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

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Abstract

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

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

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1. Introduction

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

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

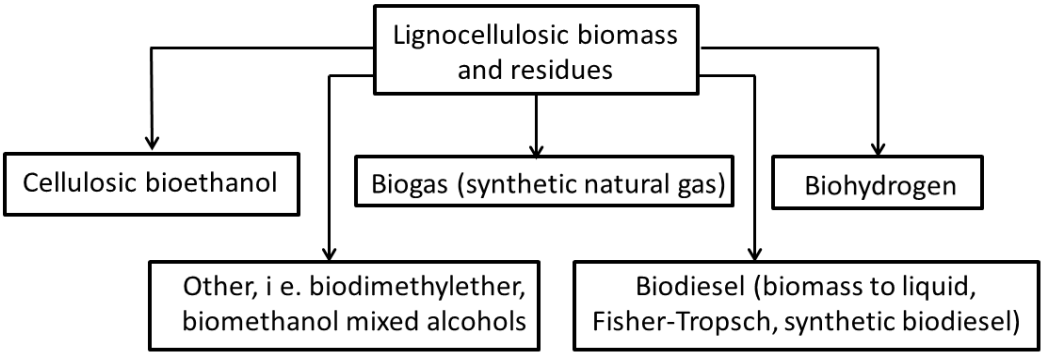


Fig. 1. Overview of biofuels from lignocellulosic biomass and residues

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

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

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

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

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

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

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

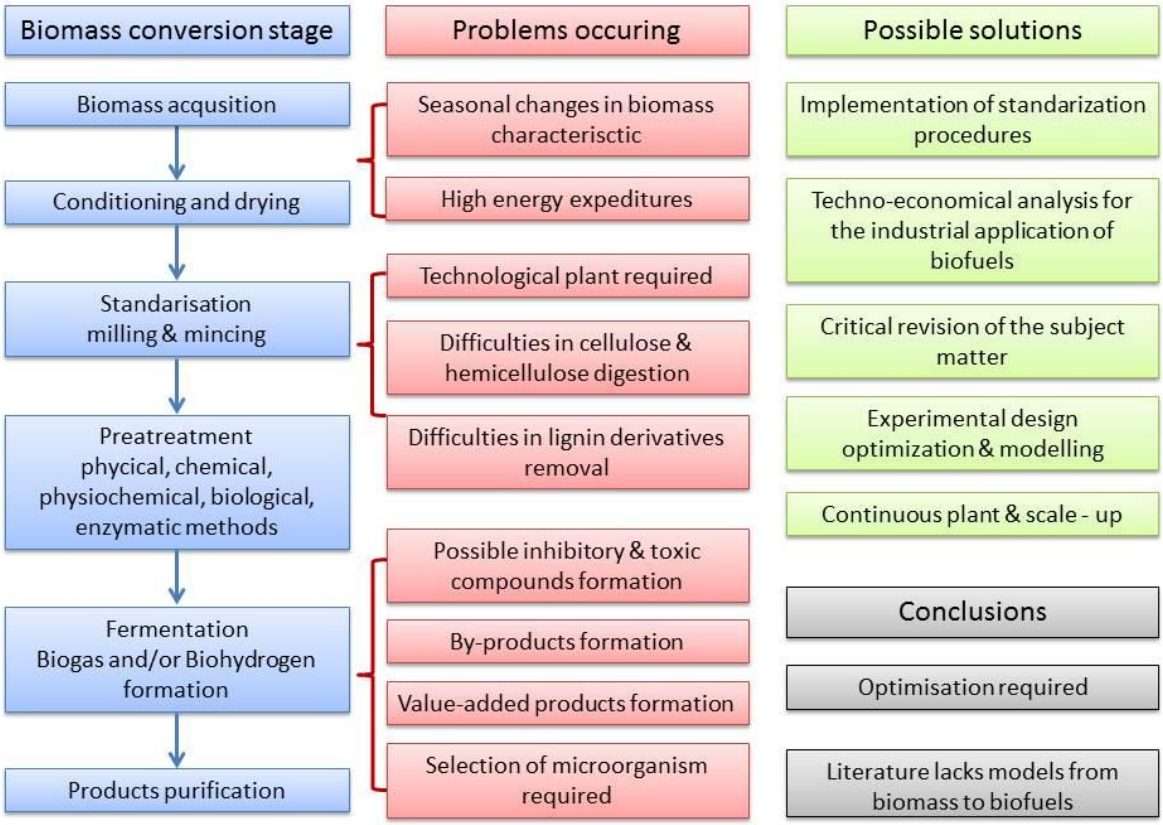


Fig. 2. Problems occuring and potential solutions encountered during the conversion of lignocellulosic biomass.

Techno-economic aspects of gaseous biofuel production

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

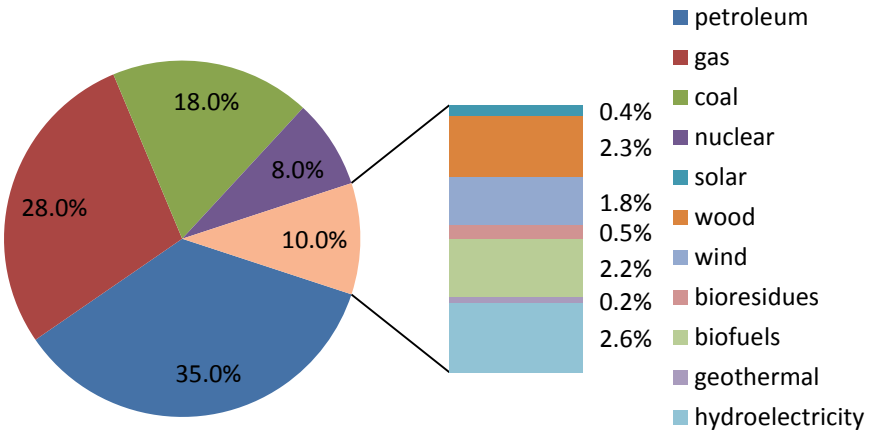
In the field of biogas production, technologies are currently successfully implemented. There are many installations producing biogas by anaerobic digestion and the improvement can be done on the basis of experience of existing plants [10–12]. The working installations for anaerobic digestion are usually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

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

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

2. Characteristics of lignocellulosic materials

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



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

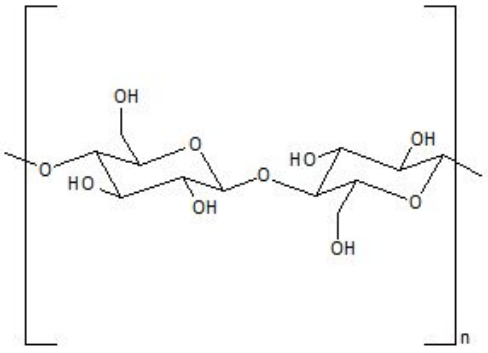
190 Lignocellulose is a main component of plants' cell walls and it is composed of cellulose
191 (about 50%), hemicellulose (about 30%) and lignin (about 20%) [23,26]. Some examples of
192 main constituents of selected lignocellulosic materials are presented in Table 1.

