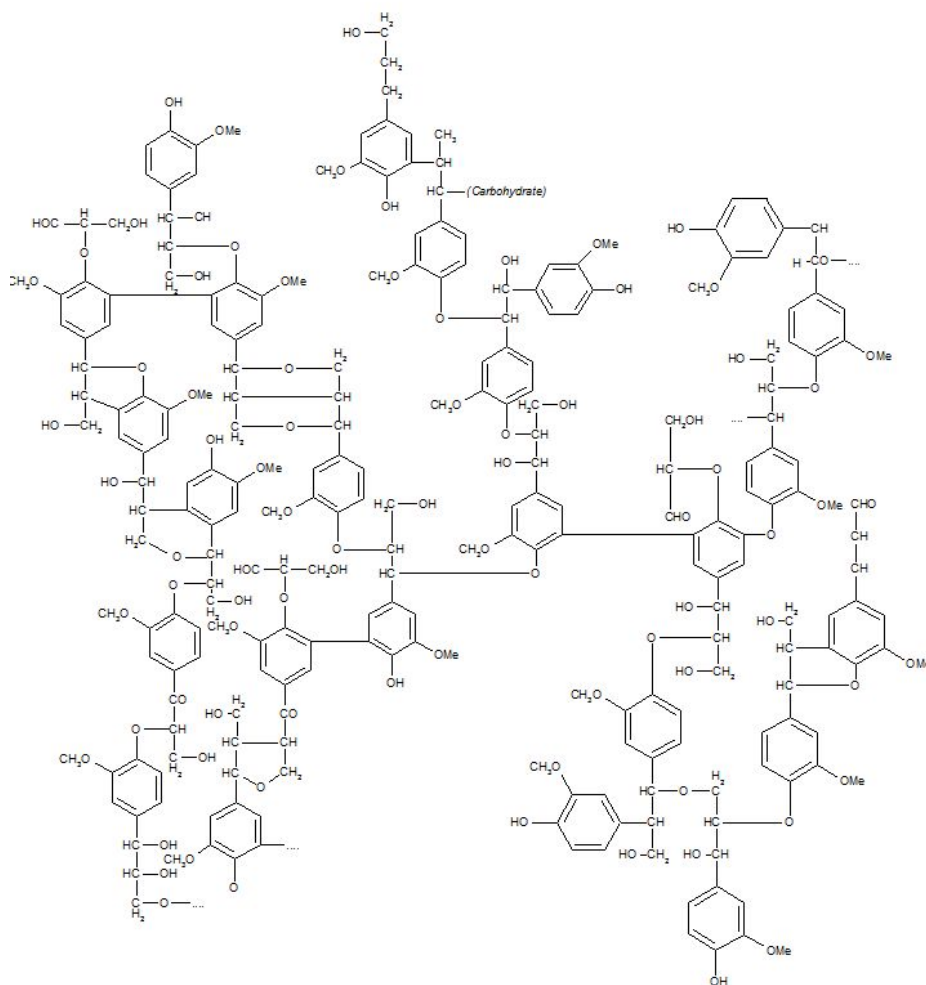


210

211 Fig. 5. Chemical structure of hemicellulose units.

212 Lignin (Fig. 6.) is a component of a plant cell wall and its main biological function is to form  
 213 an impermeable structure that protects a plant from an invasion of microbes [33,34]. Lignin is  
 214 an irregular polymer formed by enzyme-initiated polymerization of coniferyl alcohol in  
 215 hardwoods, coniferyl and sinapyl alcohols in softwoods or coumaryl alcohol plus both above  
 216 mentioned alcohols in grasses. Lignin bonds the cellulose and hemicellulose fibers through a  
 217 variety of linkages[32]. Many aspects of lignin chemistry remain undefined. Moreover,  
 218 lignins are extremely resistant to chemical and enzymatic degradation.





219  
220 structure of lignin units.

Fig. 6. Chemical

221 Extractives are a minor fraction of wood compounds, up to 5 % m/m. These are both  
222 lipophilic and hydrophilic compounds, classified as follows: terpenoids and steroids, fats and  
223 waxes, phenolic constituents and inorganic components [32,35,36].

224 An overview of chemical composition and structure of lignocellulosic biomass is presented in  
225 Table 2.

226

227 Table. 2. Characteristics of lignocellulosic biomass components

228

Discriminant	Cellulose	Hemicellulose	Lignin
Composition	Three-dimensional linear molecular	Inhomogeneous with small crystalline regions	Amorphous, nonlinear
Polymers	$\beta$ -Glucan	Polyxylose, Galactoglucomannan, Glucomannan	G Lignin; GS Lignin, GSH Lignin
Polymerization	$10^2$ - $10^5$	Under 200	Up to 4000
Subunits	<i>D</i> -pyran glucose	<i>D</i> -xylose, mannose, <i>L</i> -arabinose, galactose, glucuronic	<i>p</i> -hydroksyphenylpropane, syringylpropane, guaiacylpropane

Bonds between subunits	$\beta$ -1,4-glucosidic bonds	acid, $\beta$ -1,4-glucosidic bonds – main chains; $\beta$ -1,3; $\beta$ -1,6-glucosidic bonds – side chains	C-C bond, ether bonds (mainly $\beta$ -O-4)
Bonds between components	Without chemical bonds	Bonds with lignin	Bonds with hemicellulose

229  
230 Utilization of lignocellulosic biomass as a substrate for bioconversion processes requires the  
231 decomposition of lignocellulosic polymers into hexoses and pentoses. Among the above  
232 mentioned components of lignocelluloses, mainly lignin is responsible for so called biomass  
233 recalcitrance. The natural carbohydrate-lignin shields must be disrupted to enable the lignin  
234 removal prior to biomass hydrolysis and fermentation [37,38]. What is more, production of  
235 biofuels requires a pre-treatment step before the effective run of bioconversion processes, like  
236 anaerobic digestion or fermentation [35]. Therefore, initial pretreatment procedures are  
237 required to enhance the release of soluble sugars. Unfortunately, each pretreatment method is  
238 energy-consuming and does not remove the total lignin content. Thus, fermentative  
239 processing of lignocellulosic biomass and residues is always affected by lignin derivatives.

### 240 3. Mechanisms of biogas and biohydrogen fermentation from lignocellulosic 241 biomass

242

#### 243 3.1. Dark fermentation to biogas

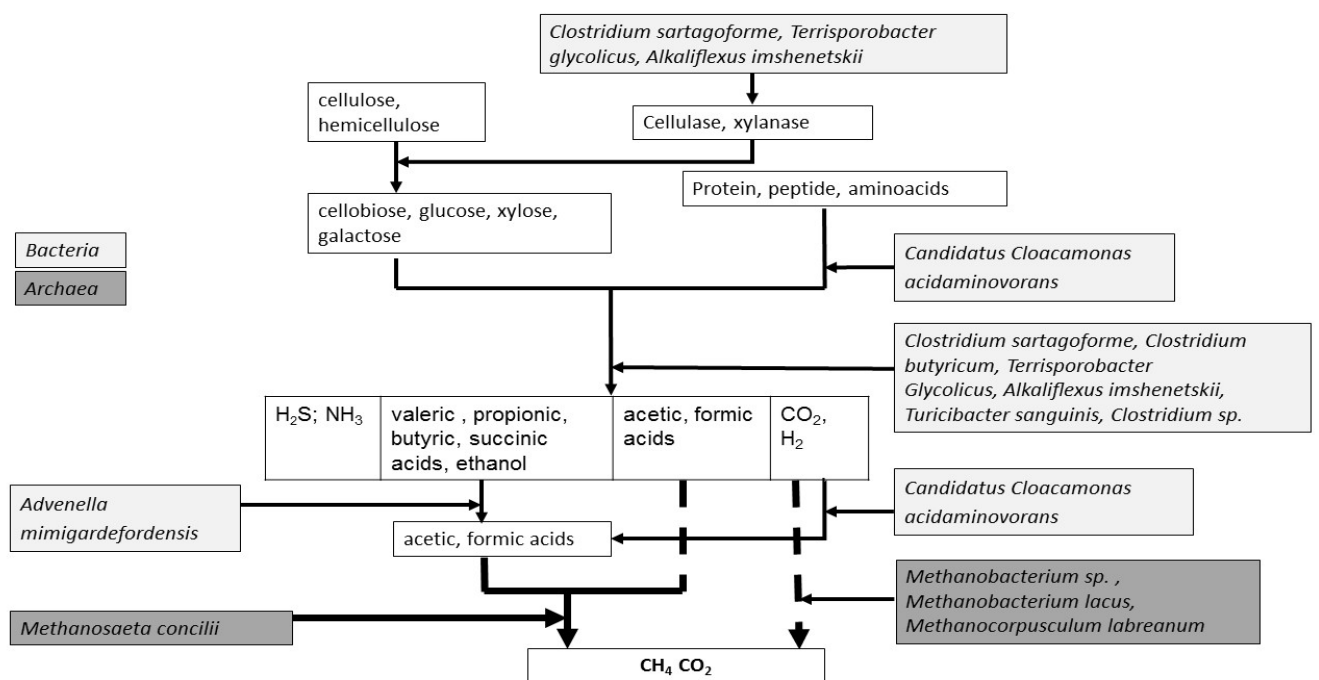
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245 Biogas is a biofuel composed mainly of methane (50 ÷ 75%), carbon dioxide (up to 40 %) and  
246 other minor constituents such as ammonia, hydrogen sulfide, hydrogen and nitrogen[1]. The  
247 biggest potential for clean energy production in combination with various biodegradable  
248 wastes is biogas production through anaerobic digestion (AD) process. The role of AD in the  
249 treatment of organic materials differing in the C/N ratio, i.e. agricultural wastes, wastewater  
250 sludges, municipall solid wastes or mixed substrates, still increases [39].Anaerobic digestion  
251 is a multi-step process carried out by a consortia of highly diversified\_microorganisms and  
252 requires strictly anaerobic conditions. Such conditions enables the transformation of organic  
253 matter into carbon dioxide and methane. In the first stage of AD, complex organic polymers  
254 i.e. proteins, lipids and carbohydrates, are hydrolyzed to simple soluble monomers like  
255 amino-acids, long-chain fatty acids and sugars. Then, in the second stage the monomers are  
256 converted by fermentative bacteria to a mixture of volatile fatty acids (VFA) and other minor  
257 products. The process is called acid genesis. In the third stage, acetogenic bacteria convert the  
258 VFA to acetate, CO<sub>2</sub> and H<sub>2</sub>. In the fourth stage, methanogenesis takes place [38]. Different  
259 microbial populations have specific optimum working conditions and are inhibited by several  
260 proceses parameters such as pH, temperature, alkalinity, concentration of free ammonia,  
261 hydrogen, sodium, potassium, VFA or heavy metals. In the AD process, all organic material  
262 can be diggested. The degree of such convesrion depends on the complexity and variety of the  
263 substrate materials. The AD technology is an attractive energy source for the production of  
264 heat and electricity and it enables to obtain a proportion of energy output to energy input  
265 equal to about 28:1 [38,40], which is a well-satisfactory result.

266 Production of biogas from different types of biomass is a topic of plenty of papers [41–47].  
 267 Anaerobic digestion of lignocellulosic biomass towards biogas production has been well  
 268 described and it is possible either by processing of only lignocellulosic substrates or mixing  
 269 them with i.e. municipal organic wastes (co-fermentation) [1]. Ge at al. [44] reviewed the  
 270 application of a solid-state AD to processing of lignocellulosic biomass. Besides the most  
 271 popular large-scale AD processes of liquid-AD (less than 15% of total solids), solid-state AD  
 272 (more than 15% of total solids) tends to be more effective technology for lignocelluloses  
 273 processing.

274 Metabolic pathways related to biogas generation are highly complicated. This kind of  
 275 fermentation is carried using microbial consortia; therefore the possible course of the process  
 276 may only be estimated as a result of experimental investigations. The course and the  
 277 mechanism of fermentation according to Tian experiment [48] is given in Figure 7.

278



279

280 Fig. 7. Analysis of metabolic pathways from lignocellulosic biomass to biogas according to  
 281 Tian et al. [48]

282 The type of microorganism present in the consortium, proposed to be responsible for given  
 283 metabolic pathway is estimated based on the clustering analysis.

### 284 3.2. Dark fermentation to biohydrogen

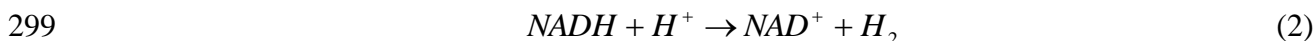
285 Biomass-based fermentative hydrogen production by microorganisms capable of conversion  
 286 of waste to valuable acids and alcohols with simultaneous liberation of biohydrogen is tested  
 287 for different types of biomass and process parameters. Because of arising food versus fuel  
 288 debate, it is crucial to consider only such feedstocks that do not compete with the food  
 289 request. Therefore, agricultural and forestry residues and wastes seem to be the most  
 290 interesting sources of biomass, as their exploitation leads to energy recovery [49].

291 Anaerobic or facultative anaerobic bacteria are able to generate biohydrogen by means of dark  
 292 fermentation [50]. To estimate the theoretical yields of biohydrogen, the glucose

293 biotransformation reaction is widely accepted as reference. The first step of all metabolic  
 294 pathways (Table 3) is the metabolism of glucose towards pyruvate, according to reaction (1)  
 295 [51]:



297 Reaction (1) may be described as the source of hydrogen which is generated during the  
 298 subsequent regeneration of produced *NADH* in reaction (2):



300 However, it is *acetyl-coA* that defines whether the hydrogen yield is 4 or 2 mol  $H_2$ /mol  
 301 glucose and the maximum yield depends on the microbial enzymatic system [52–55].

302 Strictly anaerobic and facultative anaerobic bacteria use ferredoxin oxidoreductase *Fd<sub>ox</sub>* for  
 303 *acetyl-coA* production (reaction (3)), which can be further metabolized to acetate or butyrate  
 304 [32]:



306 *Enterobacter*, ie. *Enterobacter aerogenes* and *Escherichia coli* under anaerobic conditions use  
 307 pyruvate – formate lyase to generate *acetylCoA*, as given in reaction (4) [56,57]:



309 Table 3. Maximum theoretical biohydrogen yield in various metabolic pathways.

Type of metabolic pathway	Reaction	Maximum theoretical yield [mol $H_2$ /mol glucose]	$\Delta G^0$ [kJ/mol]	References
acetic fermentation	$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$	4	-206,3	[58,59]
acetic and formic fermentation	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO^- + 2HCOOH + 4H^+ + 2H_2$	4	-209,1	[60]
butyric fermentation	$2HCOOH \rightarrow 2CO_2 + 2H_2$	4	-6	[60]
butyric fermentation	$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COO^- + 2HCO_3^- + 3H^+ + 2H_2$	2	-254,8	[61]

310  
 311 Beside the products mentioned in Table 3, glucose fermentation may lead to formation of  
 312 other products, such as propionic acid, succinic acid, lactic acid, 2,3-butanediol, ethanol,  
 313 isopropanol and butanol [49,62]. Nevertheless, above named substances should be considered  
 314 as undesired by-products, as they lower the overall hydrogen yield.

