

Review

Current Status of the Pyrolysis and Gasification Mechanism of Biomass

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Abstract: The development of the world economy goes hand in hand with increased energy consumption and global warming caused by greenhouse gases. These issues can be tackled by implementing promising technologies of power generation. They differ from the known ones in that new energy resources are involved, e.g., mixtures of various types of biomass, provided that hazardous gas emissions during the production process are minimized. The development of high-potential energy-efficient and environmentally friendly technologies which use biofuel in the energy industry requires scientific evidence for the mechanisms, conditions, and characteristics of physical and chemical processes during pyrolysis and gasification of biomass, including its multicomponent types. This article analyzes the world technologies and research findings in the field of biomass pyrolysis and gasification. The effect of a group of factors on the intensity and completeness of gasification and pyrolysis of biofuel compositions has been determined. These factors include the size, shape, and surface structure of biomass particles; component composition and properties of fuel mixtures; mechanism and intensity of heat supply; and the temperature field in the reactor filled with solid and gaseous products. The most effective values of these characteristics have been established.

Keywords: ecology; environmental; biomass; pyrolysis; gasification; gas; tar; char



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1. Introduction

At present, great importance is attributed to renewable energy, when environmental problems associated with fossil fuels are solved. Different types of biomass, including wood, energy crops, agricultural and forestry waste, algae, etc., are the main available sources of renewable energy. Biomass offers the greatest potential for meeting the energy needs of modern society, both for developed and emerging markets worldwide [1]. The major advantages of this type of fuel include its variety, wide availability, generation volumes, reasonably fast reproducibility, and numerous alternative conversion technologies (for instance, combustion, gasification, and pyrolysis). Depending on the conversion method, biomass can simultaneously serve as a source of liquid, gaseous, and solid fuel (e.g., liquid motor biofuel, biogas, and solid fuel pellets). The data of the World Bioenergy Association reveals [2] that the structure of the global bioenergy consumption in 2016 was as follows: 4.9%—liquid biofuel, 91.8%—traditional consumption of biomass considering the present-day types of solid biofuel, 2.2%—biogas, and 1.1%—municipal solid waste (MSW) processing. Producing energy from biomass may significantly promote the commitments under the Kyoto Protocol to reducing greenhouse gases and solving problems pertaining to climate change [3].

Biomass can be converted to energy by using thermochemical and biochemical methods [4]. Biochemical methods, including anaerobic digestion and fermentation, constitute

the transformation of cellulose and hemicellulose into biofuel at the stages of hydrolysis [5] and fermentation [6]. At present, biochemical methods are cost-intensive, and involve problems with using lignin-rich biomass [6,7]. Moreover, these methods are sporadic in nature. They are characterized by relatively slow speed, and the resulting product is diluted with a great amount of water recirculating in the production process. In the present study, these processes were not considered.

Thermochemical conversion technologies (combustion [8], gasification [6] and pyrolysis [3]) make it possible to convert feedstock to useful energy. Brief characteristics of the above-mentioned processes are presented in Table 1.

Table 1. Biomass conversion methods.

Type of Conversion	Benefits	Drawbacks
Thermochemical Conversion		
Combustion	The scale of setups varies from small to industrial ones in the range of 50–3000 MW. Conversion efficiency is between 20% and 40%. Biomass can be co-fired with coal.	Biomass moisture content should be less than 50%. The process develops at a high temperature (800–1000 °C).
Gasification	The produced gas with a higher heating value of 4–6 MJ/m ³ can be burned directly or used (after cleaning) as a fuel for gas engines and turbines. Syngas production from biomass makes it possible to obtain methanol and hydrogen, each of which can be used as a fuel for transportation.	The gas with a higher heating value of 4–6 MJ/m ³ is not appropriate for pipeline transportation due to its low energy density. The production of methanol with a higher heating value of 9–11 MJ/m ³ requires gasification involving oxygen.
Pyrolysis	Bio-oil can be used in engines and turbines; it also serves as feedstock for oil refineries.	Low heat stability and high corrosiveness.

Biomass combustion is used widely for commercial purposes to produce heat and power [9]. The technology is commercially available, and poses minimal risk for investors. The end product of combustion is thermal energy used for heating and/or electrification. However, the efficiency of energy production from biomass is not high: approximately 20% for small enterprises, and no more than 40% for large and modern power-generating facilities [9]. Such technologies provide an economic and competitive advantage, provided that waste as initial feedstock is used. Considering that biomass combustion technologies are widespread and well understood [1,10,11], it is interesting to explore biomass pyrolysis and gasification in this review.