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 β-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].

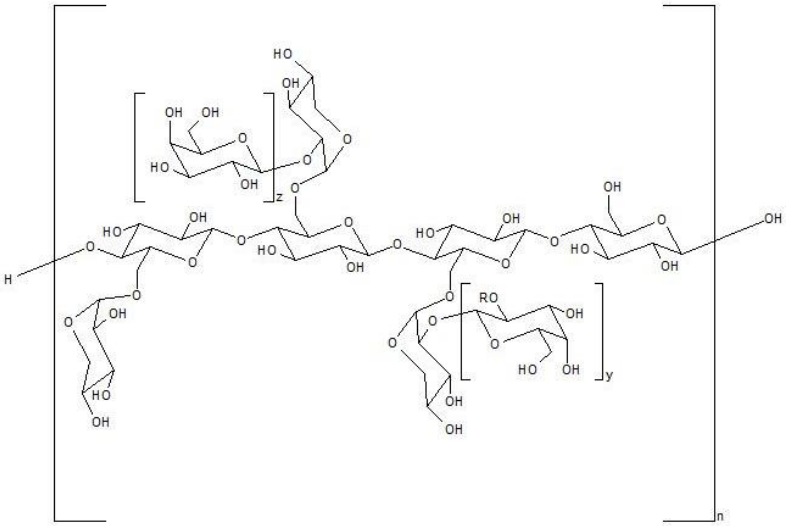


Fig. 5. Chemical structure of hemicellulose units.

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

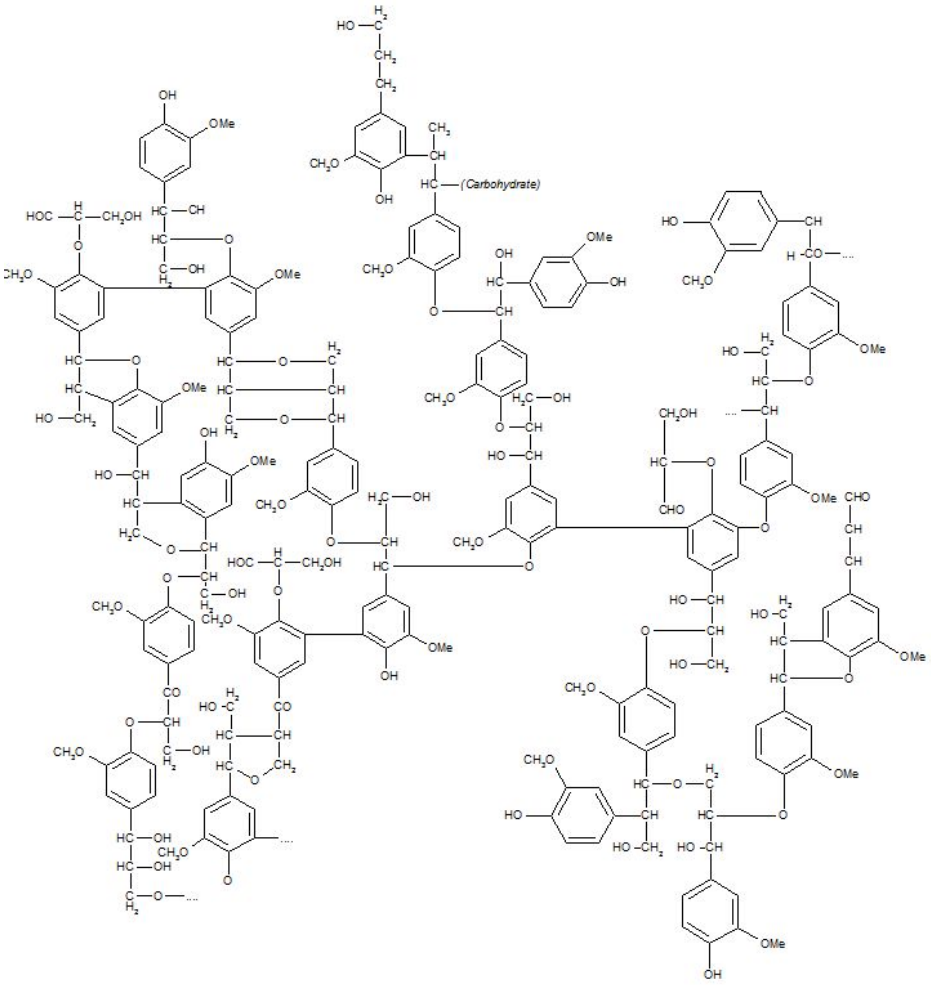


Fig. 6. Chemical structure of lignin units.

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

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

Table. 2. Characteristics of lignocellulosic biomass components

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

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

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

3. Mechanisms of biogas and biohydrogen fermentation from lignocellulosic biomass

3.1. Dark fermentation to biogas

Biogas is a biofuel composed mainly of methane (50 ÷ 75%), carbon dioxide (up to 40 %) and other minor constituents such as ammonia, hydrogen sulfide, hydrogen and nitrogen[1]. The biggest potential for clean energy production in combination with various biodegradable wastes is biogas production through anaerobic digestion (AD) process. The role of AD in the treatment of organic materials differing in the C/N ratio, i.e. agricultural wastes, wastewater sludges, municipall solid wastes or mixed substrates, still increases [39].Anaerobic digestion is a multi-step process carried out by a consortia of highly diversified_microorganisms and requires strictly anaerobic conditions. Such conditions enables the transformation of organic matter into carbon dioxide and methane. In the first stage of AD, complex organic polymers i.e. proteins, lipids and carbohydrates, are hydrolyzed to simple soluble monomers like amino-acids, long-chain fatty acids and sugars. Then, in the second stage the monomers are converted by fermentative bacteria to a mixture of volatile fatty acids (VFA) and other minor products. The process is called acid genesis. In the third stage, acetogenic bacteria convert the VFA to acetate, CO_2 and H_2. In the fourth stage, methanogenesis takes place [38]. Different microbial populations have specific optimum working conditions and are inhibited by several proceses parameters such as pH, temperature, alkalinity, concentration of free ammonia, hydrogen, sodium, potassium, VFA or heavy metals. In the AD process, all organic material can be diggested. The degree of such convesrion depends on the complexity and variety of the substrate materials. The AD technology is an attractive energy source for the production of heat and electricity and it enables to obtain a proportion of energy output to energy input equal to about 28:1 [38,40], which is a well-satisfactory result.