315 4. Problems of lignocellulosic biomass conversion

316 4.1. Pretreatment method selection

317 Pre-treatment of lignocellulosic biomass include physical, chemical, physicochemical and  
 318 biological methods. Size reduction of biomass by means of fragmentation, grinding, milling  
 319 or rolling is realized during physical pre-treatment. Decomposition of lignocellulose to simple  
 320 compounds via various chemical reactions (hydrolysis, oxidation, ozonolysis, and application  
 321 of solvents) is realized during chemical pre-treatment. Physicochemical methods aim at the  
 322 decomposition of lignocelluloses by means of joint action of chemical oxidation and thermal  
 323 treatment. Biological treatment makes use of decay fungi, bacteria and enzymes. Examples of  
 324 lignocellulosic pre-treatment methods are listed in Table 4.

325 Table 4. Pre-treatment methods of lignocellulosic biomass

Pre-treatment type	Method	Mechanism / result	Reference
Physical	Fragmentation	Destruction of lignocellulosic chain to smaller parts with exposed chemically-active groups	[63]
	Microwaves	Reduction of cellulose crystal structure	[64]
	Sonification	Cleavage of lignocellulosic hydrogen bonds	[65]
	Spray drying with gamma radiation	Cleavage of $\beta$ -1,4-glycosidic bonds	[66]
	Pyrolysis	Cellulose carbonation	[34]
Chemical	Acid hydrolysis	Cellulose decomposition and lignin dissolution	[67]
	Alkaline hydrolysis	Lignocellulose saponification, lignin structure modification	[68]
	Oxidation and ozonation	Lignin and hemicellulose dissolution	[69]
	Treatment with ionic liquids	Removal of cellulose from lignocelluloses	[70]
	Treatment with solvents	Lignin dissolution, cleavage of hemicellulose bonds	[71]
Physicochemical	Steam explosion	Hemicellulose and lignin dissolution	[72]
	Carbon dioxide explosion	Lignin and hemicelluloses decomposition	[73]
	Ammonia fiber explosion	Lignin removal	[74]
Biological	White rot	Hemicellulose and lignin decomposition	[75–78]
	Brown rot	Lignin decomposition	

Soft rot	Hemicellulose and lignin decomposition
Bacterial treatment	Hemicellulose and lignin decomposition
Enzymatic treatment	Hemicellulose and cellulose decomposition
Pickling	Hemicellulose decomposition

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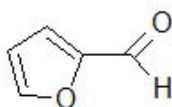
327 As shown in Table 4, there are many methods of pre-treatment of lignocellulosic biomass.  
 328 Mechanical pre-treatment typically forerun further chemical treatment as milled and minced  
 329 material is homogenic. Mechanical treatment is the most energy-intensive processing stage,  
 330 followed by treatment with physical, chemical, or physicochemical and biological methods.  
 331 Research interest is increasingly turning towards methods that allow the selective removal of  
 332 these fractions of lignocellulosic biomass, which as a result of hydrolysis may be the source  
 333 of fermentation inhibitors. This is why the selective methods gain importance.  
 334 An influence of the molecular organization as well as the cell wall structure on the  
 335 pretreatment efficiency is still not defined [79]. An important parameter for the selection of  
 336 the biomass pretreatment methods is the substrate accessibility. Unfortunately, it is not  
 337 possible to precisely predict the effectiveness of a pretreatment with one method of analysis.  
 338 However, finding out the mechanisms of the changes in the structure during bioconversion  
 339 may improve the effectiveness of the pre-treatment [80]. Pre-treatment causes changes in the  
 340 physical structure of biomass which further affects other steps of processing i.e. enzymatic  
 341 hydrolysis. Based on SEM images (scanning electron microscopy), it has been proven that the  
 342 pre-treated pine wood surface is different than that of raw pine wood. Pores formed as a result  
 343 of high levels of residual lignin removal were only present in the pre-treated wood [81].  
 344 Unfortunately, the pre-treatment of lignocellulosic biomass leads to formation of substances  
 345 that inhibit further biochemical conversion processes. For example, acid hydrolysis leads to  
 346 formation of phenolic compounds and furans that are detrimental for enzymatic hydrolysis as  
 347 well as latter fermentation. Prevention of formation of unwanted chemical substances or so  
 348 called detoxification of pre-treated lignocellulosic biomass may be controlled by several  
 349 means [82,83]. These strategies include a selection of chemical or enzymatic hydrolysis  
 350 conditions e.g. by application of alkaline instead of acid hydrolysis. Moreover, liquid-liquid,  
 351 liquid-solid extraction or microbial treatment may help to overcome the problem of formation  
 352 of fermentation inhibitors.

#### 353 4.2. Inhibitory and toxic products

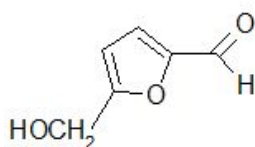
354 The utilization of monosugars present in lignocellulosic structures requires highly efficient  
 355 hydrolysis. During the hydrolysis, beside free sugars, other substances named inhibitors i.e.  
 356 lignin derivatives are formed [84]. Therefore, detoxification of hydrolysates is necessary prior  
 357 to fermentation. The presence of lignin and cellulose-lignin structures in biomass is  
 358 responsible for its ineffective hydrolysis and fermentation because both fractions are water-  
 359 insoluble. It is known that elimination of lignin results in an increase of the biomass  
 360 digestibility [37] and contrary, the presence of lignin inhibits the biomass hydrolysis mainly  
 361 due to the toxicity of lignin derivatives as well as non-specific adsorption of hydrolytic  
 362 enzymes within the structure of lignocelluloses. The delignification, i.e. the extraction of  
 363 lignin by means of chemicals, leads to so called biomass swelling. Thanks to biomass

364 swelling, the lignin structure is altered which results in an increase of the area of  
365 lignocellulose fibers exposed to cellulolytic enzymes.

366  
367 Lignin derivatives such as 5-hydroxymethyl-2-furaldehyde (HMF) and 2-furaldehyde are  
368 formed by dehydration of hexoses and pentoses. The concentration of furans varies depending  
369 on the type of material and the pretreatment procedure. Furfural is found in lower  
370 concentrations than HMF. However, even low concentrations of furfural inhibits fermentation  
371 [85]. Moreover, both furfural (Fig. 8.) and HMF (Fig. 9.) inhibit the growth of yeast and  
372 decrease ethanol yield [86–88].  
373



374 Fig. 8. Chemical structure of furfural



375  
376 Fig. 9. Chemical structure of 5-hydroxymethyl-2-furaldehyde (HMF)

377  
378 Weak acids such as acetic acid are formed by deacetylation of hemicelluloses. Formic and  
379 levulinic acids are products of HMF degradation under acidic conditions at elevated  
380 temperatures. A variety of phenolic compounds are generated when lignin breakdown occurs.  
381 The knowledge of the biomass source is crucial to predict the amount and the type of phenolic  
382 compounds present in hydrolysates because lignin has different degrees of methylation, and  
383 internal bonding and association with hemicellulose and cellulose in the plant cell wall are  
384 species-dependent[89].  
385

#### 386 4.3. Main product yield and by-product formation

387 Fermentations carried out by bacteria of diversified metabolic pathways or via mixed cultures  
388 often lead to byproducts formation. However, it is believed that selection of proper conditions  
389 can direct the microbial metabolism towards main product generation, eliminating by-product  
390 formation. In the case of biohydrogen production, even though a wide range of single type of  
391 microorganisms (*Methylotherms*, *Rumen bacteria*, *Methanogenic bacteria*, *Archaea*, *E. coli*,  
392 *Enterobacter*, *Citrobacter*, *Alcaligenes*, *Bacillus*, *Clostridium sp.*, *Clostridium butyricum*, *C.*  
393 *acetobutyricum*, *C. beijerinckii*, *C. thermolacticum*, *C. tyrobutyricum*, *C. thermocellum*, *C.*  
394 *paraputrificum*, *Enterobacter aerogenes*, *E. cloacae*, *Caldicellulosiruptor saccharolyticus*,  
395 *Thermoanaerobacterium sp.*, *T. thermosaccharolyticum*, *Thermotoga sp.*, *T. maritima*, *T. elfii*  
396 [90–94]) is capable to generate hydrogen via dark fermentation, mixed consortia seem to be a  
397 better alternative. Mixed consortia under strictly determined conditions [95,96] allow for a  
398 broad choice of feedstocks, including a variety of natural sources, anaerobically digested  
399 sludge, animal manure, sewage sludge, compost and soil. Different products and by-products  
400 of lignocellulosic hydrolysates bioconversion are given in Table 5.

401 The fermentation of lignocellulosic biomass is often considered not only as a source of  
402 gaseous fuels, such as biogas or biohydrogen, but also as a source of value-added products is  
403 obtained. The fermentation gas products can be separated very easily from the components of  
404 the fermentation broths. Proper selection of a microorganism or a mixture of microorganisms

405 or control of the process conditions, by affecting the pH during fermentation, temperature or  
406 oxygen content allows the fermentation to be directed to obtain bio components, which are  
407 difficult to obtain in the chemical synthesis. Such an approach creates a chance for a better  
408 usage of the raw material, and in the future may become the direction of more detailed  
409 research, depending on the complexity of the structure of by-products and their synthesis.

410 High yields of main products require selection not only of proper microorganisms, but also of  
411 the appropriate fermentation conditions. In Table 6 operating conditions and yields of  
412 hydrogen production by dark fermentation from various renewable resources are presented.



413 Table 5. Products and by-products generated during dark fermentation from lignocellulosic hydrolysates

414

Lignocellulosic substrates	Used microorganisms	Used enzymes	Possible products		References
			Gaseous biofuels	Other possibly valuable products	
Glucose, hemicellulose sugars	Mixed anaerobic microflora	-	Biohydrogen	Butyric acid, acetic acid	[97]
Delignified hydrolysate of lignocellulosic biomass	Anaerobic bacteria	Cellulase	Biogas	Lactic acid, citric acid, acetic acid	[98]
Glucose, hemicellulose sugars	<i>Lactobacillus species</i>	Cellulase	Biohydrogen	Lactic acid, succinic acid	[99]
Delignified hydrolysate of lignocellulosic biomass	<i>Acetobacter sp.</i>	Cellulase	Biohydrogen	Acetic acid	[100]
Cellulose, glucose rich hydrolysates	<i>Penicillium luteum, P. citrinum, Aspergillus niger, A. wentii, A. clavatus, Mucor piriformis, Citromyces pfefferianus, Paecilomyces divaricatum, Trichoderma viride, Yarrowia lipolytica, Candida guilliermondii</i>	Cellulase	Biohydrogen	Citric acid	[101]
Delignified hydrolysate of lignocellulosic biomass	<i>Mannheimia succiniciproducens</i>	Cellulase	Biohydrogen	Succinic acid	[102]
Delignified hydrolysate of lignocellulosic biomass	<i>Actinobacillus succinogenes</i>	Cellulase	Biohydrogen	Succinic acid	[103]
Cellulose	<i>Anaerobiospirillum succiniciproduens</i>	Cellulase	Biohydrogen	Succinic acid	[104,105]
Cellulose, hemicellulose	<i>Mannheimia succiniciproducens</i>	Cellulase xylanase	Biohydrogen	Succinic acid	[104,105]



Delignified hydrolysate of lignocellulosic biomass	<i>Xanthophyllomyces dendrorhous</i>	Cellulase complex β-Glucosidase	Biogas	Astaxanthin	[104,105]
Hemicellulose, xylose rich hydrolysates	Genetically modified <i>Saccharomyces cerevisiae</i> , <i>Pichia stipiti</i> ,	Xylanase	Biohydrogen	Bioethanol	[80,106]
Hemicellulose, mixed sugars, xylose rich hydrolysates	<i>Escherichia coli</i> , <i>Klebsiella</i> , <i>Erwinia</i> , <i>Lactobacillus</i> , <i>Bacillus</i> , <i>Clostridia</i>	Xylanase	Biohydrogen	Low concentrations of bioethanol	[80]
Hemicellulosic hydrolysates from barley straw, corn stover and switch grass	<i>Clostridium acetobutylicum</i> , <i>Clostridium beijerinckii</i>	-	-	ABE (acetone; butanol; ethanol)	[107,108]
Xylose from hemicellulose hydrolysates	<i>Candida guilliermondii</i>	-	-	Xylitol	[106]
Hemicellulosic hydrolysates, xylose, arabinose	<i>Candida entomaea</i> , <i>Pichia guilliermondii</i>	-	-	Arabitol	[109]
Hemicellulosic hydrolysates	<i>Bacillus polymyxa</i> , <i>Klebsiella pneumoniae</i> ( <i>Aerobacter aerogenes</i> ), <i>Bacillus subtilis</i> , <i>Serratia marcescens</i> and <i>Aerobacter hydrophilia</i>	-	-	2,3-butylene glycol	[110]
Hexoses, pentoses, disaccharides, uronic acid	<i>Klebsiella pneumoniae</i>	-	-	2,3-butylene glycol	[111–113]
Hemicellulosic sugars, xylose, arabinose, and glucose	<i>Lactobacillus pentosus</i> , <i>Lactobacillus brevis</i>	-	-	Lactic acid	[114,115]
Hemicellulosic sugars	<i>Aspergillus niger</i> .	-	-	Citric acid	[106]
Hemicellulosic sugars	<i>Clostridium tyrobutyricum</i>	-	Biohydrogen	Butyric acid	[116]



415 Table 6. Operating conditions and yields of hydrogen production by dark fermentation using selected renewable resources