Gasification is considered to be the most efficient biomass-to-fuel conversion method. The process develops at elevated temperatures (650–1200 °C) in the presence of gasification agents (air, oxygen, steam, carbon dioxide), with syngas as the resulting product [7,12]. Air gasification yields a producer gas with a higher heating value of 4–6 MJ/nm³ (low-calorific gas). This gas can be burned in boilers and in gas engines or turbines after treatment, yet it is not appropriate for pipeline transportation due to low energy density. Gasification using oxygen yields intermediate heating value gas (10–12 MJ/m³) suitable for limited pipeline transportation and can be used as syngas to produce power/heat or converted into diesel range hydrocarbons by means of Fischer–Tropsch synthesis, or into dimethyl ether or gasoline range hydrocarbons [13]. Steam (pyrolytic) gasification yields an intermediate heating value gas with a greater heat of combustion (15–20 MJ/m³). This is a two-stage process implemented in two fluidized bed reactors. The main benefits of gasification over direct combustion of biomass are minimal emissions of pollutants and high heat efficiency [14,15]. In addition, integrated gasification combined cycle (IGCC) with carbon capture and storage (CCS) is now widespread [16–18]. CCS in gasification projects is considered a promising technology for cost-effective CO₂ reduction (81–91%). The main advantages of IGCC with CCS include: (i) reduction of anthropogenic emissions (SO₂ and NO_x), as compared to combustion in boilers; (ii) reduction of energy losses during separation and capture of CO₂ from synthesis gas; and (iii) production of

valuable by-products: sulfur (for example, almost all of the sulfur in fuel can be recovered), nitrogen (from an air separation unit), and CO₂ (from a CO₂ capture unit) [16–18]. At the same time, gasification technologies, especially IGCC with CCS [16], involve considerable investment, which is much higher than the respective costs when traditional methods of fossil fuel utilization are applied.

Pyrolysis is endothermic decomposition of feedstock developing under oxygen deficiency. Pyrolysis is the first stage in combustion and gasification; it is followed by complete or partial oxidation of primary products. The end products of biomass pyrolysis are pyrolysis oil (bio-oil), non-condensable gases, and carbon-rich residue (char). The bio-oil yield occurs at temperatures from 350 to 500 °C [19]. At higher temperatures, the molecules of liquid and solid residue are destroyed to produce smaller molecules that pass to the gas medium. The yield of biomass pyrolysis products can be increased if the following conditions are fulfilled: (i) char—low temperatures and heating rates; (ii) liquid products—average temperatures, high heating rates and short gas residence time; and (iii) gas—high temperatures, low heating rate, and long gas residence time.

Pyrolysis oil can be utilized in diesel engines and power generation units in distributed generation, as well as at large power plants (as an alternative to fuel oil). Shihadeh et al. [20] showed that when pyrolysis oil is used in internal combustion engines, its efficiency is identical to the thermal efficiency of diesel fuel. However, the ignition delay of pyrolysis oil was longer [20]. Bio-oils do not yet have a wide industrial application due to existing limitations on the fuel quality, high viscosity, low stability and sustainability, and corrosiveness [19,21].

Pyrolysis yields from 10 to 35% char. Depending on the composition and physical properties of char, it can be used in different industrial processes: as solid fuel in boilers, activated carbon production, carbon nanotube manufacturing, etc. [22]. The producer gas resulting from pyrolysis can be converted after treatment into syngas, which can be utilized in engines and turbines, industrial incineration plants, and in methanol production [23].

The presented information is generalized in Table 2 with data about the typical products obtained using different methods of biomass conversion.

Table 2. Typical product yields obtained by biomass conversion.

Process		Conditions	Result		
Pyrolysis	Fast	Moderate temperature (600–800 °C), short residence time particularly vapor (from 10 to 200 °C/s)	Liquid 75%	Char 12%	Gas 13%
	Slow	Low temperature (300–500 °C), very long residence time (under 1 °C/s)	30%	35%	35%
Gasification		High temperature (650–1200 °C), long residence times (from 1 to 100 °C/s)	5%	10%	85%

There are several well-established pyrolysis and gasification plants in different parts of the world, the most well-known of them are in Canada, the USA, Finland, and others. Table 3 [21,24] lists some industrial pyrolysis and gasification units.