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

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

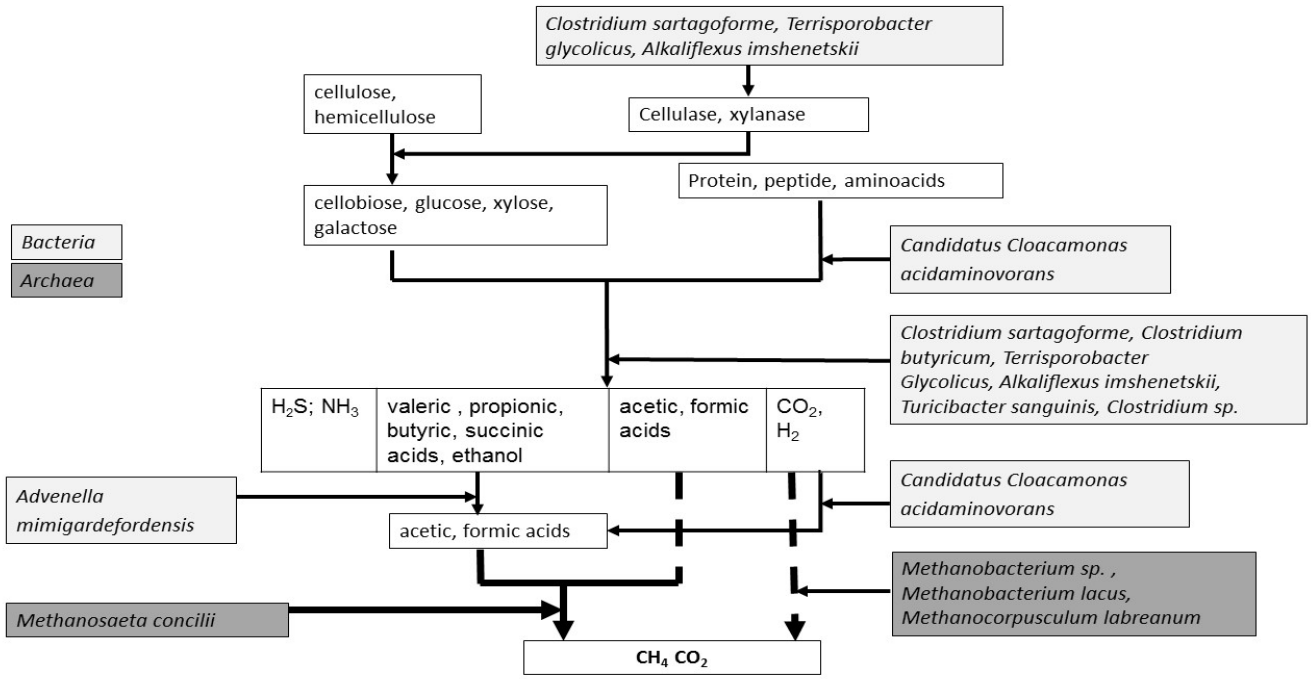


Fig. 7. Analysis of metabolic pathways from lignocellulosic biomass to biogas according to Tian et al. [48]

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

3.2. Dark fermentation to biohydrogen

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

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

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

$$C_6H_{12}O_6 + 2NAD^+ \rightarrow 2CH_3COCOO^- + 4H^+ + 2NADH \quad \Delta G^0 = -121{,}1\frac{kJ}{mol} \qquad (1)$$

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

$$NADH + H^+ \rightarrow NAD^+ + H_2 \qquad (2)$$

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

Strictly anaerobic and facultative anaerobic bacteria use ferredoxin oxidoreductase Fd_{ox} for *acetyl-coA* production (reaction (3)), which can be further metabolized to acetate or butyrate [32]:

$$Puryvate + CoA + Fd_{ox} \leftrightarrow acetylCoA + CO_2 + Fd_{red} \qquad \Delta G^0 = -19{,}2\frac{kJ}{mol} \qquad (3)$$

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

$$Puryvate \; + \; CoA \leftrightarrow acetylCoA \; + \; formate \qquad \Delta G^0 = -16{,}3\frac{kJ}{mol} \qquad (4)$$

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

Type of metabolic pathway	Reaction	Maximum theoretical yield [mol H_2/mol glucose]	ΔG^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	$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO^- + 2HCOO^- + 4H^+ + 2H_2$	4	-209,1	[60]
	$2HCOOH \rightarrow 2CO_2 + 2H_2$	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]

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

4. Problems of lignocellulosic biomass conversion

4.1. Pretreatment method selection

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

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 β-1,4-glycosidic bonds	[66]
Chemical	Pyrolysis	Cellulose carbonation	[34]
	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

As shown in Table 4, there are many methods of pre-treatment of lignocellulosic biomass. Mechanical pre-treatment typically forerun further chemical treatment as milled and minced material is homogenic. Mechanical treatment is the most energy-intensive processing stage, followed by treatment with physical, chemical, or physicochemical and biological methods. Research interest is increasingly turning towards methods that allow the selective removal of these fractions of lignocellulosic biomass, which as a result of hydrolysis may be the source of fermentation inhibitors. This is why the selective methods gain importance.

An influence of the molecular organization as well as the cell wall structure on the pretreatment efficiency is still not defined [79]. An important parameter for the selection of the biomass pretreatment methods is the substrate accessibility. Unfortunately, it is not possible to precisely predict the effectiveness of a pretreatment with one method of analysis. However, finding out the mechanisms of the changes in the structure during bioconversion may improve the effectiveness of the pre-treatment [80]. Pre-treatment causes changes in the physical structure of biomass which further affects other steps of processing i.e. enzymatic hydrolysis. Based on SEM images (scanning electron microscopy), it has been proven that the pre-treated pine wood surface is different than that of raw pine wood. Pores formed as a result of high levels of residual lignin removal were only present in the pre-treated wood [81].

Unfortunately, the pre-treatment of lignocellulosic biomass leads to formation of substances that inhibit further biochemical conversion processes. For example, acid hydrolysis leads to formation of phenolic compounds and furans that are detrimental for enzymatic hydrolysis as well as latter fermentation. Prevention of formation of unwanted chemical substances or so called detoxification of pre-treated lignocellulosic biomass may be controlled by several means [82,83]. These strategies include a selection of chemical or enzymatic hydrolysis conditions e.g. by application of alkaline instead of acid hydrolysis. Moreover, liquid-liquid, liquid-solid extraction or microbial treatment may help to overcome the problem of formation of fermentation inhibitors.