Substrate	Microorganism/ Reactor type	Organic products in fermentation broth	Conditions: pH/Temp.	Hydrogen productivity/yield	References
Organic municipal solid waste 110 g TVS/ dm <sup>3</sup> /d	Mixed cultures/ CSTR Semi-continuous	Butyric acid, acetic acid	pH = 5.0 T = 50°C	5.7 dm <sup>3</sup> H <sub>2</sub> / dm <sup>3</sup> / d	[117]
Kitchen garbage	Anaerobic digester sludge/ CSTR Continuous	Butyric acid, acetic acid, ethanol , lactic acid	pH = 5.0 T = 55°C	1.7 dm <sup>3</sup> H <sub>2</sub> / dm <sup>3</sup> /d  66 cm <sup>3</sup> H <sub>2</sub> /g VS	[118]
Potato steam peels 10 g glucose/ dm <sup>3</sup>	Mixed culture/ Batch	Acetic acid, lactic acid	pH = 6.9 T = 75 °C	12.5 mmol H <sub>2</sub> / dm <sup>3</sup> h  3,8 mol H <sub>2</sub> /mol glucose	[119]
Simulated food waste: fish 5%; meat 10%; bread 10%; apple 10%; kiwi 6%; banana 9%; pear 10%; onion 5%; lettuce 5%; carrot 5%; cabbage 10%; potato 15%	Mixed culture from digested sludge/ CSTR Continuous	Acetic acid, butyric acid, caproic acid, valeric acid	pH = 5.5 T = 34°C	20.5 dm <sup>3</sup> H <sub>2</sub> /kg VS	[120]
Liquid swine manure 13.94 g COD/ dm <sup>3</sup>	Mixed cultures from anaerobic digester/ ASBR Batch	Acetic acid, butyric acid, valeric acid, ethanol, Propionic acid	pH = 5.0 T = 37°C	0.1 dm <sup>3</sup> H <sub>2</sub> /dm <sup>3</sup> /h	[121]
Cattle wastewater 1.3 g COD/dm <sup>3</sup>	Sewage sludge/ Batch	butyric acid, acetic acid, ethanol, propionic acid	pH = 5.5 T = 45°C	0.34 dm <sup>3</sup> /dm <sup>3</sup> h	[122]



Dairy manures 70 g/dm <sup>3</sup>	<i>Clostridium sp/</i> CSABR Continuous	Butyric acid, acetic acid, ethanol, propionic acid, butanol	pH = 5.0 T = 36°C	31.5 cm <sup>3</sup> /g TVS	[123]
Cheese whey wastewater 10 g/dm <sup>3</sup>	Mixed cultures (anaerobic bacteria from UASB reactor)/ Batch	Acetic acid, butyric acid, propionic acid, heptanoic acid, valeric acid	pH = 4.5 T = 55°C	1.1cm <sup>3</sup> H <sub>2</sub> /gVSS*h	[124]
Palm oil mill effluent 59 g COD/dm <sup>3</sup>	Mixed cultures (isolated from cow dung) / USAB Continuous	-	pH = 5	73dm <sup>3</sup> /d	[125]
<i>Jatropha curcas</i> – biodiesel industry residue	Mixed cultures (from activated sludge)/ CSTR Continuous	Butyric acid, ethanol, acetic acid, propionic acid, valeric acid	pH = 5.5 T = 37°C	3.65 dm <sup>3</sup> /((dm <sup>3</sup> *d) 148cm <sup>3</sup> H <sub>2</sub> /g carbohydrate	[126]
Wheat straw 5 g/dm <sup>3</sup>	<i>Thermoanaerobacterium thermosaccharolyticum</i> M18/ Batch	Acetic acid, butyric acid, ethanol, butanol, propionic acid	T = 60°C pH = 7	0.11 mmol/ dm <sup>3</sup> h	[127]
Sugarcane bagasse 1%	<i>Caldicellulosiruptor saccharolyticus</i> / Batch	-	T = 70°C	18,21 dm <sup>3</sup> H <sub>2</sub> /kg 2.3 mol H <sub>2</sub> /mol glucose	[128]
Delignified wood fibers 0.1 g/dm <sup>3</sup>	<i>Clostridium thermocellum</i> 27405/ Batch	Acetic acid, ethanol, formic acid	T = 60°C	2.32 mol H <sub>2</sub> /mol glucose	[90]
Swine manure	Mixed cultures in swine manure/ Batch polyethylene jar reactor	-	T = 35°C pH = 4.7-5.9	1.63 mol H <sub>2</sub> / mol glucose (HRT 16 h)	[129]

416 COD – chemical oxygen demand; VS – volatile solids; TVS – total volatile solids; ASBR – anaerobic sludge blanket reactor; CSTR –  
417 continuously-stirred tank reactor; CSABR – continuously stirred anaerobic bioreactor; USAB – upflow anaerobic sludge blanket reactor; d – day;  
418 HRT – hydraulic retention time



419 Information presented in Table 6 indicates that hydrogen production by dark fermentation  
420 has been investigated for various types of renewable resources, including municipal wastes  
421 and sludges, waste food as well as lignocellulosic waste and biomass. Glucose yield is widely  
422 accepted as reference for the description of the hydrogen yield. The hydrogen production is  
423 realised either by selected or native microorganisms at various conditions of pH and  
424 temperature. However, due to ununiform units of hydrogen productivity and yield, it is not  
425 easy to compare the results of investigations of different authors. Moreover, reported studies  
426 lack information regarding the energy requirements for the fermentative production of  
427 hydrogen.

428 Interestingly, enzymes may be added-value products formed as a result of dark fermentation  
429 of lignocellulosic biomass. During bioconversion with different microorganisms and solid  
430 substrates, the production of a variety of enzymes, such as  $\alpha$ -amylase, cellulase, xylanase,  
431 protease, fructosyl transferase, chitinase, pectinase was reported [130–136]. Recovery of  
432 added-value products from a fermentation broth can be an additional source of income,  
433 allowing the development of waste streams and improving the economy of the proposed  
434 technology.

## 435 5. Recent developments in modeling of fermentation processes

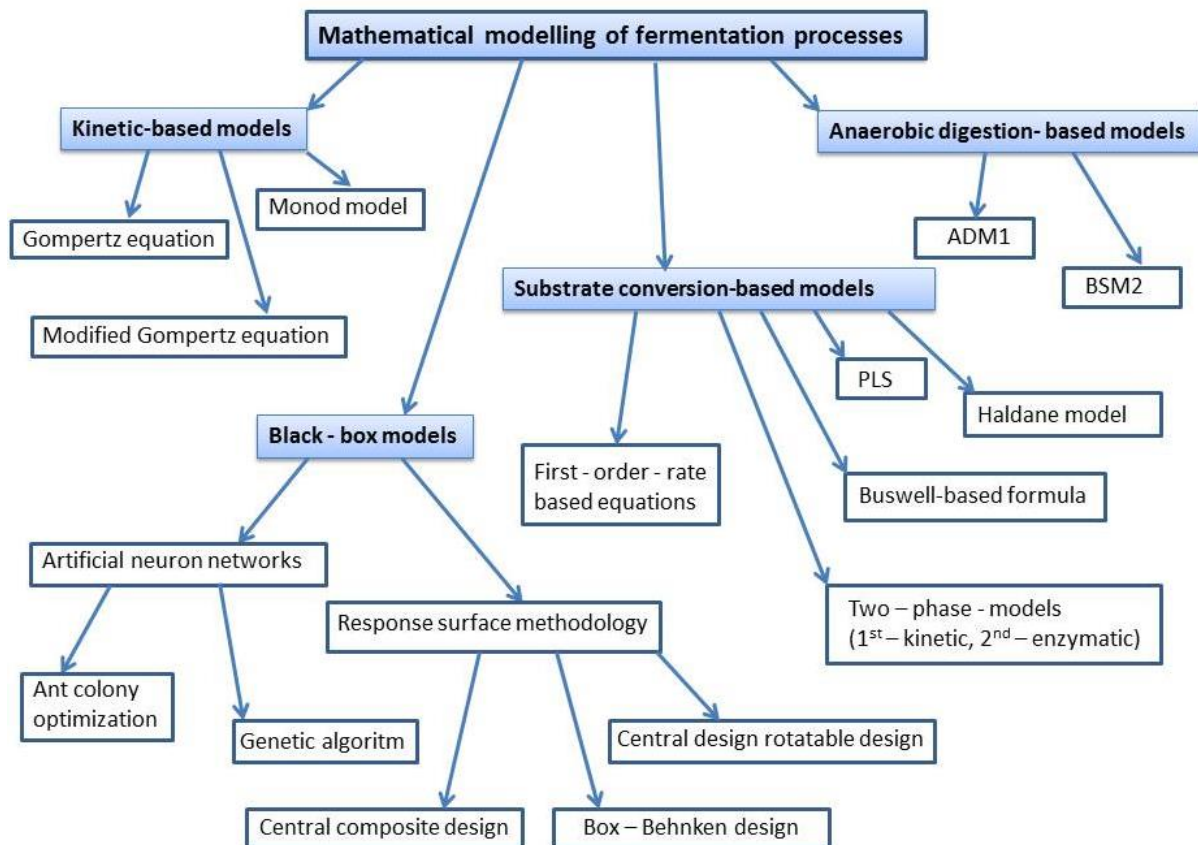
436 The use of mathematical models can help to explore the phenomena occurring during  
437 various processes. The production of biogas and biohydrogen from biomass is realized via  
438 biochemical processes accomplished by the combined action of microorganisms, which  
439 metabolize the organic substrates into a mixture of both gaseous and liquid compounds. Such  
440 processes of microbiological fermentation are complex and require further research to be  
441 fully understood. Additionally, the efficiency of fermentation processes corresponds to the  
442 optimum only in rarest cases and thus it is highly needed to reveal the phenomena  
443 governing such processes. Modeling of a bioprocess is a representation of the biological,  
444 chemical and physical processes occurring in the bioreactor [137] and aims at selection and  
445 optimization of several process parameters affecting the biofuel production (i.e. pH, volatile  
446 fatty acids, temperature, substrate quantity, alkalinity) [138]. Therefore, prediction of the  
447 fermentation process leading to biofuel production is important to i) save time and increase  
448 resources utilization efficiency, ii) transform from lab-scale to industrial scale and iii) design  
449 the system including appropriate operational factors [139].

### 450 5.1. Classification of models

451 There are many models that have been tested on data obtained during fermentation processes  
452 for gaseous biofuels production; however there is no universal classification of such models.  
453 I.e., according to Lauwers et al. [140], there are two main approaches of model classification:  
454 (1) dynamic or non-dynamic, and (2) white-, grey- or black-box. Dynamic models use several  
455 ordinary differential equations. Such models are generally based on mass-balance  
456 considerations and generates predictions continuous in time. Non-dynamic models link  
457 substrate to products by means of stoichiometry (i.e. models include calculations with C, H, N  
458 and O and the obtained gas yield) and predicts time-independent variables. White-box models  
459 are deductive and use *a priori* information. Grey-box models are mechanistically inspired  
460 models including parameter estimation procedures. Black-box models are data-driven models  
461 that link input directly to the output.

462 On the other hand, the mathematical models for anaerobic digestion may be divided as  
 463 follows [140]: mechanistically inspired models, reduced complexity models and data-driven  
 464 models. Mechanistically inspired models express the kinetics of particular stages of biogas  
 465 production according to i.e. Monod-type kinetics, Haldane kinetics or Andrews kinetics.  
 466 Examples of the most popular models of this group are ADM1 (Anaerobic Digestion Model  
 467 no. 1) and parts of BSM2 (Benchmark Simulation Model no. 2). Reduced complexity models  
 468 present equations expressing mass balance and process kinetics and may be used for control  
 469 strategies even for large-scale plants. Data-driven models, on the other hand, aim at predicting  
 470 the behavior of the system without any pre-knowledge of the occurring process. These are  
 471 either black-box models or fuzzy logic. The examples of tools for the design of black-box  
 472 models are PCR ([wyjaśnić](#)), PLS ([wyjaśnić](#)), ANN ([wyjaśnić](#)), neuro-fuzzy systems and SVM  
 473 (Support Vector Machines).

474 Another classification is proposed by Lubken et al. [141]. Mathematical models of anaerobic  
 475 digestion may be divided into three main groups: stoichiometry-based models, rate-limiting  
 476 step models and multispecies models. Stoichiometry-based models assume that biochemical  
 477 composition decides about the anaerobic digestibility of an organic substrate (models apply  
 478 i.e. Buswell formula, Boyle equation, the specific methane yield). The rate-limiting step  
 479 approach highlights the need for the description of the rate-limiting step during the anaerobic  
 480 digestions. The models apply Haldane kinetics, Andrew kinetics, Contois model or Monod  
 481 model. These are dynamic mathematical models and are similar to some of mechanistically  
 482 inspired models discussed by Lauwers et al.[140]. Multispecies models account for the  
 483 complex microbiological consortia responsible for the anaerobic processes. An example of  
 484 such model is ADM1.



485

486 Fig. 10. Classification of models for fermentation processes.

487 The diversity of raw materials and the complexity of the fermentation processes during the  
488 bioconversion of lignocellulose to biofuels cause that there are many ways of approaching the  
489 mathematical description of these processes. As presented earlier, based on the works by  
490 Lauwers et al.[140] and Lubken et al. [141], it is possible to adopt different criteria for  
491 modeling. Due to the lack of a universal classification of the models, the authors of the  
492 present work reviews recent advances on modeling of fermentative conversion of  
493 lignocellulosic biomass to biofuels. The authors propose a classification of the most  
494 commonly used models into four groups: i) ADM1-based models, ii) substrate conversion-  
495 based models, iii) kinetic-based models and iii) black-box models, as given in Figure 10.  
496 Further discussion precedes in accordance with the proposed classification.

## 497 5.2. ADM1-based models

498 Anaerobic Digestion Model No. 1 (ADM1) [142] is a consolidation of a variety of different  
499 mathematical models. The ADM1 is the most commonly used model for optimisation of AD  
500 process. It is a structured model based on a system of ordinary differential equations that  
501 represent the interactions between the substrate, microorganisms and products in anaerobic  
502 digestion. ADM1 describes 19 biochemical reactions, 3 equations referring to the mass  
503 transfer phenomena between liquid and gas phases and an additional 6 acid-base kinetic  
504 processes that are involved in the bioconversion of complex organic substrates into methane,  
505 carbon dioxide and inert byproducts. It includes 24 components, and 56 stoichiometric and  
506 kinetic parameters for assuming the biological processes and additional parameters for  
507 determining the physico-chemical processes occurring in the system.

508 The original ADM1 model describes complex substrates by their complete organic and  
509 inorganic composition. The organic components considered within the model are  
510 carbohydrates, proteins, lipids, sugars, amino acids (AA), long chain fatty acids (LCFA),  
511 volatile fatty acids (VFA: acetic, propionic, butyric and valeric acids) as well as particulate  
512 and soluble inert substrates. The main inorganic components taken into account are  
513 ammonium nitrogen and bicarbonate; the others are anions (phosphate, sulphate, nitrate, etc.)  
514 and cations (calcium, potassium, magnesium, etc.). The organic components and molecular  
515 hydrogen are expressed as chemical oxygen demand (COD), whereas inorganic nitrogen and  
516 inorganic carbon species are expressed through their molecular concentrations.