The purpose of the study is to systematize the knowledge of the mechanisms, conditions, and characteristics of physical and chemical processes under the thermal decomposition of biofuel in a gas medium. These encompass pyrolysis and gasification of biomass for efficient waste management and greenhouse gas emission control, as well as for the joint production of gaseous and solid products with high-potential energy generation.

This research singles out mechanisms and stages of pyrolysis and gasification of biomass, defines the most typical types for biomass used for pyrolysis and gasification, as well as analyzing the main factors (temperature, biomass composition, size of particles) that determine the efficiency of these processes. The novelty of this research comes from performing a comparative analysis of literature data on the subject of biomass pyrolysis and gasification. The issues related to the physical and chemical aspects of pyrolysis and gasification, conditions, and significant factors affecting the qualitative and quantitative

characteristics of end products of biomass pyrolysis and gasification will be discussed in detail in the study. The literature data under consideration will be generalized and presented for illustrative purposes as tables listing the benefits and drawbacks of thermochemical methods of biomass conversion, pyrolysis products, known commercial pyrolysis and gasification plants, types of biomass in use and their properties, and several parameters affecting the efficiency of the processes, as well as the most significant research findings in the field of biomass pyrolysis and gasification. The conducted review and analysis results of recent achievements are meant to aggregate the experimental data to develop mathematical models of biomass pyrolysis and gasification in the future. These would make it possible to reliably predict the characteristics of end products when widely varying the parameters of significant factors. Without doubt, this will promote the development of practical applications.

Table 3. Worldwide current pyrolysis and gasification operating plants.

Plant Name	Location	Units	Capacity
Pyrolysis			
Red arrow, WI	Canada	Circulating fluidized bed	1700 kg/h
Dyna Motive	Canada	Bubbling fluidized bed	400 kg/h
Bio-alternative	USA	Fixed bed	2000 kg/h
Battelle	USA	Catalytic pyrolysis technology	1000 kg/h
Empyro	Netherlands	Flash pyrolysis	5000 kg/h
Bioliq	Germany	Fast pyrolysis	500 kg/h
BEST Energy	Australia	Bubbling fluidized bed	300 kg/h
Fortum	Finland	-	350 kg/h
Unión Fenosa	Spain	Bubbling fluidized bed	200 kg/h
IRR manufacturing	South Africa	-	1000 kg/h
Gasification			
Great plains synfuels plant	USA	Fixed bed dry bottom	16,000 t/day
Energos Gasification Plant	Norway	two-stage thermal treatment process	78,000 t/year
Red Rock Bio	USA	TCG Global steam reforming	136,000 tons/year
Shaanxi Weihe Fertilizer Co	China	General Electric	1500 t/day
Yunnan Yuntianhua Group Tian'an Chemical Co., Ltd.	China	-	2700 t/day

2. Mechanisms and Stages of Biomass Pyrolysis and Gasification

Biomass is a system with a rather complex structure. A group of processes, phase transformations, and chemical reactions in a condensed phase and gas medium proceed in biomass when it is heated. Below are equations describing the main processes and transformations, taking into account typical stages of biomass conversion [6,25,26]: drying, pyrolysis, and gasification (Figure 1). There are reactors in which most of these processes run simultaneously [6,25–27].

These processes are intended for producer gas generation. The term “synthesis gas” is quite often used, though it has a rather strict ratio of component concentrations: $H_2/(2CO + 3CO_2) = 1.05$. Impurities have been removed from it, and it is used as feed-stock for the synthesis of chemical organic compounds currently produced from oil. It is unreasonable to set such requirements for the gas used as fuel. It is also incorrect to refer to biomass-derived producer gas as biogas. Biogas is obtained from biomass using biotechnologies. It consists mainly of methane (CH_4). Producer gas contains a small amount of CH_4 .

The following stages are typical of the process: drying, pyrolysis, gasification, and condensation. These stages can be separated from each other by using intermediate chambers or different heating temperature ranges, and varying the type of medium (inert, reducing, oxidizing).