4.2. Inhibitory and toxic products

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

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

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

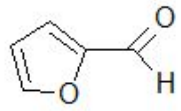


Fig. 8. Chemical structure of furfural

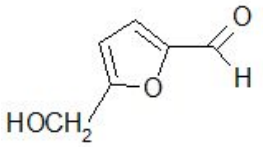


Fig. 9. Chemical structure of 5-hydroxymethyl-2-furaldehyde (HMF)

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

4.3. Main product yield and by-product formation

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

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

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

High yields of main products require selection not only of proper microorganisms, but also of the appropriate fermentation conditions. In Table 6 operating conditions and yields of 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	*Lactobacillus species*	Cellulase	Biohydrogen	Lactic acid, succinic acid	[99]
Delignified hydrolysate of lignocellulosic biomass	*Acetobacter* sp.	Cellulase	Biohydrogen	Acetic acid	[100]
Cellulose, glucose rich hydrolysates	*Penicillium luteum, P. citrinum, Aspergillus niger, A. wentii, A. clavatus, Mucor piriformis, Citromyces pfefferianus, Paecilomyces divaricatum, Trichoderma viride, Yarrowia lipolytica, Candida guilliermondii*	Cellulase	Biohydrogen	Citric acid	[101]
Delignified hydrolysate of lignocellulosic biomass	*Mannheimia succiniciproducens*	Cellulase	Biohydrogen	Succinic acid	[102]
Delignified hydrolysate of lignocellulosic biomass	*Actinobacillus succinogenes*	Cellulase	Biohydrogen	Succinic acid	[103]
Cellulose	*Anaerobiospirillum succiniciproduens*	Cellulase	Biohydrogen	Succinic acid	[104,105]
Cellulose, hemicellulose	*Mannheimia succiniciproducens*	Cellulose xylanase	Biohydrogen	Succinic acid	[104,105]

Delignified hydrolysate of lignocellulosic biomass	*Xanthophyllomyces dendrorhous*	Cellulase complex β-Glucosidase	Biogas	Astaxanthin	[104,105]
Hemicellulose, xylose rich hydrolysates	Genetically modified *Saccharomyces cerevisiae, Pichia stipiti,*	Xylanase	Biohydrogen	Bioethanol	[80,106]
Hemicellulose, mixed sugars, xylose rich hydrolysates	*Escherichia coli, Klebsiella, Erwinia, Lactobacillus, Bacillus, Clostridia*	Xylanase	Biohydrogen	Low concentrations of bioethanol	[80]
Hemicellulosic hydrolysates from barley straw, corn stover and switch grass	*Clostridium acetobutylicum, Clostridium beijerinckii*	-	-	ABE (acetone; butanol; ethanol)	[107,108]
Xylose from hemicellulose hydrolysates	*Candida guilliermondii*	-	-	Xylitol	[106]
Hemicellulosic hydrolysates, xylose, arabinose	*Candida entomaea, Pichia guilliermondii*	-	-	Arabitol	[109]
Hemicellulosic hydrolysates	*Bacillus polymyxa, Klebsiella pneumoniae (Aerobacter aerogenes), Bacillus subtilis, Seratia marcescens* and *Aerobacter hydrophia*	-	-	2,3-butylene glycol	[110]
Hexoses, pentoses, disaccharides, uronic acid	*Klebsiella pneumoniae*	-	-	2,3-butylene glycol	[111–113]
Hemicellulosic sugars, xylose, arabinose, and glucose	*Lactobacillus pentosus, Lactobacillus brevis*	-	-	Lactic acid	[114,115]
Hemicellulosic sugars	*Aspergillus niger.*	-	-	Citric acid	[106]
Hemicellulosic sugars	*Clostridium tyrobutyricum*	-	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^3/d	Mixed cultures/ CSTR Semi-continuous	Butyric acid, acetic acid	pH = 5.0 T = 50°C	5.7 dm^3 H_2/ dm^3/ 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^3 H_2/ dm^3/d 66 cm^3 H_2/g VS	[118]
Potato steam peels 10 g glucose/ dm^3	Mixed culture/ Batch	Acetic acid, lactic acid	pH = 6.9 T = 75 °C	12.5 mmol H_2/ dm^3h 3,8 mol H_2 /mol glucose	[119]
Simulated food waste: fish5%; meat 10%;bread 10%; apple 10%; kiwi 6%; banana 9%; pear 10%; onion5%; 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^3 H_2/kgVS	[120]
Liquid swine manure 13.94 g COD/ dm^3	Mixed cultures from anaerobic digester/ ASBR Batch	Acetic acid, butyric acid, valeric acid, ethanol,	pH = 5.0 T = 37°C	0.1 dm^3 H_2 /dm^3/h	[121]
Cattle wastewater 1.3 g COD/dm^3	Sewage sludge/ Batch	Propionic acid butyric acid, acetic acid, ethanol, propionic acid	pH = 5.5 T = 45°C	0.34 dm^3/dm^3h	[122]

Dairy manures 70 g/ dm^3	*Clostridium sp/* CSABR Continuous	Butyric acid, acetic acid, ethanol, propionic acid, butanol	pH = 5.0 T = 36°C	31.5 cm^3/g TVS	[123]
Cheese whey wastewater 10 g/dm^3	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^3 H_2/gVSS*h	[124]
Palm oil mill effluent 59 g COD/dm^3	Mixed cultures (isolated from cow dung) / USAB Continuous	-	pH = 5	73dm^3/d	[125]
Jatropha curcas – 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^3/(dm^3*d) 148cm^3H_2/g carbohydrate	[126]
Wheat straw 5 g/dm^3	*Thermoanaerobacterium thermosaccharolyticum M18/* Batch	Acetic acid, butyric acid, ethanol, butanol, propionic acid	T = 60°C pH = 7	0.11 mmol/ dm^3h	[127]
Sugarcane bagasse 1%	*Caldicellulosiruptor saccharolyticus/* Batch	-	T = 70°C	18,21 dm^3 H_2/kg 2.3 mol H_2/mol glucose	[128]
Delignified wood fibers 0.1 g/dm^3	*Clostridium thermocellum 27405/* Batch	Acetic acid, ethanol, formic acid	T = 60°C	2.32 mol H_2/ 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_2/ mol glucose (HRT 16 h)	[129]