517 The ADM1 model includes five steps of biochemical degradation of complex organic  
518 material: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. The first  
519 step is the disintegration of complex particulates into carbohydrates, proteins, lipids,  
520 particulate and soluble inert substrates. Disintegration can include an array of processes such  
521 as lysis, non-enzymatic decay, phase separation and physical breakdown. In the second step,  
522 the particulate monomers (carbohydrates, proteins and lipids or fats) are successively  
523 disintegrated to sugars, AA and LCFA, by the hydrolytic bacterial species. The aim of the  
524 disintegration and hydrolysis is the breakdown and solubilization of substrates. Then, the  
525 soluble products of hydrolysis are fermented to mixed VFA, hydrogen and carbon dioxide by  
526 the acidogenes. Finally, methane can be produced via two different pathways: either via  
527 heterotrophic methanogenesis of acetate to methane and carbon-dioxide by acetoclastic  
528 methanogens archaea or via autotrophic methanogenesis of both hydrogen and carbon dioxide  
529 to methane, by hydrogenophilic methanogenic archaea.

530  
531 The ADM1 model was originally developed for sewage sludge, but the growing number of  
532 papers reported the application of the model in the areas of lignocellulosic biomass waste or

533 energy crops. An overview of recent adaptations and extensions of ADM1 for biomass wastes  
534 is given in Table 7.

535 The modified ADM1 was investigated for various types of waste biomass as a feedstock .  
536 Lubken et al. [143] simulated biogas production using cattle manure and rape-oil as co-  
537 substrates. The authors proposed to replace the COD by measurement of volatile solids to  
538 characterize the substrate and recommended the inhibition effect of pH to be included in the  
539 model. Boubaker et al. [144] investigated the mesophilic anaerobic co-digestion (AcoD)  
540 process of olive mill wastewater and olive mill solid waste. The authors suggested a  
541 modification taking into account the inhibition of methanogenesis step by high concentrations  
542 of total VFA. Derbal et al. [145] applied ADM1 to simulate anaerobic co-digestion of organic  
543 fraction of municipal solid wastes in mesophilic conditions. The authors note the limitation of  
544 ADM1 model in complex processes of AcoD by the fact that only a part of the input kinetic  
545 parameters were obtained by analysis and the rest of them were adopted from the literature.  
546

547 The anaerobic biodegradability of agro-wastes was used to characterize the substrates and  
548 considered as the basis input to the model [146]. The modification of the original ADM1  
549 includes the implementation of H<sub>2</sub>S in liquid and gaseous phases in the processes that  
550 occurred during anaerobic digestion. The proposed model was validated with the mono-  
551 substrate and co-substrate cases in batch and continuous reactors.

552 Zhao et al. [147] divided the lignocellulosic substrate into three fractions: slowly  
553 hydrolysable, readily hydrolysable and inert parts. Such an approach allowed for better  
554 understanding of the degradation kinetics. Koch et al. [148] used the modified ADM1 for the  
555 validation of the digestion of grass silage as the single substrate, including the separation of  
556 inert decay products and a solid-influenced hydrolysis function reflecting nitrogen  
557 incorporation and release. It was shown that only changes of hydrogen inhibition constants  
558 and maximum uptake of acetate rate were necessary to fit the measurements. The extended  
559 model, used by Esposito et al. [149], considered two separate influent substrates, i.e. sewage  
560 sludge and organic fraction of municipal solid waste, which were modeled with different  
561 biodegradation kinetics. The sewage sludge biodegradation modeling was based on the  
562 original ADM1. A surface-based kinetics, depending on the particle size distribution of the  
563 solid waste, was used to model the disintegration process of organic fraction of municipal  
564 solid waste. The proposed model includes the effect of the two key process parameters of the  
565 CSTR AcoD process on the methane production rate i.e. particle size and the organic loading  
566 rate [149].

567 The effect of the different feed composition and loading rates on the biogas composition and  
568 the biogas formation rate was developed for the AcoD process [150]. The main distinction of  
569 the proposed modification includes the transfer coefficients for substrates with different  
570 digestibility. The modified ADM1 was calibrated on the laboratory scale digester with the  
571 feed containing a mixture of cow manure and corn silage. The results of the simulations for  
572 single substrates and the feed mixture of corn silage, cow manure, grass silage and rapeseed  
573 oil were presented and verified with the literature data and experimental results. It was shown  
574 that planning or operational decisions of AD processes can be made with the aid of the model  
575 for substrates of different composition.  
576

577 Girault et al. [151] proposed a procedure of a waste characterization based on experimental  
578 degradation kinetics. This fractionation procedure enables to identify a single fraction of COD  
579 for which hydrolysis is a rate – limiting step and a single fraction of COD for which  
580 hydrolysis is a non rate-limiting. Thus, the optimization of the input state variable dataset is  
581 possible, especially for lignocellulosic biomass as the feedstock. Additionally, the effects of  
582 the substrate to inoculum ratio and the origin of the inoculum were investigated. The results





583 showed that the tested operating parameters had no significant impact on the fractionation  
584 results, because COD fractionation is mainly limited by temporal variability of the substrate  
585 properties [151].

586  
587 Rivas-Garcia et al. [152] performed series of numerical experiments based on the ADM1 to  
588 investigate the interactions among the microbial populations. These interactions lead to  
589 inhibition of methane production because of acidification of the medium. The experimental  
590 results reported by [153] for the AD of dairy manure were used to validate the model. It was  
591 found that the concentration of acetate – degrading bacteria is a key indicator in a substrate  
592 and inoculum formulations to secure and efficient digester performance.

593  
594 Shi et al. [154] used the mathematical model, proposed by Zhao et al. [147] and additionally  
595 based on the ADM1, for the modeling of AcoD process of complex wastes, i.e. the mixture of  
596 dairy manure and spent mushroom, with an emphasis of anaerobic hydrolysis of  
597 lignocellulosic wastes. Dairy manure was modeled according to original ADM1. Spent  
598 mushroom substrate was divided into cellulose and hemicellulose, which was hydrolyzed into  
599 the carbohydrates and the inert solids. Then, the carbohydrates were hydrolyzed into soluble  
600 sugars and soluble inert fraction. The optimization of HRT (hydraulic retention time),  
601 substrate ratio and pH value on biogas production were investigated. Process of AcoD of  
602 maize silage and cow manure was used for calibration and verification of the modified ADM1  
603 model [155,156]. The proposed model includes fractionation of influent on the basis of the  
604 extended Weender analysis and a function describing an influence of the solids on the  
605 hydrolysis process. The least satisfactory fitting of experimental to simulated results was  
606 obtained for biogas production. It was a result of the biogas production fluctuations during the  
607 experiment. Better fitting was obtained for the concentrations of propionic, butyric and acetic  
608 acids (o co chodzi?).

609 Table 7. Recent studies using the ADM1 and its modified version for modeling of anaerobic digestion and co-digestion processes for biogas  
610 production

Feedstock	Conditions	Effluent response	ADM1 modification	References
coDS: cattle manure and renewable energy crops	38°C, HRT = 20 days	BY (Nm <sup>3</sup> /d), CO <sub>2</sub> Y(%), CH <sub>4</sub> Y(%), H <sub>2</sub> Y(ppm), Ac(mgCOD/dm <sup>3</sup> ), Pr(mgCOD/dm <sup>3</sup> )	Measurement of VS instead of COD to characterize organic matter; modified pH inhibition form	[143]
coDS: mixture of OMW and OMSW with aerobic activated sludge	37±2°C, HRT = 36, 24 and 12 days	BY(dm <sup>3</sup> /d), CO <sub>2</sub> Y(%), CH <sub>4</sub> Y(%), pH, TVFA(gCOD/ dm <sup>3</sup> )	Including TVFA amount inhibition in the acetate uptake	[144]
coDS: mixture of MSW and WWTPS	37°C, HRT = 27 days	BY(dm <sup>3</sup> /d), CO <sub>2</sub> Y(%), CH <sub>4</sub> Y(%), TCOD (kgCOD/m <sup>3</sup> ), SCOD (kgCOD/m <sup>3</sup> ), TVFA(kgCOD/dm <sup>3</sup> ), pH, IC(kmol/m <sup>3</sup> ), IN(kmol/m <sup>3</sup> )		[145]
moDS: orange, apple, pig manure or rape; coDS: pig manure(60%, total weight )+ glycerin (40%, total weight)	35°C, HRT = 20 days	BY (Nm <sup>3</sup> /kgVS), CH <sub>4</sub> Y(%), pH, VS(g/ dm <sup>3</sup> ), TAN(g/ dm <sup>3</sup> ), SCOD (g/ dm <sup>3</sup> ), alkalinity (gCaCO <sub>3</sub> / dm <sup>3</sup> )	The inhibition of acetoclastic methanogens by hydrogen sulfide, agro-wastes characterization by the anaerobic biodegradability	[146]
moDS: Cattail	39±1°C, HRT = 36, 24 and 12 days	CH <sub>4</sub> (kgCOD/m <sup>3</sup> ), VFA(kgCOD/m <sup>3</sup> )	Including fractionation of influent	[147]
moDS: grass silage	38°C	BY(dm <sup>3</sup> /d), CO <sub>2</sub> Y(%), CH <sub>4</sub> Y(%), H <sub>2</sub> Y(ppm), TAN(g/kg), TN(g/kg), TVFA/alkalinity(-), TS(%), Ac(g/kg), Bu(g/kg)	Including fractionation of influent on the basis of the extended Weender analysis, including function describing the influence of solids on the hydrolysis process	[148]
coDS: OFMSW and sewage sludge	MWWTP digester	COD(kgCOD/m <sup>3</sup> ), CH <sub>4</sub> Y(kmol), MPR(kmol/d), pH,	Including the surface based kinetics at OFMSW disintegration process	[149]



coDS: mixture of cow manure and corn silage	35°C	HMA(kgCOD/m <sup>3</sup> ), AMA(kgCOD/m <sup>3</sup> ) BY (N dm <sup>3</sup> /d), CH <sub>4</sub> Y(N dm <sup>3</sup> /d),	including the transfer coefficients for substrates with different digestibility	[150]
moDS: waste activated sludge or pig slurry	38°C	MPR(Ndm <sup>3</sup> CH <sub>4</sub> /(L <sub>inoculum</sub> h)	including degradation kinetics accounting the effects of substrate to inoculum ratio and the origin of the inoculum	[151]
moDS: cattle manure	35°C	BY(v/v), VS(g/ dm <sup>3</sup> ), VFA(g/ dm <sup>3</sup> ), pH	including the interactions between the microbial populations in an anaerobic digester	[152]
coDS: dairy manure and spent mushroom substrate	35°C, HRT = 12, 20 and 28 days	BY (dm <sup>3</sup> /d), pH	including anaerobic hydrolysis of lignocellulose biomass	[154]
coDS: maize silage, cattle manure at a ratio of 49:51 (% VS).	39°C	BY (L/d), CH <sub>4</sub> Y(%), pH, Ac(kgCOD/m <sup>3</sup> ), Pr(kgCOD/m <sup>3</sup> ), Va(kgCOD/m <sup>3</sup> ),	including fractionation of influent on the basis of the extended Weender analysis, including function describing the influence of solids on the hydrolysis process	[154,156]
coDS: food waste and slurry of MSW	mesophilic conditions, HRT = 20 days	BY(m <sup>3</sup> /d), active methanogens (kgCOD/m <sup>3</sup> ), AcA(kgCOD/m <sup>3</sup> ) VFA(kgCOD/m <sup>3</sup> )	including recycling sludge	[157]
moDS: swine manure fibers, coDS: swine manure fibers and AAS pretreated manure fibers	38°C, HRT = 25 days	BY (m <sup>3</sup> /d), CH <sub>4</sub> Y(%), Ac(kgCOD/m <sup>3</sup> ), Bu(kgCOD/m <sup>3</sup> ), Pr(kgCOD/m <sup>3</sup> )	including recycling sludge	[158]
moDS: food waste or green waste	37°C	CH <sub>4</sub> Y(dm <sup>3</sup> /day), TAN(g/ dm <sup>3</sup> ), TS(g/ dm <sup>3</sup> ), VS(g/ dm <sup>3</sup> ), TVFA(gCOD/ dm <sup>3</sup> ), BA(gCaCO <sub>3</sub> / dm <sup>3</sup> ), pH	Including improved methodology for substrate characterization involving a combined biochemical and kinetic approach	[153]

611 AAS – aqueous ammonia soaking, Ac-acetate concentration in effluent, AcA- acetic acid, AMA - acetoclastic methanogenic archaea concentration, BA – bicarbonate alkalinity, Bu – butyrate, BY – biogas yield, coDS  
612 – co-substrate batch, CH<sub>4</sub>Y - methane yield, CO<sub>2</sub>Y – carbon dioxide yield, IC – inorganic carbon, HMA - hydrogen trophic methanogenic archaea concentration, IN – inorganic nitrogen, moDS – mono-substrate batch,  
613 MPR – methane production rate, MSW - municipal solid waste, MWWTP – municipal wastewater treatment plant, OFMSW- organic fraction of municipal solid waste, OMSW - olive mill solid waste, OMW - olive  
614 mill wastewater, Pr - propionic acid concentration in effluent, SOW – solid organic waste, TAN – total ammonia nitrogen, TN – total nitrogen, TS – total solids, Va – valeric acid, VFA - volatile fatty acids, VS- volatile  
615 solids, WAS – waste activated sludge, WWTPS - wastewater treatment plant sludge, TVFA – total volatile fatty acids

616 Mathematical modeling of AD process, including the effects of sludge recycling on the  
617 stability of digestion, was studied by Rathnasiri [157]. The feedstock was organic fraction of  
618 food waste. An increase of the recycled biomass caused an increase of the biogas production  
619 rate, due to the increase of the methanogens activity and the enhancement of acetic acid  
620 conversion. It was found that the reactor stability decreases with an increase of OLR and the  
621 reactor was completely inhibited when input OLR was doubled. Instability was confirmed by  
622 accumulation of volatile fatty acid and inhibition of strict methanogens.  
623

624 Jurado et al. [158] tested the methane production from swine manure treated by the aqueous  
625 ammonia soaking in CSTR digesters for mesophilic conditions. Addition of the pretreated  
626 manure fibers to the feedstock resulted in an increase by 22% in biogas production and by  
627 98% of methane yield compared to manure fibers without treatment. The modeling of AcoD  
628 by ADM1 showed that the disintegration and hydrolysis of the solid matrix of swine manure  
629 preceded extremely slowly. In the case of mixture of swine manure and pretreated manure  
630 fibers, the disintegration and hydrolysis rate increased significantly.  
631

632 Poggio et al. [153] developed an improved methodology for substrate characterization based  
633 on the direct substrate analysis and the data from experiments in bioreactors. Four substrate  
634 fractionation models were integrated into ADM1 and evaluated for their ability to fit the  
635 experimental and simulated data. The method was tested using data from short batch testing  
636 and semi-continuous experiments with the food waste and green waste as influent. The best  
637 prediction of methane production, biogas composition, totals and volatile solids, ammonia and  
638 alkalinity were obtained for the fractionation models based on data from batch test.  
639

640 ADM1 is also utilized to model the anaerobic digestion in more complex systems like BSM2  
641 (Benchmark Simulation Model no. 2). BSM2 is an example of a plant-wide modeling in  
642 which the anaerobic digestion is regarded as a unit stage. BSM2 is a model-based complex  
643 tool for development, evaluation and analysis of plant-wide control strategies for wastewater  
644 treatment plants [140,159,160], including all steps of treatment occurring in primary clarifier,  
645 activated sludge tanks (anaerobic and aerobic), secondary clarifier as well as the sludge  
646 thickener, sludge dewatering unit and storage tank. Among all the stages of wastewater  
647 treatment, anaerobic digestion (AD) is a key process for sludge treatment and its operation is  
648 of great importance for the overall performance of a wastewater treatment plant. This is  
649 because the biogas is the final product of the AD process and its production may be an  
650 indicator of the digester performance [161].