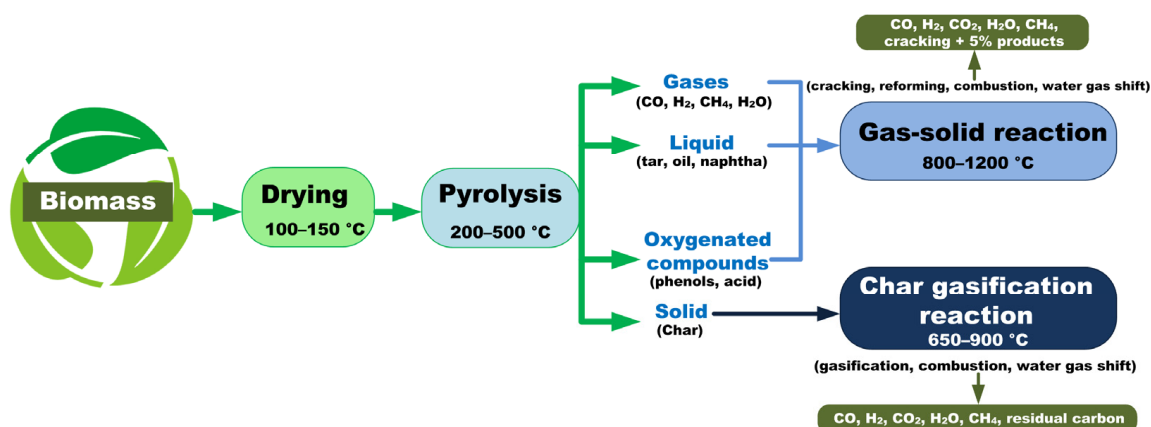


Figure 1. Mechanisms and stages of pyrolysis and gasification.

2.1. Drying

Drying is the first step of fuel preparation [28]. The moisture content of the initial fuel has a significant effect on gasification. High-moisture fuels are unable to maintain a sustainable combustion front in the layer, due to great energy demands for water evaporation.

By choosing the correct thermal mode in the reactor, wet fuel can be gasified under the conditions of steam-air blowing without adding any external steam. According to thermodynamic calculations, high content of moisture reduces the efficiency of the process, but increases the content of hydrogen in the producer gas. Water in the solid fuel can be physically or chemically bound. Since coal, biomass, peat, and other solid fuels are porous, their drying proceeds in the same way.

At the initial stage of drying, the content of moisture decreases almost linearly with time. This region is referred to as the period of the constant drying rate. During this period, the drying rate is determined by the external mass exchange of the surface with the surrounding gas medium. Unbound moisture is the first to evaporate, followed by inherent moisture evaporating in a quasi-steady mode. As soon as moisture content becomes critical, the drying rate starts decreasing. The period of the falling drying rate begins. At the same time, the rate of moisture diffusion inside the particle becomes lower than that of the external mass exchange. Thus, experimental data about the coefficient of moisture diffusion in the material makes it possible to calculate the rate and duration of fuel drying.

2.2. Pyrolysis

Thermal decomposition (pyrolysis) of biomass (which is usually implemented in industrial plants at temperatures exceeding 550 °C) is a complex of transformations resulting in gaseous products and a solid residue [29]. Pyrolysis proceeds under oxidizer deficiency. When biomass is heated, the proportions of gas, liquid, and semicoke produced depend on the pyrolysis mode and type of the system used. Three main components of biomass participating in pyrolysis are distinguished [30]: cellulose, hemicellulose, and lignin. Hemicellulose decomposes at a temperature from 250 to 400 °C and generates 20% semicoke when heated to 720 °C; higher temperatures (from 310 to 430 °C) are required for cellulose to decompose with 8% semicoke produced; lignin decomposes at 300–530 °C with the production of approximately 55% semicoke [30]. At lower temperatures, hydrocarbons depolymerize to produce smaller particles. Dehydration occurs at about 300 °C, with the production of unsaturated polymers and semicoke. A further temperature growth leads to extensive rupture of C–C and C–H with the production of oxygenates C_{2–4} and products: CO, CO₂, H₂, and CH₄ [13].