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

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

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

5. Recent developments in modeling of fermenation processes

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

5.1. Classification of models

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

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

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

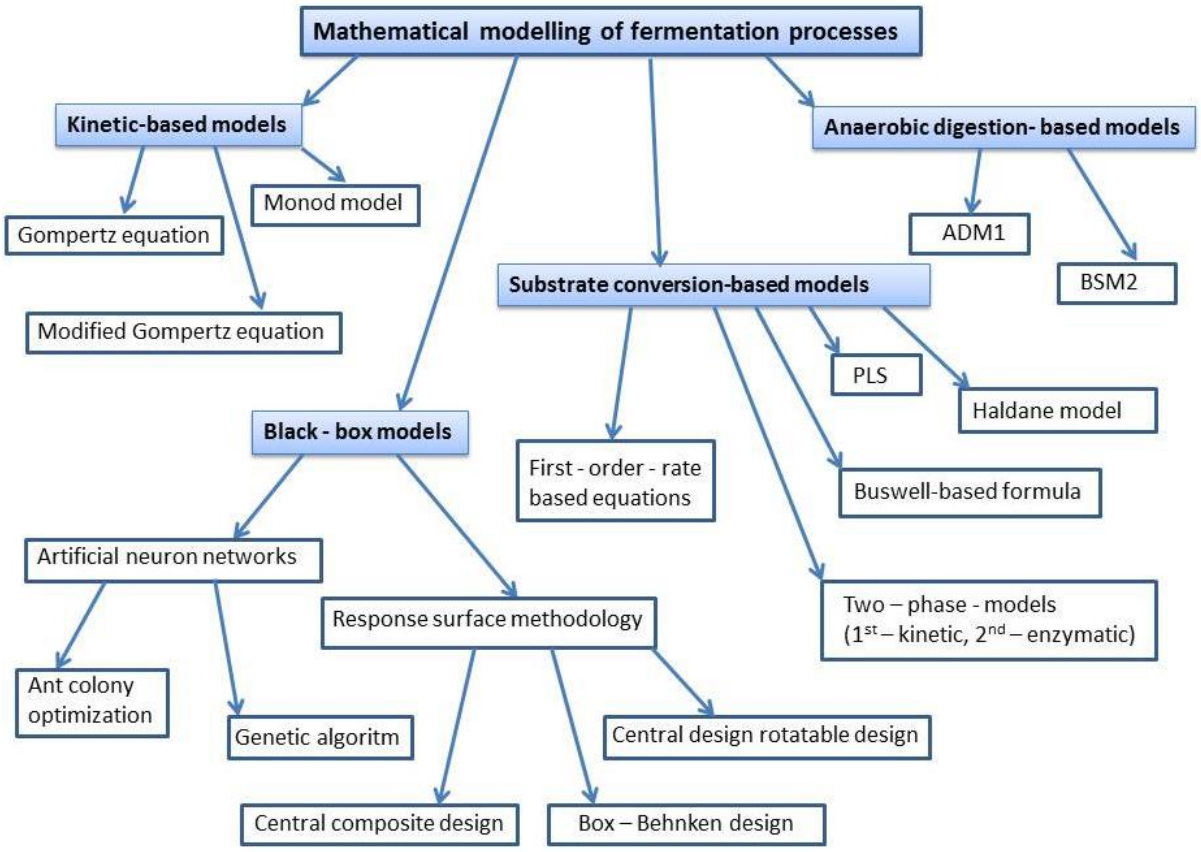


Fig. 10. Classification of models for fermentation processes.

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

5.2. ADM1-based models

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

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

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

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

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

The modified ADM1 was investigated for various types of waste biomass as a feedstock . Lubken et al. [143] simulated biogas production using cattle manure and rape-oil as co-substrates. The authors proposed to replace the COD by measurement of volatile solids to characterize the substrate and recommended the inhibition effect of pH to be included in the model. Boubaker et al. [144] investigated the mesophilic anaerobic co-digestion (AcoD) process of olive mill wastewater and olive mill solid waste. The authors suggested a modification taking into account the inhibition of methanogenesis step by high concentrations of total VFA. Derbal et al. [145] applied ADM1to simulate anaerobic co-digestion of organic fraction of municipal solid wastes in mesophilic conditions. The authors note the limitation of ADM1 model in complex processes of AcoD by the fact that only a part of the input kinetic parameters were obtained by analysis and the rest of them were adopted from the literature.

The anaerobic biodegradability of agro-wastes was used to characterize the substrates and considered as the basis input to the model [146]. The modification of the original ADM1 includes the implementation of H_2S in liquid and gaseous phases in the processes that occurred during anaerobic digestion. The proposed model was validated with the mono-substrate and co-substrate cases in batch and continuous reactors.

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

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

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

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

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

Shi et al. [154] used the mathematical model, proposed by Zhao et al. [147] and additionally based on the ADM1, for the modeling of AcoD process of complex wastes, i.e. the mixture of dairy manure and spent mushroom, with an emphasis of anaerobic hydrolysis of lignocellulosic wastes. Dairy manure was modeled according to original ADM1. Spent mushroom substrate was divided into cellulose and hemicellulose, which was hydrolyzed into the carbohydrates and the inert solids. Then, the carbohydrates were hydrolyzed into soluble sugars and soluble inert fraction. The optimization of HRT (hydraulic retention time), substrate ratio and pH value on biogas production were investigated. Process of AcoD of maize silage and cow manure was used for calibration and verification of the modified ADM1 model [155,156]. The proposed model includes fractionation of influent on the basis of the extended Weender analysis and a function describing an influence of the solids on the hydrolysis process. The least satisfactory fitting of experimental to simulated results was obtained for biogas production. It was a result of the biogas production fluctuations during the experiment. Better fitting was obtained for the concentrations of propionic, butyric and acetic 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^3/d), CO_2Y(%), CH_4Y(%), H_2Y(ppm), Ac($mgCOD/dm^3$), Pr($mgCOD/dm^3$)	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^3/d), CO_2Y(%), CH_4Y(%), pH, TVFA($gCOD/ dm^3$)	Including TVFA amount inhibition in the acetate uptake	[144]
coDS: mixture of MSW and WWTPS	37°C, HRT = 27 days	BY(dm^3/d), CO_2Y(%), CH_4Y(%), TCOD ($kgCOD/m^3$), SCOD ($kgCOD/m^3$), TVFA($kgCOD/dm^3$), pH, IC($kmol/m^3$), IN($kmol/m^3$)		[145]
moDS: orange, apple, pig manure or rape; coDS: pig manure(60%, total weight)+ glycerin (40%, total weight)	35°C, HRT = 20 days	BY ($Nm^3/kgVS$), CH_4Y(%), pH,VS(g/ dm^3), TAN(g/ dm^3), SCOD (g/ dm^3), alkalinity ($gCaCO_3/ dm^3$)	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_4 ($kgCOD/m^3$), VFA($kgCOD/m^3$)	Including fractionation of influent	[147]
moDS: grass silage	38°C	BY(dm^3/d), CO_2Y(%), CH_4Y(%),H_2Y(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($kgCOD/m^3$), CH_4Y(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^3), AMA(kgCOD/m^3) BY (N dm^3/d), CH_4Y(N dm^3/d),	including the transfer coefficients for substrates with different digestibility	[150]
moDS: waste activated sludge or pig slurry	38°C	MPR(Ndm^3 CH4/($L_{inoculum}$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^3), VFA(g/ dm^3), 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^3/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_4Y(%), pH, Ac(kgCOD/m^3), Pr(kgCOD/m^3), Va(kgCOD/m^3),	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^3/d), active methanogens (kgCOD/m^3), AcA(kgCOD/m^3) VFA(kgCOD/m^3)	including recycling sludge	[157]
moDS: swine manure fibers, coDS: swine manure fibers and AAS pretreated manure fibers	38°C, HRT = 25 days	BY (m^3/d), CH_4Y(%), Ac(kgCOD/m^3), Bu(kgCOD/m^3), Pr(kgCOD/m^3)	including recycling sludge	[158]
moDS: food waste or green waste	37°C	CH_4Y(dm^3/day), TAN(g/ dm^3), TS(g/ dm^3), VS(g/ dm^3), TVFA(gCOD/ dm^3), BA(g$CaCO_3$/ dm^3), pH	Including improved methodology for substrate characterization involving a combined biochemical and kinetic approach	[153]