651 It is well known that the input characterization is a major challenge for modeling of anaerobic  
652 digestion processes. In the BSM2, the degradation of particulate substrates in anaerobic  
653 digestion is modified compared to original ADM1. This is because there is an activated  
654 sludge treatment prior to AD and an interface is needed to convert the state variables from  
655 activated sludge directly to the products of disintegration rather than to overall particulate  
656 composite material. Such an approach allows for adapted composition depending on substrate  
657 and separates the feed from dead biomass. The disintegration step is fixed for dead biomass  
658 and as the disintegration step is rate limiting, the hydrolysis rates must be adjusted to obtain a  
659 realistic degradation rate [160]. Additionally, when various substrates are co-digested, Arnell  
660 et al. [162] propose to implement a function for long-chain fatty acids inhibition to the  
661 modified ADM1 for BSM2.

662 The AD process is the important clean technology for simultaneous organic waste treatment  
663 and production of alternative sources of energy like biogas. As described above, the  
664 technology of anaerobic co-digestion is intensively developed as a valuable solution for the  
665 disposal of different types of organic wastes with the sewage sludge. The composition of two

666 or more substrates provides better nutrient balance and may favor positive interactions, as  
667 well as dilute the inhibitors concentrations and increase the biogas production. Mathematical  
668 modeling of the AcoD process is most often based on ADM1 model. Among different process  
669 parameters affecting the yield and rate of biogas generation, the pH of the pulp, temperature,  
670 substrate composition, biomass pre-treatment method and digestion time seem to be the most  
671 important ones. The results of recently published studies showed that substrate  
672 characterization is ultimately the most influential model input on methane production  
673 prediction. In general, an increased fractionation model complexity led to better fit but with  
674 increased uncertainty. Furthermore, hydrolysis is assumed to be the first limiting step in AD  
675 process, especially for substrates with high content of solid fraction. The development of  
676 feedstock characterization methods and accurate calculations of kinetic factors to provide the  
677 required model inputs was still a bottleneck to a broader adoption of ADM1 model. The  
678 presented literature review clearly depicts that selection of proper digestion conditions as well  
679 as the prediction of the yield and quality of biogas may be substantially aided with  
680 mathematical modeling.

681 The above presented literature review shows that chemical composition and biodegradability are  
682 the key factor for the biogas production process. Substrate characterization is one of the most  
683 influential model input for methane flow prediction. Besides the knowledge of the process  
684 dynamics, a proper structural identification plays the key role in the success of the  
685 optimization process. Determination of substrate composition of agricultural waste and  
686 biomass from energy crops is complicated for materials rich in fibers and consisting of several  
687 main components, such as cellulose, hemicellulose and lignin. Additionally, in the recent  
688 years the process of anaerobic combined digestion (AcoD) has been recommended to enhance  
689 the biogas production of the digester. Mixing the carbon – rich substrates (lignocellulosic  
690 biomass) with the nitrogen - rich wastes (animal manure, food waste) improve the process  
691 stability and the balance of nutrient content. Therefore, the modeling of AcoD process needs  
692 to predict the impact of the mixing ratio of two or more substrates, loading rates and the  
693 selection of the pretreatment method of substrates.

694 The ADM1 was originally developed for modeling biogas production from sewage sludge;  
695 however, its structure is a standard for further modifications and allows for modeling of  
696 biogas production by anaerobic degradation for various substrates. The application of the  
697 ADM1 to simulate the production of biogas is a very challenging task, due to the rapid  
698 development of biogas plants operating with agricultural waste and biomass from energy  
699 crops as a feedstock.

### 701 5.3. Substrate conversion-based models

702

703 The other group includes models based on a substrate conversion for the estimation of the  
704 biofuels production yield. Monlau et al. [21] investigated the relation between the  
705 compositional and structural features of lignocellulosic biomass on the biogas production. It is  
706 because without the determination of composition as well as the structural properties it is  
707 impossible to evaluate the potential of methane production from the lignocellulosic biomass.  
708 For the evaluation of biogas production estimated by BMP (Biological Methane Potential or

709 Biomethane Potential,  $\frac{ml_{CH_4}}{g_{TS}}$ ), a multilinear partial least square (PLS) model was developed.

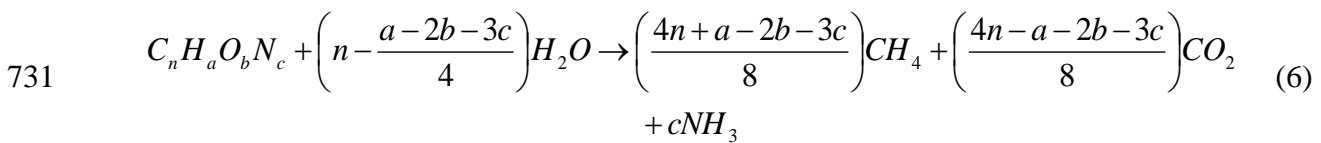
710 The PLS analysis was performed in a full cross validation, so called leave-one-out cross  
711 validation procedure. Following equation was proposed, considering the compositional as  
712 well as structural parameters most significantly affecting the biogas production:

713  
 714  $BMP = 303.14 - 4.53 \cdot Lig + 0.77 \cdot SolSu + 1.28 \cdot Pro - 1.59 \cdot Cri + 0.61 \cdot Am + 1.33 \cdot Ua$  (5)  
 715

716 where: Lig – lignin,  $\frac{g}{gTS}$ , SolSu – soluble sugars,  $\frac{g}{gTS}$ , Pro – protein,  $\frac{g}{gTS}$ , Cri –  
 717 crystalline cellulose,  $\frac{g}{gTS}$ , Am – amorphous holocelluloses,  $\frac{g}{gTS}$ , Ua – uronic acids,  $\frac{g}{gTS}$ ;  
 718 where TS – total solids.  
 719

720 The proposed model (equation 5) may be used to estimate methane yields in relation to  
 721 compositional and structural properties of lignocellulosic biomass, however it does not inform  
 722 about the substrate degradation rates. Moreover, no abiotic or biotic factors i.e. pH, particle  
 723 size, porosity etc. are taken into account.  
 724

725 Li et al. [47] investigated the methane production potential, biodegradability of substrates and  
 726 kinetics depending on various organic substrates, including lignocellulosic biomass. The  
 727 authors [47] applied following Buswell formula for calculation of the theoretical methane  
 728 yield based on the elemental composition of organic substrates ( $TMY_{ele}$ ,  $\frac{ml_{CH_4}}{g_{VS}}$ ; VS – volatile  
 729 solids):  
 730



733 
$$TMY_{ele} = \frac{22.4 \cdot 1000 \cdot \left( \frac{4n + a - 2b - 3c}{8} \right)}{12n + a + 16b + 14c}$$
 (7)  
 734

735 Where: VS – volatile solids.

736 Theoretical methane yield based on the organic composition ( $TMY_{org}$ ,  $\frac{ml_{CH_4}}{g_{VS}}$ ) is expressed  
 737 by the following formula:  
 738

739 
$$TMY_{org} = \frac{373VFA + 496Pro + 1014Lip + 415Carb + 727Lig}{100}$$
 (8)  
 740

740 Where: VFA – volatile fatty acids, Pro – protein, Lip – lipids, Carb – carbohydrates.  
 741

742 Anaerobic biodegradability of the substrate was calculated by dividing the experimental  
 743 methane yield by either elemental or organic TMY.

744 Mirmohamadsadeghi et al. [40] investigated the biogas production from hardwood elm,  
 745 softwood pine and agricultural waste rice straw using biomass pretreatment with organosolv  
 746 method. For such purpose, lignocellulosic biomass was treated at elevated temperatures (150  
 747 and 180°) with 75% ethanol solution and sulfuric acid as a catalyst. Kinetics of AD process  
 748 was described by the equation analogous to the first-order rate equation.

749 Li et al. [47] applied a first-order kinetic model to determine the extent and the rate of a  
 750 substrate biodegradation:

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$$B = B_0[1 - \exp(-kt)] \quad (9)$$

Where: B – cumulative methane yield, B<sub>0</sub> – ultimate methane yield, k – first-order rate constant, t – digestion time.

As lignocellulosic biomass is not easily biodegradable, mainly due to the complex structure of lignin and other polysaccharides constituting the cell wall, the investigation of the influence of lignin on methane production is highly important. Therefore, Li et al. [47] proposed a useful set of data (including i.e. EMY, TMY, BD and k values) to help to solve the problem.

Fedailaine et al. [137] studied the modeling of bio kinetics of anaerobic digestion. Following aspects were analyzed and incorporated into the model: microbial activity, substrate degradation and methane production. The established model is based on mass balances on the substrate, biomass and methane production. Simplifying assumptions to the model include the tightness of the bioreactor, perfect agitation and uniformity in the reactor. Additionally, the growth kinetics obeys the substrate inhibition model (Haldane model), the factor that limits the bacterial growth is the presence of organic substrate and the suspended biomass contributes to the biodegradation of the substrate.

Kinetics of biogas production from lignocellulosic ensiled forage ley with addition of endogenous cellulolytic enzymes during the AD process was investigated by Speda et al. [41]. The applied induced enzyme solution contained enzymes apparently active and stable in the environment of anaerobic digestion. It was found that the addition of enzymes increased both the rate and yield of biomethane production. The kinetic studies revealed that the biogas production process may be divided into two phases: the first phase represents the gas production as a result of hydrolysis of easily accessible material, while the second phase represents the biogas production from the digestion of less microbiologically accessible materials i.e. lignocelluloses. Both above named stages may be described by 1<sup>st</sup> order kinetics and the rate of the second phase is increased by the enzymes addition. Selected research of biogas production from lignocellulosic biomass is presented in Table 8.

Table 8. Selected research on fermentative conversion of lignocellulosic biomass to biogas

Feedstock	Biomass pre-treatment	AD conditions	Applied model	Parameters investigated	Reference
Corn straw	Mechanical, thermal, biological with complex microbial agents	AD incubator with a shaker, mesophilic conditions	BMP	pH, digestion time, type of biological treatment	[163]
Hardwood elm, softwood pine, waste rice straw	Mechanical, organosolv (ethanol, H <sub>2</sub> SO <sub>4</sub> ), thermal (150 and 180°C)	Effluent from mesophilic digester as inoculum; glass digester vessel, mesophilic AD	1 <sup>st</sup> order kinetics model	Pre-treatment conditions, substrate type, digestion time	[40]
Ensiled	No information	Addition to	BMP	Time, effect	[41]

forage ley		AD endogenous enzymes collected from methanogenic microbial community		of enzymes addition	
Pulp and paper sludge	Thermal (80°C, 90 min)	Cow dung as inoculum, 30 ÷ 38°C, mechanical mixing	BMP, modified Gompertz model, logistic function model, transference function model	Substrate concentration, pH, time	[164]

785 AD – anaerobic digestion BMP – Biological Methane Potential

#### 786 5.4. Kinetic-based models

787  
788 This group of models includes unstructured kinetic models, in which microorganisms are  
789 usually considered to be a component or reactant in the system. In recent years, modified  
790 Gompertz model, developed by Zwietering et al. [165] has been widely used for nonlinear  
791 modeling of the typical cumulative biogas or biohydrogen production course. The data is  
792 fitted to the modified Gompertz equation assuming the gas production in batch mode is a  
793 function of the specific growth rate of microorganisms in the bio digesters. The equation can  
794 be written as follows:

$$795 \quad P = A \cdot \exp \left\{ - \exp \left[ \frac{U_m e}{A} (\lambda - t) + 1 \right] \right\} \quad (10)$$

796  
797 where  $P$  is the cumulative volume of specific gas production ( $m^3$ ),  $A$  the gas production  
798 potential ( $m^3$ ),  $U_m$  the maximum production rate ( $m^3/h$ ),  $\lambda$  the lag phase time or the minimum  
799 time required to produce gas (h),  $t$  incubation time (h) and  $e$  is the constant equal to 2,718.

800  
801 In a batch test,  $P$  increases very slowly with increasing cultivation time from 0 to 1, and then  
802 increases rapidly almost at the rate of  $U_m$  and with a further increase of the cultivation time, it  
803 finally reaches an asymptotic value  $A$ . The values of  $A$ ,  $U_m$  and  $\lambda$  are determined for each  
804 batch test by best fitting between experimental and estimated modeled data using non-linear  
805 regression.

#### 806 *Biogas production*

807 Kinetics of biogas production from lignocellulosic biomass mixed with fresh cattle dung (1:3)  
808 was studied by Das Ghatak and Mahanta [166]. The investigated lignocellulosic feedstock  
809 included bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk. Lignocellulosic  
810 biomass was mixed with cattle dung for the purpose of increasing its carbon to nitrogen ratio  
811 so as to obtain optimal conditions for anaerobic digestion. Authors [166] applied the modified  
812 Gompertz equation to model the anaerobic digestion in thermophilic range i.e. within 45 –



813 55°C. A good correlation between the experimental data and data predicted by the model was  
814 obtained.

815 Abdelhay et al. [167] investigated the biogas production from green waste (grass and leaves)  
816 mixed with organic part of municipal waste. For the simulation of the biogas production, they  
817 have used the modified Gompertz equation. They have applied the design of experiment with  
818 two levels of each investigated parameter as well as the response surface modeling. The input  
819 data included total solids and leachate volumetric fraction while the response variables were  
820 biogas production and methane content.

821 Das Ghatak and Mahanta [168] developed a model for evaluating the effect of temperature on  
822 the rate of biogas production from various lignocellulosic biomass substrates. They applied a  
823 modified Gompertz equation, validating it as being useful for prediction of the biogas  
824 production from lignocellulosic biomass mixed with cattle dung under given conditions.  
825 Selected studies using the modified Gompertz equation for modeling of fermentative  
826 production of biogas are presented in Table 9.