2.3. Gasification of Carbonaceous Residue

Biomass gasification is a method of thermochemical conversion which includes converting chemical structures of biomass at elevated temperatures ($>700\text{ }^{\circ}\text{C}$) in the presence of a gasifying agent (air/ O_2 /steam/ CO_2 or a combination of these). Biomass is gasified in order to convert feedstock with a low calorific value into gaseous products with an average calorific value [31]. In addition to H_2 , CO , CO_2 , and CH_4 , untreated syngas also contains tars, lighter hydrocarbons, N_2 , and sulfur compounds, as well as traces of chloride. These decrease the gas quality. Among all these syngas components, H_2 and CO are the most essential. Pyrolysis and gasification are interdependent processes. The gasification of the carbonaceous residue of biomass after pyrolysis is the process of interaction of carbon in a solid state with gaseous pyrolysis products CO , H_2 , and CO_2 . It proceeds in the following way:

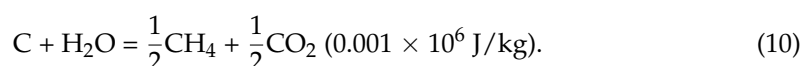
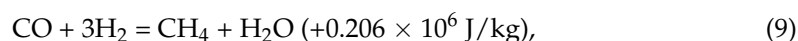
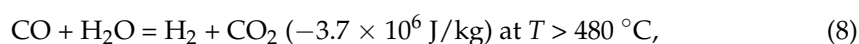
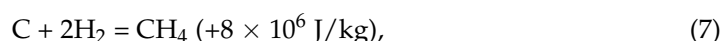
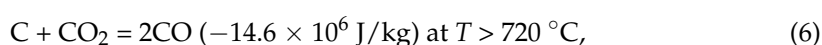
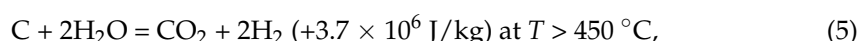
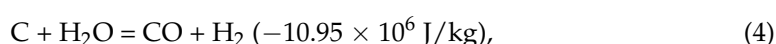
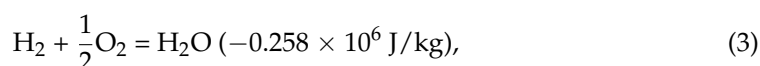
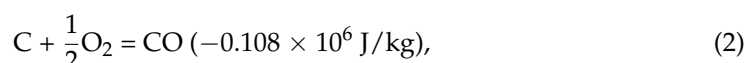
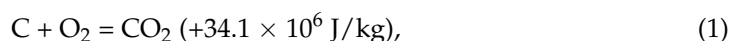
- $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ (absorbed heat, i.e., endothermic effect $-14.6 \cdot 10^6\text{ J/kg}$) [32],
- $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ (absorbed heat, i.e., endothermic effect $-10.9 \cdot 10^6\text{ J/kg}$) [32],
- $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$ (proceeds only at temperatures above $500\text{ }^{\circ}\text{C}$ with heat released, i.e., exothermic effect $+8 \cdot 10^6\text{ J/kg}$) [29]. These reactions develop on the surface and in the pores of biomass particles.

Thus, the main purpose of biomass gasification is the production of gas, while maximizing H_2 concentrations and minimizing the tar content.

2.4. Pyrolysis and Gasification

The processes, phase transformations and chemical reactions described in the three previous sub-sections can be consecutive or parallel. The pyrolysis and gasification of biomass particles can be controlled by varying the initial concentrations of H_2O and CO_2 in the gas medium.

The main reactions of such interactions are as follows [29,32–35]:



The explanations in line with the concepts [29,32–35] are presented below. Most of the oxygen (pure oxygen or oxygen of the air), supplied to the gas generator, is spent on the reactions (1)–(3). This releases thermal energy required for the drying of the solid residue, destruction of chemical bonds, and temperature increase in the gasification zone, as well as for the reactions (4)–(9). The reactions (4,5) are the main gasification reactions. They are endothermic and proceed in a high-temperature and low-pressure zone. The reaction (6) is a primary reaction during the combustion of carbon (endothermic). It is much slower than that of combustion (1) under the same temperatures. The reaction (7) describes the interaction of carbon with hydrogen to produce methane. The rate of this reaction is not

high, except under the conditions of high pressure. The interaction (8) is very important for hydrogen synthesis. A temperature increase (over 600 °C) facilitates the reaction (9) towards methane generation. It is quite slow under relatively low temperatures. The reaction (10) is quite neutral in terms of heat release.

To use the gas obtained from biomass pyrolysis and gasification as an energy-efficient (with a high calorific value) and environmentally friendly (with a low content of SO_x and NO_x) fuel, factors influencing its composition should be carefully analyzed. The following sections focus on these parameters.