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 – co-substrate batch, CH_4Y - methane yield, CO_2Y – carbon dioxide yield, IC – inorganic carbon, HMA - hydrogen trophic methanogenic archaea concentration, IN – inorganic nitrogen, moDS – mono-substrate batch, 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 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 solids, WAS – waste activated sludge, WWTPS - wastewater treatment plant sludge, TVFA – total volatile fatty acids

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

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

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

ADM1 is also utilized to model the anaerobic digestion in more complex systems like BSM2 (Benchmark Simulation Model no. 2). BSM2 is an example of a plant-wide modeling in which the anaerobic digestion is regarded as a unit stage. BSM2 is a model-based complex tool for development, evaluation and analysis of plant-wide control strategies for wastewater treatment plants [140,159,160], including all steps of treatment occurring in primary clarifier, activated sludge tanks (anaerobic and aerobic), secondary clarifier as well as the sludge thickener, sludge dewatering unit and storage tank. Among all the stages of wastewater treatment, anaerobic digestion (AD) is a key process for sludge treatment and its operation is of great importance for the overall performance of a wastewater treatment plant. This is because the biogas is the final product of the AD process and its production may be an indicator of the digester performance [161].
It is well known that the input characterization is a major challenge for modeling of anaerobic digestion processes. In the BSM2, the degradation of particulate substrates in anaerobic digestion is modified compared to original ADM1. This is because there is an activated sludge treatment prior to AD and an interface is needed to convert the state variables from activated sludge directly to the products of disintegration rather that to overall particulate composite material. Such an approach allows for adapted composition depending on substrate and separates the feed from dead biomass. The disintegration step is fixed for dead biomass and as the disintegration step is rate limiting, the hydrolysis rates must be adjusted to obtain a realistic degradation rate [160]. Additionally, when various substrates are co-digested, Arnell et al. [162] propose to implement a function for long-chain fatty acids inhibition to the modified ADM1 for BSM2.

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

or more substrates provides better nutrient balance and may favor positive interactions, as well as dilute the inhibitors concentrations and increase the biogas production. Mathematical modeling of the AcoD process is most often based on ADM1model. Among different process parameters affecting the yield and rate of biogas generation, the pH of the pulp, temperature, substrate composition, biomass pre-treatment method and digestion time seem to be the most important ones. The results of recently published studies showed that substrate characterization is ultimately the most influential model input on methane production prediction. In general, an increased fractionation model complexity led to better fit but with increased uncertainty. Furthermore, hydrolysis is assumed to be the first limiting step in AD process, especially for substrates with high content of solid fraction. The development of feedstock characterization methods and accurate calculations of kinetic factors to provide the required model inputs was still a bottleneck to a broader adoption of ADM1 model. The presented literature review clearly depicts that selection of proper digestion conditions as well as the prediction of the yield and quality of biogas may be substantially aided with mathematical modeling.

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

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

5.3. Substrate conversion-based models

The other group includes models based on a substrate conversion for the estimation of the biofuels production yield. Monlau et al. [21] investigated the relation between the compositional and structural features of lignocellulosic biomass on the biogas production. It is because without the determination of composition as well as the structural properties it is impossible to evaluate the potential of methane production from the lignocellulosic biomass. For the evaluation of biogas production estimated by BMP (Biological Methane Potential or Biomethane Potential, $\frac{ml_{CH_4}}{g_{TS}}$), a multilinear partial least square (PLS) model was developed. The PLS analysis was performed in a full cross validation, so called leave-one-out cross validation procedure. Following equation was proposed, considering the compositional as well as structural parameters most significantly affecting the biogas production:

$$BMP = 303.14 - 4{,}53 \cdot Lig + 0.77 \cdot SolSu + 1.28 \cdot Pro - 1.59 \cdot Cri + 0.61 \cdot Am + 1.33 \cdot Ua \quad (5)$$

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

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

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

$$C_nH_aO_bN_c + \left(n - \frac{a-2b-3c}{4}\right)H_2O \rightarrow \left(\frac{4n+a-2b-3c}{8}\right)CH_4 + \left(\frac{4n-a-2b-3c}{8}\right)CO_2 + cNH_3 \quad (6)$$

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

Where: VS – volatile solids.