827  
828 Table 9. Recent studies applying the modified Gompertz equation for modeling of  
829 fermentative biogas production

Feedstock	Inoculum	Conditions	Investigated parameters	Modeled factors	References
Bamboo dust, saw dust, sugarcane bagasse, rice straw, rice husk mixed with fresh cattle dung	Cattle dung	45 ÷ 55°C, addition of water to feedstock (3:1)	Substrate type, temperature, digestion time	Cumulative biogas production	[166]
Pulp and paper sludge	Cow dung	80°C, 90 min	Substrate concentration, pH, time	Methane production	[164]
Grass and leaves mixed with municipal waste	Leachate or anaerobic sludge from wastewater treatment plant	38°C, fermentation for 20 days	Total solids, leachate fraction	Biogas production, methane concentration	[167]
Lignocellulosic materials	Cattle dung	Batch fermentation, total solids < 9%	temperature	Biogas rate	[168]

830

### 831 *Biohydrogen production*

832 The course and the yield of biohydrogen production by dark fermentation is mainly affected  
833 by the biomass pretreatment method. The effect of pretreatment was investigated for e.g.  
834 poplar leaves [169], soybean straw [170], and wheat straw [171]. Quemeneur et al. [172]  
835 tested the influence of lignocellulosic-derived compounds formed during the pretreatment  
836 processes. These byproducts may inhibit microbial growth and reduce fermentability. In all  
837 these studies, the Gompertz equation was used for modeling the kinetics of hydrogen  
838 formation. Selected studies applying the modified Gompertz equation are given in Table 10.

839 The effects of pretreatment conditions and feedstock biomass concentration on the hydrogen  
840 production for de-oiled *Jatropha* waste were investigated by Kumar et al. [173]. The hydrogen  
841 production kinetics was evaluated by Gompertz and Monod models. Monod model was used  
842 to explain the influence of residual sugar concentration in the hydrolysates on HPR. The  
843 results showed that the best pretreatment methods are acid and enzymatic hydrolyzes and  
844 their combination. Reilly et al. [174] predicted cumulative hydrogen production from  
845 simultaneous saccharification and fermentation of wheat straw pretreated with calcium  
846 carbonate. The alkali pretreatment removed over one-third of hemicellulose from the straw. It  
847 resulted in easier access of the supplemented cell wall degrading enzymes into the material  
848 and higher hydrogen production. The waste activated sludge treated by the low pressure wet  
849 oxidation was applied for the hydrogen production by dark fermentation [175]. The hydrogen  
850 yield was determined by Gompertz model for the fermentation using glucose, treated sludge  
851 or the mixture of the treated sludge and glucose as the substrate. The hydrogen production  
852 was the lowest for the sole treated sludge. However, concentrations of polysaccharides and  
853 proteins present in the liquid phase increased after the treatment.

854  
855 The other important factor regarding fermentative conversion of biomass to hydrogen is the  
856 composition of substrates. Cheng et al.[4] used the two-stage system for the co-production of  
857 hydrogen and methane from cornstalk. Batch hydrogen fermentation was performed in a  
858 continuously stirred tank reactor. The cumulative hydrogen volume increased and hydrogen  
859 yield decreased as the cornstalk concentration in feedstock increased. The effect of cornstalk  
860 addition on hydrogen production from sewage sludge was investigated by Liu [176].  
861 Cumulative hydrogen volume and maximum hydrogen production rates at various total solid  
862 ratios between cornstalk and sewage sludge were simulated by the modified Gompertz model.  
863 The results showed that the hydrogen yield and energy yield increased with the increase of  
864 cornstalk concentration in the feedstock. The effect of the various waste activated sludge to  
865 food waste ratios on the efficiency of the hydrogen production in mesophilic dark  
866 fermentation was modeled with the modified Gompertz equation [177]. The highest yield of  
867 hydrogen and the highest energy yield were observed for sole food waste fermentation. It  
868 corresponds to results of VS removal efficiency for co-digestion. However, the maximum  
869 specific hydrogen production rate followed opposite trend. Fermentation of synthetic  
870 lignocellulosic hydrolysate was performed with the variable sugar concentration in the  
871 feedstock and with addition of furfural [86]. The substrate-to-microorganism ratio was used  
872 for evaluation of the feedstock composition. Results indicated a significant interaction  
873 between substrate-to-microorganism ratio and furfural concentration. The effect of initial  
874 sugar and biomass concentration on the hydrogen formation was tested for waste paper as the  
875 raw material [178]. It was reported that final cumulative hydrogen formation increased with  
876 the initial sugar concentration up to 18,9 g/l and decreased with further increase of the sugar  
877 content. The highest cumulative hydrogen formation was obtained at the initial biomass  
878 concentration equal to 0,5 g/l and then decreased if the biomass concentration increased. It  
879 may have been due to hydrogen consumption by homoacetogenic bacteria with the purpose of  
880 acetic acid production. Gonzales et al. [179] performed dark fermentation on different types  
881 of lignocellulosic biomass: empty palm fruit bunch, rice husk or pine tree wood pellets. The  
882 highest value of hydrogen yield was obtained for rice husk, while the lowest for empty palm  
883 fruit bunch. Generation of inhibitory byproducts such as hydroxymethylfurfural and furfural  
884 was observed during acid pretreatment for empty palm fruit bunch and pine tree wood pellets.

885  
886 The effect of pH on hydrogen production was investigated for batch fermentation of  
887 pretreated oil palm empty fruit bunch [180]. The highest cumulative hydrogen production,  
888 hydrogen yield and hydrogen production rate were obtained at pH = 5,5. It corresponds to the

889 observed increase of acetic and butyric acids formation with a decrease of pH [19]. Zhang et  
 890 al. [181] stated the improvement of the hydrogen production at various mixed cultures  
 891 systems compared to mono-culture system from hydrolysates derived from *Miscantus* after  
 892 hydrothermal pretreatment with dilute acids. The pretreatment process was carried out under  
 893 different process parameters (temperature, pH, retention time) to obtain the hydrolysates with  
 894 different glucose to xylose ratio. It was observed, based on the modeling of the experimental  
 895 results, that the enhancement of hydrogen production is possible for xylose – rich  
 896 lignocellulosic hydrolysates. Argun and Dao [182] reported the effect of varying inoculum  
 897 addition on hydrogen formation rate and yield from waste peach pulp during dark  
 898 fermentation. Hydrogen yield increased with the increase of the inoculum ratio from 0 to 5%.  
 899 Concentration of inoculum higher than 5% did not improve the hydrogen yield.

901 Table 10. Recent studies using the modified Gompertz equation for modeling of fermentative  
 902 hydrogen production

Feedstock	Inoculum	Conditions	Investigated parameters	Modeled factors	References
Pretreated poplar leaves	Mixed cultures from cracked cereal	35°C	Pretreatment method	HY (cm <sup>3</sup> H <sub>2</sub> /g dry poplar leaves)	[169]
Pretreated soybean straw	Mixed cultures from cracked cereal	35°C, pH = 7	Pretreatment method	HY (cm <sup>3</sup> H <sub>2</sub> /g substrate)	[170]
Wheat straw	Heat – pretreated mesophilic anaerobic digested sludge	37°C, pH = 5,5	Enzyme addition	HY (cm <sup>3</sup> H <sub>2</sub> /g VS)	[171]
Lignocellulose – derived compounds	Heat – pretreated anaerobic digested sludge	37°C, pH = 5,5	Inhibitor addition	HY (mol H <sub>2</sub> /mol xylose)	[172]
Alkali pretreated cornstalk	Heat – pretreated anaerobic sewage sludge	37°C, pH = 7	Cornstalk to sewage sludge proportion	HY (cm <sup>3</sup> H <sub>2</sub> /g VS), EY (kJ/g VS)	[4]
Alkali pretreated cornstalk	<i>C. thermocellum</i> 7072	55°C	Substrate concentration, stirring speed	HY (cm <sup>3</sup> H <sub>2</sub> /g cornstalk)	[176]
Waste activated sludge and food waste	Heat – pretreated activated sludge	37°C, pH = 5,5	Composition of substrate	HY (cm <sup>3</sup> H <sub>2</sub> /g VS), EY (kJ/g VS)	[177]
Acid hydrolyzed oil palm empty fruit bunch	Palm oil mill waste sludge	35°C, pH = 5÷7	pH	HY (mol H <sub>2</sub> /mol xylose), HPR (mmol/ dm <sup>3</sup> /h)	[180]
<i>Miscantus</i>	<i>Clostridium</i>	35°C,	Composition	HY (mol	[181]

hydrothermal pretreatment with dilute acids	<i>beijerinckii</i> /Co-culture of <i>Clostridium beijerinckii</i> and <i>Geobacter matallireducens</i>		of inoculum, glucose to xylose ratio in lignocellulosic hydrolysates	H <sub>2</sub> /mol xylose), HPR (mmol/ dm <sup>3</sup> /h)	
Ca(OH) <sub>2</sub> pretreatment wheat straw	Digested sewage sludge	35°C, pH = 6,25	Time of pretreatment process, concentration of Ca(CO) <sub>3</sub> formed during pretreatment processes	H (cm <sup>3</sup> H <sub>2</sub> /g VS),	[174]
Heat and acid de-oiled Jatropha waste pretreated by enzyme, acid, alkali, heat and ultrasonification	Heat-treated sludge	55°C, pH = 7	Pretreatment method, feedstock biomass concentration	HY (cm <sup>3</sup> H <sub>2</sub> /g VS), HPR (mmol/ dm <sup>3</sup> /d)	[173]
Synthetic lignocellulosic hydrolysate	Mesophilic anaerobic digester sludge	37°C, pH = 5,5	Furfural concentration	HY (cm <sup>3</sup> H <sub>2</sub> /mol sugars <sub>initial</sub> ), H <sub>2</sub> cumulative (cm <sup>3</sup> )	[86]
Heat pretreatment waste peach pulp	Anaerobic sludge	37°C,	Inoculum concentration	HY (cm <sup>3</sup> H <sub>2</sub> /g starch), HPR (mL/h)	[182]
Paper waste	Heat - treated acidogenic phase of anaerobic treatment plant	37°C, pH = 6,8	Initial sugar and biomass concentration	H (cm <sup>3</sup> )	[178]
Empty palm fruit bunch, rice husk, pine tree wood pellets	Heat – treated anaerobic digester sludge	35°C, pH = 7	Type of lignocellulosic biomass	HY (mol H <sub>2</sub> /mol total sugar), HPR (ml H <sub>2</sub> /dm <sup>3</sup> /d)	[179]
Low-pressure wet oxidation pretreatment waste sludge or the mixture of treated	Heat – treated anaerobic digester sludge	36°C, pH = 7	Pretreatment conditions	HY (mol H <sub>2</sub> /mol SCDO),	[175]

sludge and  
glucose

903 EY – energy yield, HPR – hydrogen production, HY – hydrogen yield, SCOD – soluble chemical oxygen  
904 demand

905  
906

907 Modified Gompertz equation is a simple kinetic model used to describe the progress of  
908 product formation, mainly H<sub>2</sub> or some soluble metabolite products. Modeling of the  
909 fermentative hydrogen production process includes the mathematical description of the other  
910 process components of the dark fermentation such as kinetics of microbial growth and the  
911 substrate utilization. Simple kinetic models are used for this purpose, although only a few  
912 works refer to processes using complex organic substrates. Boni et al. [183] developed and  
913 calibrated the model based on the classic Monod equation for the description of hydrogen  
914 production from organic wastes. The solution of Monod equation for the two steps i.e. the  
915 substrate consumption and the cell growth are as follows:

$$916 \quad \frac{dS}{dt} = -\frac{1}{Y} \left( \frac{\mu_m \cdot S}{k_s + S} \right) X \quad (11)$$

917

$$918 \quad \frac{dX}{dt} = \left( \frac{\mu_m \cdot S}{k_s + S} \right) X - k_d X \quad (12)$$

919 where:  $S$  is the concentration of substrate (g COD/m<sup>3</sup>),  $t$  is the time (h),  $Y$  is the ratio between  
920 the rate of bacterial growth and the rate of substrate utilization (mg VSS/mg COD),  $\mu_m$  is the  
921 maximum specific growth rate (1/d),  $k_s$  is the half-velocity constant (g COD/m<sup>3</sup>),  $X$  is the  
922 concentration of the cells (g COD/m<sup>3</sup>),  $k_d$  is the endogenous decay coefficient (1/d).

923

924 The important factors considered in the model are the cell death (a first-order decay rate is  
925 assumed) and temperature effects, according to the van Hoff-Arrhenius relationship.

926

927 Is well known that at high substrate concentration, the cell growth is inhibited and the  
928 hydrogen production is reduced. Among different substrate inhibition models, the Haldane-  
929 Andrew equation (equation 13) and the Han-Levenspiel equation (equation 14) are  
930 recommended for the description of the inhibitory nature of substrates [184,185]:

$$931 \quad \mu = \frac{1}{X} \frac{dX}{dt} = \mu_m \frac{S}{k_s + S + \frac{S^2}{k_i}} \quad (13)$$

$$932 \quad \mu = \frac{1}{X} \frac{dX}{dt} = \mu_m \left( 1 - \frac{C}{C_m} \right) \quad (14)$$

933 Where:  $\mu$  is the specific growth rate (1/d),  $k_i$  is the inhibition constant (g COD/m<sup>3</sup>),  $C$  is the  
934 inhibitor concentration (g COD/m<sup>3</sup>),  $C_m$  is the maximum inhibitor concentration or the  
935 concentration of inhibitor above which biomass growth ceases (g COD/m<sup>3</sup>).

936 The literature research indicates that hydrogen production and fermentation kinetics vary with  
937 the composition and characteristics of the substrate. Above mentioned substrate inhibition  
938 models are able to provide satisfactory description of data for hydrogen production using  
939 simple substrates (glucose, sucrose or xylose). However, they do not adequately predict the  
940 results of processes occurring from different types of complex organic wastes.

941 The Gompertz model describes the progress of hydrogen production process with high values  
942 of correlation coefficient values between the experimental and model-fitted data. This model

943 has the ability to describe a broad range of factors influencing the batch fermentative  
 944 biohydrogen production process. However, the three model parameters (the cumulative  
 945 volume of hydrogen production, the gas production potential and the lag phase time) are  
 946 determined on the basis of experimentally measured hydrogen evolution data. Because of that,  
 947 the model parameters are restricted to specific experimental conditions and cannot be used to  
 948 predict fermentative process under varying combination of multiple substrates, bacterial  
 949 strains and process parameters. Utility of Gompertz model is also limited. The model cannot  
 950 be used for the prediction of volatile fatty acid formation and substrate consumption.  
 951 Modeling of hydrogen production from complex organic substrates by dark fermentation  
 952 requires also the modeling of other bioprocesses i.e. hydrolysis or acidogenesis. In the  
 953 literature there is a lack of such a kinetic model incorporating various parameters affecting  
 954 fermentative hydrogen production.