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

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

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

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

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

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

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

Where: B – cumulative methane yield, B_0 – 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 1st 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_2SO_4), thermal (150 and 180^{o}C)	Effluent from mesophilic digester as inoculum; glass digester vessel, mesophilic AD	1st 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^oC, 90 min)	Cow dung as inoculum, $30 \div 38^oC$, mechanical mixing	BMP, modified Gompertz model, logistic function model, transference function model	Substrate concentration, pH, time	[164]

AD – anaerobic digestion BMP – Biological Methane Potential

5.4. Kinetic-based models

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

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

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

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

Biogas production

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

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

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

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

Table 9. Recent studies applying the modified Gompertz equation for modeling of 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]

Biohydrogen production

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

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

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

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

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

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

Feedstock	Inoculum	Conditions	Investigated parameters	Modeled factors	References
Pretreated poplar leaves	Mixed cultures from cracked cereal	35°C	Pretreatment method	HY (cm^3 H_2/g dry poplar leaves)	[169]
Pretreated soybean straw	Mixed cultures from cracked cereal	35°C, pH = 7	Pretreatment method	HY (cm^3 H_2/g substrate)	[170]
Wheat straw	Heat – pretreated mesophilic anaerobic digested sludge	37°C, pH = 5,5	Enzyme addition	HY (cm^3 H_2/g VS)	[171]
Lignocellulose – derived compounds	Heat – pretreated anaerobic digested sludge	37°C, pH = 5,5	Inhibitor addition	HY (mol H_2/mol xylose)	[172]
Alkali pretreated cornstalk	Heat – pretreated anaerobic sewage sludge	37°C, pH = 7	Cornstalk to sewage sludge proportion	HY (cm^3 H_2/g VS), EY (kJ/g VS)	[4]
Alkali pretreated cornstalk	*C. thermocellum 7072*	55°C	Substrate concentration, stirring speed	HY (cm^3 H_2/g cornstalk)	[176]
Waste activated sludge and food waste	Heat – pretreated activated sludge	37°C, pH = 5,5	Composition of substrate	HY (cm^3 H_2/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_2/mol xylose), HPR (mmol/ dm^3/h)	[180]
Miscantus	*Clostridium*	35°C,	Composition	HY (mol	[181]

hydrothermal pretreatment with dilute acids	*beijerinckii* /Co-culture of *Clostridium beijerinckii* and *Geobacter matallireducens*		of inoculum, glucose to xylose ratio in lignocellulosic hydrolysates	H_2/mol xylose), HPR (mmol/ dm^3/h)	
$Ca(OH)_2$ pretreatment wheat straw	Digested sewage sludge	35°C, pH = 6,25	Time of pretreatment process, concentration of $Ca(CO)_3$ formed during pretreatment processes	H (cm^3 H_2/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^3 H_2/g VS), HPR (mmol/ dm^3/d)	[173]
Synthetic lignocellulosic hydrolysate	Mesophilic anaerobic digester sludge	37°C, pH = 5,5	Furfural concentration	HY (cm^3 H_2/mol $sugars_{initial}$), H_2 cumulative (cm^3)	[86]
Heat pretreatment waste peach pulp	Anaerobic sludge	37°C,	Inoculum concentration	HY (cm^3 H_2/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^3)	[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_2/mol total sugar), HPR (ml H_2/dm^3/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_2/mol SCDO),	[175]

	sludge and glucose			

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

Modified Gompertz equation is a simple kinetic model used to describe the progress of product formation, mainly H_2 or some soluble metabolite products. Modeling of the fermentative hydrogen production process includes the mathematical description of the other process components of the dark fermentation such as kinetics of microbial growth and the substrate utilization. Simple kinetic models are used for this purpose, although only a few works refer to processes using complex organic substrates. Boni et all. [183] developed and calibrated the model based on the classic Monod equation for the description of hydrogen production from organic wastes. The solution of Monod equation for the two steps i.e. the substrate consumption and the cell growth are as follows:

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

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

where: S is the concentration of substrate (g COD/m^3), t is the time (h), Y is the ratio between the rate of bacterial growth and the rate of substrate utilization (mg VSS/mg COD), μ_m is the maximum specific growth rate (1/d), k_s is the half-velocity constant (g COD/m^3), X is the concentration of the cells (g COD/m^3), k_d is the endogenous decay coefficient (1/d).

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

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

$$\mu = \frac{1}{X}\frac{dX}{dt} = \mu_m \frac{S}{k_s + S + \frac{S^2}{k_i}} \tag{13}$$

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

Where: μ is the specific growth rate (1/d), k_i is the inhibition constant (g COD/m^3), C is the inhibitor concentration (g COD/m^3), C_m is the maximum inhibitor concentration or the concentration of inhibitor above which biomass growth ceases (g COD/m^3).

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

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

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

5.5. Black-box models

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

5.5.1. Response surface methodology

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

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

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

Substrate	Inoculum	Investigated factors	Response	Type of design	References
Biogas					
Pretreated *Tithonia diversifolia* shoot	Consortium of microorganisms	T, pH, RT, TS, VS	BY (m^3/kg TS_{fed})	CCD	[189]
Pretreated	Consortium of	T, pH, RT,	BY (m^3/kg	CCRD	[190]

Chromolaena odorata with poultry manure	microorganisms	TS, VS	VS_{fed})		
Pretreated and untreated *Carica papayas* fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	CCD	[191]
Pretreated *Carica papayas* fruit peels and poultry dropping	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	CCRD	[192]
Pretreated *Telfairia occidentalis* fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	CCRD	[193]
Food waste	Mesophilic anaerobic digestion sludge	Concentration of Ca, Mg, Co and Ni	CH_4 (cm^3)	CCD	[194]
Food waste and poultry manure	Not specified	T, pH, ratio poultry manure : food waste	CH_4 (cm^3/ VS)	CCD	[195]
Rice straw	Cow manure	temperature, pH, substrate concentration, agitation time	BY (dm^3)	CCD	[196]
		Biohydrogen			
Bean-husk: corn stalk: organic fraction of solid municipal waste	Heat-pretreated anaerobic sludge	S_0, pH, T, HRT	HY (cm^3 H_2/gVS)	BBD	[197]
De-oiled Jatropha wastes	Heat-pretreated anaerobic sludge	S_0, pH, T	HY(cumulative H_2 production)	CCD	[198]
Food wastes	Heat-pretreated anaerobic sludge	pH, T, (insignificant: inoculum size, COD)	HY(cm^3 H_2/g carbohydrate); HFR (cm^3 H_2/h)	CCD with screening	[199]
Potato waste	Heat-pretreated anaerobic sludge	S_0, pH, T, τ	HY (cm^3 H_2/g VS)	BBD	[200]
Hydrolyzed	Heat-pretreated	S_0, S_0:buffer,	HY(as	CCD	[201]

sugarcane bagasse	sludge from hydrogen pilot plant	inoculum:S_0	cumulative H_2 production)		
Waste peach pulp	Natural microflora	C/N, C/P, C/Fe, C/Ni	HY (cm^3/g COD), HFR (cm^3 H_2/h)	BBD	[202]
Waste sugarcane leaves	Anaerobic sludge	S_0, inoculum concentration, HRT	HY (cm^3/g sugar)	BBD	[203]

S_0 – initial substrate concentration, T - temperature, τ – time, HRT – hydraulic retention time; RT – retention time, TS – total solids, VS – volatile solids, COD – chemical oxygen demand; HY - H_2 yield, HFR – H_2 formation rate, BY – biogas yield, BBD – Box-Behnken design; CCD – central composite design; CCRD – central composite rotatable design

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

Biogas production

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

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

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

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

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

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

Biohydrogen production

Sekoai and Kana [197] used BBD to determine the relationship between the substrate concentration, pH, temperature and hydraulic retention time (HRT) for the hydrogen yield. The final modeling was preceded by multiple regression analysis leading to the development of a quadratic model relating the hydrogen production to the proportion of used substrates (i.e. bean husk (BH), corn stalk (CS) and organic fraction of solid municipal waste (OFSMW)). The highest yield of hydrogen was obtained from substrate mixtures excluding CS. The experimental validation of optimized hydrogen production resulted in about 4% improvement of hydrogen yield and was equal to 58.62 ml H_2/g TVS (total volatile solids).

A five-level CCD was used to model the influence of de-oiled Jatropha (substrate) concentration, pH, and temperature on biohydrogen cumulative production [198]. The optimal conditions calculated with RSM for hydrogen formation agreed with those obtained in the experiments and the cumulative hydrogen production was 307.4 cm^3 H_2 The applied methods allowed to improve the average hydrogen content from 54 to 58% of the total gas volume.

A CCD with five center points was used by Ismail et al. [199] to model and optimize the initial pH and temperature on the hydrogen yield and the hydrogen formation rate. The investigated factors were selected using a two-level factorial design which allowed skipping a chemical oxygen demand (COD) of the substrate and inoculum size as insignificant variables in the conducted experiments. The optimum hydrogen yield was 120 cm^3/g carbohydrates and maximum H_2 production rate was 35.69 cm^3/h.

The BBD was used to determine the model describing fermentative biohydrogen production, when potato-waste concentration (as a substrate), temperature, pH and time of fermentation were the investigated factors [200]. Optimized conditions allowed to obtain a 12% increase in the biohydrogen yield, resulting in production of 603.5 cm^3 H_2/g TVS.

The results of hydrogen yield from fermentation of hydrolyzed sugarcane bagasse as a substrate were used to optimize the substrate concentration, the substrate to buffer ratio and the inoculum to substrate ratio by applying CCD method [201]. The obtained hydrogen yield from experimental validation was slightly lower than those predicted by model and reached 6980 cm^3 H_2/dm^3 substrate.

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

highest values of both hydrogen yield and production rate were 460 cm^3 H_2/ g COD and 2.44 cm^3/h, respectively.

BBD with input variables of substrate concentration, inoculum concentration and HRT was used to model and optimize the hydrogen production from pretreated waste sugarcane leaves [203]. The optimal hydrogen yield was 14.2 cm^3 H_2/g of fermentable sugars in the lab-scale experiment. The developed model allowed to enhance the biohydrogen yield by 23% in a semi-pilot scale.

5.5.2. Artificial Neuron Networks

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

Biogas production

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

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

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

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

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

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

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

ANN models for predicting of ammonia and hydrogen sulfide formation was developed by Strik et al.[210]. The proposed approach was used to model the concentration of these trace compounds under dynamic conditions. Therefore, the information regarding the current concentrations of ammonia and hydrogen sulfide in both the liquid and the gaseous phases were used to predict the resulting concentration of a given component. The accuracy of H_2S prediction was 91%, while the NH_3 model estimated its concentration with the accuracy of 83%. Both models showed the potential to predict, control, reduce or avoid the formation of the trace compounds during anaerobic digestion processes.

Biohydrogen production

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

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 *Carica papayas* fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	QuickProp 5-12-1	[191]
Pretreated *Carica papayas* fruit peels and poultry dropping	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	QuickProp 5-12-1	[192]
Pretreated *Telfairia occidentalis* fruit peels	Consortium of microorganisms from cattle rumen content	T, pH, RT, TS, VS	BY (m^3/kg VS_{fed})	QuickProp 5-12-1	[193]
Food waste and poultry manure	Not specified	T, pH, ratio poultry manure : food waste	MY (cm^3/ 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_3] C/N, TS, particle size	30-day MY (L/kg VS_{feed})	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_4content	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_0 – in mixture of co-	BY (cm^3)	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	BY (dm^3)	4-10-1	[196]
Not specified	Thermophilic digesting sludge	COD loading rate, sulfate loading rate, actual [H_2S] in biogas, [S^{2-}] in reactor, BY, pH	[H_2S] in biogas	7-(2 hidden layers with 5 neurons)-1	[210]
		Nitrogen loading rate, [NH_3] in biogas, [NH_3] in reactor, total inorganic nitrogen in reactor, BY, pH, COD loading rate	[NH_3]in biogas	8-(2-hidden layers with 7 neurons)-1	
Buffalo dung compost	Anaerobic mixed consortia	Biohydrogen pH, glucose: xylose ratio, inoculum size, inoculum age	Cumulative H_2	BPNN 4-10-1	[211]
Darvill wastewater plant	Anaerobic sludge	So, Inoculum %, T°C	Cumulative H_2	BPNN 4-(6-10)-1	[212]
Waste water (sugar industry)	Mixed cultures	OLR, ORP, pH, alkalinity	HPR	BPNN 4-3-1	[213]
Wastewater treatment plant	Mixed cultures	pH, So, Xo, T°C, time	HPR	BPNN 5-6-4-1	[214]
Wastewater treatment plant	Mixed cultures	OLR, pH, VSS yield	HPR	BPNN 3-8-4-1	[215]
Cheese Whey	*Escherichia coli* Δ*hycA* Δ*lacI* (WDHL)	ORP, pH, dissolved CO_2	HPR	BPNN	[216]

S_0 – initial substrate concentration VS – volatile solids, F/E – feedstock to effluent ratio, C/N – carbon to nitrogen ratio;TS – total solids, [NH_3]- ammonia concentration, MY – methane yield, S_0 – initial substrate concentration, T - temperature, τ – time, HRT – hydraulic retention time; COD – chemical oxygen demand; LCFA – long chain fatty acids, BBD – Box-Behnken Design; CCD – central composite design; ORP: Oxidation-reduction potential; CO_2: Carbon dioxide; HPR: Hydrogen production; HRT: Hydraulic retention time; So: Initial substrate concentration, Xo= Initial biomass concentration; T°C: Temperature; SE (%): Substrate degradation efficiency; OLR: Organic loading rate; H2: Hydrogen; TOCeff : Effluent total organic carbons; VSS yield: Volatile suspended solids yield; BPNN: Back propagation neural network; HY: Hydrogen yield

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

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

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

5.5.4. Comparison of RSM and ANN models for biohydrogen

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

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

6. Concluding remarks

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

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

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

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

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

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8. References

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