## 955 5.5. Black-box models

956 Black-box models i.e. response surface methodology (RSM) or artificial neural networks  
 957 (ANN) are very attractive for the description of biotechnological processes. The relationships  
 958 between the key input process variables and the output characteristics given in the form of  
 959 equations are useful tools for both scientists and engineers. These empirical models do not  
 960 require knowledge of the mechanisms of processes that are described, but they are able to  
 961 predict the relationships between input and output variables on the basis of the set of  
 962 experimental data. This approach makes it possible to obtain reliable and statistically  
 963 significant results without knowing the details of the complex transformations and reactions  
 964 taking place during the biomass conversion processes.

### 965 5.5.1. Response surface methodology

966 In the case of complex systems, statistical methods allow to determine the empirical models  
 967 based on the well-designed experiments. These empirical models are usually used for  
 968 screening and characterization of variables or the process optimization. A lot of experimental  
 969 design methods are proposed [186] and some of them have been adopted for modeling and  
 970 optimization of gaseous biofuel production via fermentation route with RSM as the most  
 971 frequently used. RSM is used to i) determine the sensitivity of the efficiency of biohydrogen  
 972 or biogas to the factors including substrate type and its initial concentration, temperature, time  
 973 or pH [187,188]; ii) to assess the importance of the individual factors; iii) to find the level of  
 974 variables to provide the optimum fermentation course; and iv) to find the factor range that  
 975 produces the best combination of several different response (like yield of the produced gas,  
 976 process rate, concentration of impurities in the generated gas stream provided they are taken  
 977 into account).

978 The collected data concerning the biohydrogen and biogas production processes modeled with  
 979 RSM methods are given in Table 11.

980 Table 11. Application of RSM in modeling of biogas production and biohydrogen

Substrate	Inoculum	Investigated factors	Response	Type of design	References
Biogas					
Pretreated <i>Tithonia diversifolia</i> shoot	Consortium of microorganisms	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg TS <sub>fed</sub> )	CCD	[189]
Pretreated	Consortium of	T, pH, RT,	BY (m <sup>3</sup> /kg	CCRD	[190]

<i>Chromolaena odorata</i> with poultry manure	microorganisms	TS, VS	VS <sub>fed</sub> )		
Pretreated and untreated <i>Carica papayas</i> fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	CCD	[191]
Pretreated <i>Carica papayas</i> fruit peels and poultry dropping	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	CCRD	[192]
Pretreated <i>Telfairia occidentalis</i> fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	CCRD	[193]
Food waste	Mesophilic anaerobic digestion sludge	Concentration of Ca, Mg, Co and Ni	CH <sub>4</sub> (cm <sup>3</sup> )	CCD	[194]
Food waste and poultry manure	Not specified	T, pH, ratio poultry manure : food waste temperature, pH, substrate concentration, agitation time	CH <sub>4</sub> (cm <sup>3</sup> / VS)	CCD	[195]
Rice straw	Cow manure		BY (dm <sup>3</sup> )	CCD	[196]
Biohydrogen					
Bean-husk: corn stalk: organic fraction of solid municipal waste	Heat-pretreated anaerobic sludge	S <sub>0</sub> , pH, T, HRT	HY (cm <sup>3</sup> H <sub>2</sub> /gVS)	BBD	[197]
De-oiled <i>Jatropha</i> wastes	Heat-pretreated anaerobic sludge	S <sub>0</sub> , pH, T	HY(cumulative H <sub>2</sub> production)	CCD	[198]
Food wastes	Heat-pretreated anaerobic sludge	pH, T, (insignificant: inoculum size, COD)	HY(cm <sup>3</sup> H <sub>2</sub> /g carbohydrate); HFR (cm <sup>3</sup> H <sub>2</sub> /h)	CCD with screening	[199]
Potato waste	Heat-pretreated anaerobic sludge	S <sub>0</sub> , pH, T, τ	HY (cm <sup>3</sup> H <sub>2</sub> /g VS)	BBD	[200]
Hydrolyzed	Heat-pretreated	S <sub>0</sub> , S <sub>0</sub> :buffer,	HY(as	CCD	[201]

sugarcane bagasse	sludge from hydrogen pilot plant	inoculum:S <sub>0</sub>	cumulative H <sub>2</sub> production)		
Waste peach pulp	Natural microflora	C/N, C/P, C/Fe, C/Ni	HY (cm <sup>3</sup> /g COD), HFR (cm <sup>3</sup> H <sub>2</sub> /h)	BBD	[202]
Waste sugarcane leaves	Anaerobic sludge	S <sub>0</sub> , inoculum concentration, HRT	HY (cm <sup>3</sup> /g sugar)	BBD	[203]

981 S<sub>0</sub> – initial substrate concentration, T - temperature,  $\tau$  – time, HRT – hydraulic retention time; RT – retention  
 982 time, TS – total solids, VS – volatile solids, COD – chemical oxygen demand; HY - H<sub>2</sub> yield, HFR – H<sub>2</sub>  
 983 formation rate, BY – biogas yield, BBD – Box-Behnken design; CCD – central composite design; CCRD –  
 984 central composite rotatable design  
 985

986 The central composite design (CCD) and the Box-Behnken design (BBD) enable an efficient  
 987 use of experimental test runs in comparison to factorial experiments [204], because it is  
 988 possible to obtain enough information from relatively small number of experiments. Both of  
 989 above mentioned design methods provide good results for practical problems, especially for  
 990 long-term and time consuming bioprocesses.

#### 991 *Biogas production*

992 The five-level CCD was applied to determine RSM model of biogas formation during  
 993 anaerobic digestion of pretreated Mexican sunflower [189]. Investigated factors that  
 994 influenced the biogas production were temperature, pH, retention time, total solids (TS) and  
 995 volatile solids (VS). The calculated values of biogas yield using a developed regression model  
 996 equation were slightly overestimated in comparison to those obtained in experiments. The  
 997 highest biogas yield was 2249 l /kg TS. The similar method was used to model and optimize  
 998 the biogas production from *Carica papayas* fruit peels [191]. The values of the biogas yield  
 999 predicted by RSM were usually higher than the experimental values. Based on the optimized  
 1000 values of process parameters, the predicted biogas yield was 189.5 l/kg (VS).

1001 The five-level central composite rotatable design (CCRD) was used to obtain a model for  
 1002 biogas production from pretreated Siam weed and poultry manure [190]. The used inlet  
 1003 variables were temperature, pH, retention time, TS and VS. The fitting of results of the biogas  
 1004 yield (in m<sup>3</sup>/kg of VS) from experiments and calculated values from the model equation was  
 1005 about 90%. The highest yield of biogas depended on the type of weed pretreatment and it was  
 1006 3.884 l/kg VS for a substrate sample pretreated with mechanical, chemical and thermal  
 1007 methods, and 2.554 l/kg VS for a substrate pretreated using mechanical and chemical methods  
 1008 only. Similar approach was adopted for modeling and optimization of biogas production from  
 1009 *Carica papaya* peels and poultry dropping [192]. The biogas yield for optimally determined  
 1010 conditions was 3.979 l/ kg VS. The model-based calculated values of biogas yield were higher  
 1011 than experimental values and the accuracy of the predicted values was 91.8%. The same  
 1012 method was used to obtain the model equation of biogas production in anaerobic digestion of  
 1013 peels of fluted pumpkin [193]. Accuracy of predicted biogas yield was about 90% and the  
 014 optimal yield value was in the range from 1.629 to 1.695 l/kg VS, depending on the substrate  
 015 pretreatment method.

016 Concentrations of micronutrient supplement containing Ca, Mg, Co and Ni were optimized  
 017 using CCD of experimental tests for biogas production from food waste [194]. The  
 018 investigated variables were divided into two groups: Ca-Mg and Co-Ni, and each given pair  
 019 was modeled separately. The response variable was cumulative methane production, similarly  
 020 for both cases. It was found that the optimal concentration of micronutrient supplement could



1021 enhance methane production by 2.7 times than a control methane volume. The accuracy of  
1022 prediction for Ca-Mg and Co-Ni was about 88%.

1023 The optimal combination of parameters i.e. temperature, pH and the ratio of poultry manure  
1024 to food waste for methane production in anaerobic digestion was determined using CCD  
1025 [195]. The highest production of methane was 535 cm<sup>3</sup>/g VS and the accuracy of the  
1026 predicted value with the model value was 99%.

1027 Prediction of the biogas production efficiency was investigated by [196]. The authors studied  
1028 the biogas production from rice straw in a floating drum anaerobic bio-digester. The  
1029 investigated factors for the process optimization were temperature, pH and substrate  
1030 concentration and agitation time. The most significant parameters were found to be the  
1031 temperature and substrate concentration.

### 1032 *Biohydrogen production*

1033 Sekoai and Kana [197] used BBD to determine the relationship between the substrate  
1034 concentration, pH, temperature and hydraulic retention time (HRT) for the hydrogen yield.  
1035 The final modeling was preceded by multiple regression analysis leading to the development  
1036 of a quadratic model relating the hydrogen production to the proportion of used substrates  
1037 (i.e. bean husk (BH), corn stalk (CS) and organic fraction of solid municipal waste  
1038 (OFSMW)). The highest yield of hydrogen was obtained from substrate mixtures excluding  
1039 CS. The experimental validation of optimized hydrogen production resulted in about 4%  
1040 improvement of hydrogen yield and was equal to 58.62 ml H<sub>2</sub>/g TVS (total volatile solids).

1041 A five-level CCD was used to model the influence of de-oiled *Jatropha* (substrate)  
1042 concentration, pH, and temperature on biohydrogen cumulative production [198]. The optimal  
1043 conditions calculated with RSM for hydrogen formation agreed with those obtained in the  
1044 experiments and the cumulative hydrogen production was 307.4 cm<sup>3</sup> H<sub>2</sub>. The applied methods  
1045 allowed to improve the average hydrogen content from 54 to 58% of the total gas volume.

1046 A CCD with five center points was used by Ismail et al. [199] to model and optimize the  
1047 initial pH and temperature on the hydrogen yield and the hydrogen formation rate. The  
1048 investigated factors were selected using a two-level factorial design which allowed skipping a  
1049 chemical oxygen demand (COD) of the substrate and inoculum size as insignificant variables  
1050 in the conducted experiments. The optimum hydrogen yield was 120 cm<sup>3</sup>/g carbohydrates and  
1051 maximum H<sub>2</sub> production rate was 35.69 cm<sup>3</sup>/h.

1052 The BBD was used to determine the model describing fermentative biohydrogen production,  
1053 when potato-waste concentration (as a substrate), temperature, pH and time of fermentation  
1054 were the investigated factors [200]. Optimized conditions allowed to obtain a 12% increase in  
1055 the biohydrogen yield, resulting in production of 603.5 cm<sup>3</sup> H<sub>2</sub>/g TVS.

1056 The results of hydrogen yield from fermentation of hydrolyzed sugarcane bagasse as a  
1057 substrate were used to optimize the substrate concentration, the substrate to buffer ratio and  
1058 the inoculum to substrate ratio by applying CCD method [201]. The obtained hydrogen yield  
059 from experimental validation was slightly lower than those predicted by model and reached  
060 6980 cm<sup>3</sup> H<sub>2</sub>/dm<sup>3</sup> substrate.

061 Another approach was presented in a paper by Argun and Dao [202], who applied the ratios  
062 of C/N, C/P, C/Fe and C/Ni as independent variables in the model developed using BBD. A  
063 correlation between selected investigated factors on the yield and rate of hydrogen production  
064 was obtained as a quadratic function, in which all quadratic terms were significant. The

1065 highest values of both hydrogen yield and production rate were 460 cm<sup>3</sup> H<sub>2</sub>/ g COD and 2.44  
1066 cm<sup>3</sup>/h, respectively.

1067 BBD with input variables of substrate concentration, inoculum concentration and HRT was  
1068 used to model and optimize the hydrogen production from pretreated waste sugarcane leaves  
1069 [203]. The optimal hydrogen yield was 14.2 cm<sup>3</sup> H<sub>2</sub>/g of fermentable sugars in the lab-scale  
1070 experiment. The developed model allowed to enhance the biohydrogen yield by 23% in a  
1071 semi-pilot scale.

### 1072 5.5.2. Artificial Neuron Networks

1073 Artificial Neuron Network (ANN) is an artificial intelligence tool that identifies arbitrary  
1074 nonlinear multi-parametric discriminant function directly from experimental data [205]. Just  
1075 as in the case of RSM, ANN methods are suitable for developing models of bioprocesses  
1076 without prior understanding of the kinetics of metabolic fluxes within the cell and the cultural  
1077 environment. The most widely utilized ANN architecture is the multilayered perceptron  
1078 (MLP) that approximates non-linear relationships existing between input and output variables.

### 1079 *Biogas production*

1080 ANN was used to model the biogas yield in an anaerobic digestion of untreated and pretreated  
1081 *Carica papayas* fruit peels [191], pretreated *C. papayas* fruit peels with poultry dropping  
1082 [192] and pretreated *Telfairia occidentalis* fruit peels [193]. Investigated independent  
1083 variables were temperature, pH, retention time, total solids and volatile solids. The applied  
1084 method allowed to predict biogas formation with great accuracy and indicated the temperature  
1085 to be the most important parameter affecting the biogas generation.

1086 The influence of temperature, pH and ratio of poultry manure to food waste on methane  
1087 production was investigated by Yusof et al. [195]. The excellent agreement of experimental  
1088 and predicted values with the ANN methane yield was obtained in the studied range of  
1089 parameters.

1090 Another approach to selection of input variables was demonstrated by Xu et al.[206]. Because  
1091 an anaerobic digestion of lignocellulosic biomass is sensitive to substrate composition, i.e.  
1092 cellulose, hemicellulose and lignin, the contents of cellulose, xylan and lignin were selected  
1093 as the investigated parameters. The other studied variables were extractives, volatile solids,  
1094 inoculum characteristics (alkalinity and ammonia concentration), inoculum size, C/N ratio,  
1095 total solids and particle size. It was found that lignin content and inoculum size were the most  
1096 important variables. ANN model was developed using all investigated variables, and then  
1097 tested with smaller amount variables. The methane yield prediction obtained with using  
1098 significant explanatory variables (extractives, lignin, cellulose, inoculum size) was correct.  
1099 However, when easily measurable variables (VS, particle size, C/N, TS, inoculum size) were  
1100 selected, the prediction was not satisfactory.

1101 Effect of pH, moisture content, volatile solids and volatile fatty acids on the biogas production  
1102 rate and methane content was studied for anaerobic digestion of organic fraction of municipal  
103 solid waste [207]. ANN model using free forward back propagation was adopted to optimize  
104 the methane fraction in biogas at the level of 60-70%. In the investigated systems, the overall  
105 dataset performance revealed the accuracy of about 73%.

106 Eleven investigated process variables were studied to predict the biogas flow rate by Beltramo  
107 et al. [208]. The data used for developing the ANN model were calculated with the ADM1  
108 model. The significant variables were selected on the basis of the accumulation of the

1109 pheromone trail by the Ant colony optimization (ACO) algorithm. As a result, five significant  
1110 process variables (concentration of amino acids, long chain fatty acids, carbohydrates,  
1111 proteins and lipids) or three significant variables (amino acids, carbohydrates and proteins)  
1112 were used to optimize the biogas flow by testing several ANN structures with 10, 3, and 1  
1113 hidden neurons. Good prediction of biogas flow rate was achieved for both selected input  
1114 variables and using 3 hidden neurons. The ANN model with the less significant variables was  
1115 also tested, but it showed less successful prediction performance in comparison to the models  
1116 applying the significant variables.

1117 Kana et al. [209] used ANN coupling Genetic Algorithm (GA) to model and optimize biogas  
1118 production from saw dust, cow dung, banana stem, rice bran and paper waste. Input variables  
1119 were concentrations of five co-substrates and the output variable was the biogas yield. The  
1120 used ANN structure with 2 hidden neurons allowed to develop the model satisfactorily  
1121 describing the trend of biogas volume generating in the digester, but experimental and  
1122 predicted values were significantly different. In spite of such large discrepancies, GA may be  
1123 applied to the obtained results and this method allowed for a good optimization of co-  
1124 substrate compositions ensuring high biogas yields.

1125 ANN models for predicting of ammonia and hydrogen sulfide formation was developed by  
1126 Strik et al.[210]. The proposed approach was used to model the concentration of these trace  
1127 compounds under dynamic conditions. Therefore, the information regarding the current  
1128 concentrations of ammonia and hydrogen sulfide in both the liquid and the gaseous phases  
1129 were used to predict the resulting concentration of a given component. The accuracy of H<sub>2</sub>S  
1130 prediction was 91%, while the NH<sub>3</sub> model estimated its concentration with the accuracy of  
1131 83%. Both models showed the potential to predict, control, reduce or avoid the formation of  
1132 the trace compounds during anaerobic digestion processes.

### 1133 *Biohydrogen production*

1134 Investigations devoted to biohydrogen production from lignocellulosic materials are at the  
1135 laboratory stage, as given in table 12. Published data on the modeling of the biohydrogen  
1136 formation process concern either studies on model substrates such as simple sugar solutions  
1137 or various types of biomass. The results of ANN modeling of hydrogen production from pure  
1138 sugar solutions are given in a subsection “*Comparison of RSM and ANN models determined*  
1139 *for biohydrogen*”.

1140

1141 Table 12. Applications of ANN in modeling of biohydrogen and biogas production

Substrate	Inoculum	Investigated factors	Response	Network structure	References
		Biogas			
Pretreated and untreated <i>Carica papayas</i> fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	QuickProp 5-12-1	[191]
Pretreated <i>Carica papayas</i> fruit peels and poultry dropping	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	QuickProp 5-12-1	[192]
Pretreated <i>Telfairia occidentalis</i> fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m <sup>3</sup> /kg VS <sub>fed</sub> )	QuickProp 5-12-1	[193]
Food waste and poultry manure	Not specified	T, pH, ratio poultry manure : food waste	MY (cm <sup>3</sup> /VS)	3-8-1	[195]
Hydrolyzed feedstock (corn stover, wheat straw, switch grass, leaves, yard trimming, tree trimming, maple wood, pine wood)	Mesophilic digested sewage sludge	VS, cellulose, hemicellulose and lignin content, inoculum size, pH, [NH <sub>3</sub> ] C/N, TS, particle size	30-day MY (L/kg VS <sub>feed</sub> )	Not specified	[206]
Organic fraction of municipal solids, vegetable wastes	Cow dung and anaerobic sludge form food industry	pH, Moisture content, VS, volatile fatty acids, biogas production rate, actual methane concentration in biogas	CH <sub>4</sub> content	with 2-hidden layers	[207]
Corn silage, Cow manure, Grass silage	not specified	Inert solutes, inert particulates, acetic acid, inorganic nitrogen, sugars, composites, lipids, LCFA, carbohydrates, amino acids, proteins	Biogas flow rate	several tested structures: 11-10-1, 11-3-1, 11-1-1; 5-10-1, 5-3-1, 5-1-1; 3-10-1, 3-3-1, 3-1-1	[208]
Cow dung, banana stem,	Consortium of	S <sub>0</sub> – in mixture of co-	BY (cm <sup>3</sup> )	5-2-1	[209]



rice bran, paper waste, saw dust	microorganisms from rumen content	substrate			
Rice straw	Cow manure	temperature, pH, substrate concentration, agitation time COD loading rate, sulfate loading rate, actual [H <sub>2</sub> S] in biogas, [S <sup>2-</sup> ] in reactor, BY, pH	BY (dm <sup>3</sup> )	4-10-1	[196]
Not specified	Thermophilic digesting sludge	Nitrogen loading rate, [NH <sub>3</sub> ] in biogas, [NH <sub>3</sub> ] in reactor, total inorganic nitrogen in reactor, BY, pH, COD loading rate Biohydrogen	[H <sub>2</sub> S] in biogas	7-(2 hidden layers with 5 neurons)-1	[210]
Buffalo dung compost	Anaerobic mixed consortia	pH, glucose: xylose ratio, inoculum size, inoculum age	[NH <sub>3</sub> ]in biogas	8-(2-hidden layers with 7 neurons)-1	[211]
Darvill wastewater plant	Anaerobic sludge	So, Inoculum %, T°C	Cumulative H <sub>2</sub>	BPNN 4-10-1	[212]
Waste water (sugar industry)	Mixed cultures	OLR, ORP, pH, alkalinity	Cumulative H <sub>2</sub>	BPNN 4-(6-10)-1	[213]
Wastewater treatment plant	Mixed cultures	pH, So, X <sub>0</sub> , T°C, time	HPR	BPNN 4-3-1	[214]
Wastewater treatment plant	Mixed cultures	OLR, pH, VSS yield	HPR	BPNN 5-6-4-1	[215]
Cheese Whey	<i>Escherichia coli ΔhycA ΔlacI</i> (WDHL)	OLR, pH, dissolved CO <sub>2</sub>	HPR	BPNN 3-8-4-1	[216]

142 S<sub>0</sub> – initial substrate concentration VS – volatile solids, F/E – feedstock to effluent ratio, C/N – carbon to nitrogen ratio; TS – total solids, [NH<sub>3</sub>] – ammonia concentration, MY  
143 – methane yield, S<sub>0</sub> – initial substrate concentration, T – temperature, τ – time, HRT – hydraulic retention time; COD – chemical oxygen demand; LCFA – long chain fatty  
144 acids, BBD – Box-Behnken Design; CCD – central composite design; ORP: Oxidation-reduction potential; CO<sub>2</sub>: Carbon dioxide; HPR: Hydrogen production; HRT:  
145 Hydraulic retention time; So: Initial substrate concentration, X<sub>0</sub>= Initial biomass concentration; T°C: Temperature; SE (%): Substrate degradation efficiency; OLR: Organic  
146 loading rate; H<sub>2</sub>: Hydrogen; TOC<sub>eff</sub> : Effluent total organic carbons; VSS yield: Volatile suspended solids yield; BPNN: Back propagation neural network; HY: Hydrogen  
147 yield



### 1148 5.5.3. Comparison of predictability of biogas yield with using RSM and ANN

1149

1150 Comparison of predictability of biogas yield with using RSM and ANN models was done on  
1151 the basis of results obtained for anaerobic digestions of biomass waste. Dahunsi et al. used  
1152 RSM and ANN models to optimize biogas generation from anaerobic digestion of *C. papaya*  
1153 [191], pretreated *C. papaya* fruit peels with poultry dropping [192] and from fruit peels of  
1154 fluted pumpkin [193]. The input variables were temperature, pH, retention time, total solids  
1155 and volatile solids. The predicted values of biogas yield with using RSM model were higher  
1156 than respective values predicted with ANN model and higher accuracy and efficiency were  
1157 obtained for the latter model. ANN method showed that temperature was the most significant  
1158 variable in investigated range of parameters. The higher accuracy of ANN model was  
1159 reported by Yusof et al. [195], when input variables were temperature, pH and ratio of poultry  
1160 manure to food waste. The methane yield predicted with RSM model was overestimated,  
1161 whereas values of output variables from ANN model were the most similar to those obtained  
1162 in experiments.

1163 ANN models are known for their higher generalization as well as modeling ability. Available  
1164 results of predictive output values are more accurate for ANN models compared to those  
1165 predicted by RSM models.

### 1166 5.5.4. Comparison of RSM and ANN models for biohydrogen

1167 Comparison of RSM and ANN models determined for biohydrogen production in dark  
1168 fermentation processes was done for pure sugar solutions as substrates. The most of described  
1169 studies of the modeling of biohydrogen formation relates primarily to simple sugars such as  
1170 glucose, xylose or sucrose [187,217]. Relatively little information about modeling of  
1171 biohydrogen produced in fermentation processes with lignocellulosic biomass or its  
1172 hydrolysates as a substrate is available. Models generated by RSM and ANN for biohydrogen  
1173 production were compared by Wang and Wan [218]. Independent variables were temperature,  
1174 initial pH and glucose concentrations. Predicted values of hydrogen yield were higher when  
1175 the RSM model was applied. The determined errors were much smaller for the ANN model  
1176 and this model had a much higher modeling ability than RSM model for the optimization of  
1177 fermentative hydrogen production. ANN and RSM were used to model the hydrogen  
1178 generation from model glucose solutions in an Upflow Anaerobic Sludge Blanket (UASB)  
1179 bioreactor. The hydrogen yield and COD removal efficiency were optimized on the basis of  
1180 seventeen fermentation experiments. Input variables were hydraulic retention time,  
1181 immobilized cell volumes and temperatures [219]. The analysis of such parameters as the  
1182 prediction error for biohydrogen yield, accuracy and generalization competency showed that  
1183 the application of ANN in fermentation process development gave better results than RSM.  
1184 Another research of biohydrogen production using anaerobic fermentation of glucose  
1185 solutions were carried out to investigate an influence of temperature, pH and glucose  
1186 concentration as input variables [220]. Comparison of hydrogen yield obtained with RSM and  
1187 ANN models showed that the output values were predicted with lower errors by the ANN  
1188 model. This model outperformed the RSM one, although overestimated results were obtained  
1189 for the both tested methods. In the case when sugarcane molasses have been used as a  
1190 substrate in dark fermentation, the similar predicted optimum conditions for substrate  
1191 concentration, pH and temperature, but different inoculum concentrations have been found for  
1192 ANN and RSM [212]. Better accuracy in modeling have been for ANN method, that has been  
1193 pointed as a more reliable to navigate the optimization of fermentation process. Initial

1194 molasses concentration, inoculum size and hydraulic retention time were input variables in  
1195 RSM and ANN models studied by Sewsynker-Sukai and Kana [221] to optimize biohydrogen  
1196 yield. Predicted optimum conditions for biohydrogen production were similar for both used  
1197 models in decreasing order, although ANN models were much more accurate.

## 1198 6. Concluding remarks

1199

1200 Advanced hydrolysis and fermentation are proposed for processing of lignocellulosic biomass  
1201 to produce gaseous biofuels like biogas and biohydrogen. Anaerobic digestion leading to  
1202 biogas formation is a widely used technology utilizing waste biomass such as sewage sludge  
1203 and organic fraction of municipal solid waste. Dark fermentation is applied to biohydrogen  
1204 production in a laboratory scale, usually from simple sugars. Both processes are still  
1205 developed to be applied for processing of complex low-cost resources such as lignocellulosic  
1206 biomass. The main advantages of using lignocellulosic biomass as a substrate for gaseous  
1207 biofuel production are their availability in large quantities and low price. The main  
1208 disadvantages are their relatively low yield of gaseous biofuel production and potential  
1209 instability [13,15,33,222,223].

1210 Problems with the processing of lignocellulosic biomass arise from a) pre-treatment of  
1211 biomass, which consists in facilitating the availability of biomass components that are easily  
1212 fermentable; b) the presence of toxic substances formed during the processing of biomass; c)  
1213 satisfactory yield. The use of pre-treatment, single-stage or a combination of several methods,  
1214 causes a decomposition of lignocellulosic biomass components, which are more easily  
1215 processed by microorganisms during fermentation. At the same time, pre-treatment may result  
1216 in the formation of inhibiting or toxic substances for these microorganisms. Therefore, it may  
1217 be beneficial to remove toxic components (e.g. total phenolic components when fermented to  
1218 hydrogen) and use mixed substrates as well as selected microorganisms. Product yield is very  
1219 important for the implementation of a tested technology. Among different process parameters  
1220 affecting the yield and rate of biogas and biohydrogen generation, the pH of the pulp,  
1221 temperature, substrate composition, biomass pre-treatment method and digestion time seem to  
1222 be the most significant ones.

1223 The optimization procedure of fermentation process is a useful tool to find a solution for  
1224 experimental results improvements. The most advanced and relatively universal model is  
1225 ADM1. It is used in the case of biogas generation via anaerobic digestion processes,  
1226 nevertheless it requires modification if lignocellulosic materials are the substrates. Other  
1227 proposed models can be classified as a substrate based models, kinetic based models and  
1228 black-box models. The advantage of the two first types of models is their relative simplicity  
1229 but they can be used only in the range of investigated variables, and because of the longtime  
1230 of a single experiment, their applicability is limited. The black-box models can be developed  
1231 on the basis of experimental data available in scientific publications. Their advantage is the  
1232 possibility of obtaining reliable results without knowing the mechanisms of processes  
1233 occurring during fermentation.

1234 Actually, optimization of the biomass conversion based on proposed models is focused on the  
235 selection of parameters describing hydrolysis or fermentation. The literature lacks the links  
236 between the mentioned processes. Therefore, it seems valuable to develop a procedure that  
237 will allow not only to obtain high yields of biohydrogen and biogas, but also i) to clarify and  
238 identify the key stages of process management, ii) to indicate possible production of other  
239 valuable bio components in a microbiological synthesis, iii) to minimize the formation of  
240 substances acting as inhibitors for microorganisms. The challenges for production of gaseous  
241 biofuels from lignocellulosic biomass in the near future are the identification of highly

1242 potential feedstocks, the definition of efficient conditions of saccharification, minimizing the  
1243 generation or effective separation of inhibitors, the genetic engineering development  
1244 concerning high biofuels producing strains and the designation of optimal operating strategies  
1245 through modeling and optimization procedures.

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