3. Biomass Types Used for Pyrolysis and Gasification

The following categories of biomass are distinguished in the context of pyrolysis and gasification: (i) primary wood waste, such as chips, sawdust, and tree branches; (ii) energy crops grown for the use in the energy sector, such as rapeseed, jatropha, miscanthus, and sugar cane; (iii) agricultural waste, such as sugar cane bagasse, nut shell (coconut, sunflower), corn husk, wheat straw, oil production waste (olive, rapeseed and sunflower waste), and palm seeds; and (iv) municipal solid waste, animal waste, and food waste. Table 4 presents data on types of biomass used for pyrolysis and gasification in different regions of the world.

Table 4. Characteristics of components (type of biomass) used in gasification and pyrolysis.

Component	Country	Ultimate Analysis (wt %)					Proximate Analysis (wt %)					Ref.
		C	H	O	N	S	Moisture	Volatile Matter	Fixed Carbon	Ash	Heat of Combustion (MJ/kg)	
Woody biomass												
Beech wood	Germany	44.1	6.3	49.4	0.2	0	4.7	87.6	8	0.8	19.5	[36]
Wood pellet	UK	52.3	6.8	40.7	0.16	-	6.7	84.3	15.7	0.8	20.8	[37]
Soft wood	Ukraine	45.34 ± 0.13	5.86 ± 0.04	42.45 ± 0.04	0.58 ± 0.11	0.17 ± 0.07	5.15	-	-	5.60 ± 0.38	18.23 ± 0.13	[38]
Woody biomass	Sweden	51.3	6.2	42	0.1	0.021	4.3	83.8	-	0.3	19.36	[39]
Pine	Russia	47.88	6.34	45.69	0.09	0	-	72.5	27.0	0.5	-	[40]
Pine sawdust	India	50.3	6	42.99	0.69	-	6.09 ± 0.3	78.03 ± 0.2	12.16 ± 0.1	2.07 ± 0.03	18.44 ± 0.9	[41]
Sal sawdust	India	49.83	6.01	43.56	0.58	-	8.88 ± 0.2	76.03 ± 0.1	14.09 ± 0.2	1.14 ± 0.01	18.20 ± 0.9	[41]
Pine wood chips	Canada	48.3	5.8	45.4	0.5	-	4.5	78.4	-	2.6	16.1	[42]
Sawdust	Ecuador	46.1	6.3	46.7	0.3	-	7.4	-	-	0.6	-	[43]
Pine sawdust	India	53.5	6.93	32.55	3.33	0.66	7.85 ± 0.05	77.27 ± 0.65	12.20 ± 0.15	2.78 ± 0.12	18.55 ± 0.43	[44]
Root of mango tree	Australia	45.56	6.44	47.24	0.56	0.20	5.73	67.87	22.49	3.91	18.52	[45]
Eucalyptus urophylla	Brazil	45.03	4.78	38.46	0.11	-	11.37	75.34	13.04	0.27	17.16	[46]
Herbaceous and agricultural biomass												
Miscanthus	Australia	50.73	7.08	41.95	0.14	0.10	10.67	65.65	18.34	5.34	17.00	[45]
Palm empty fruit bunches	UAE	44.7	5.97	49.05	0.74	0.18	8.73	67.51	17.47	6.28	17.2	[47]
Palm leaves	UAE	40.76	5.55	52.14	1.32	0.24	12.03	58.17	15.41	14.4	18.9	[47]
Palm leave stems	UAE	42.67	5.83	50.78	0.58	0.15	11.65	68.84	10	9.51	16.5	[47]
Corn stalks	Ukraine	36.38 ± 1.36	5.40 ± 0.13	44.08 ± 0.38	1.68 ± 0.01	0.16 ± 0.02	8.13	-	-	12.30 ± 0.87	14.24 ± 0.46	[38]
Jerusalem artichoke stalks	China	45.36	6.11	47.26	0.75	0.52	15.76	67.4	13.5	3.34	15.69	[48]
Cane	China	42.78	5.17	50.51	1.33	0.21	5.89	72.12	13.52	8.47	16.16	[48]
Gulmohar seed	India	51.3	6	40.56	2.58	-	7.09 ± 0.05	75.56 ± 0.5	15.80 ± 0.2	2.07 ± 0.12	19.65 ± 0.11	[44]
Corn cob	China	46.6	5.8	47.0	0.4	0.2	-	86.9	11.8	1.3	-	[49]
Corn cob	India	44.2	5.9	44.2	0.54	0.08	10.2	80	4.2	5.7	15.5	[41]
Palm kernel shell	UK	50.11	6.24	42.16	1.50	0	6.70	67.52	22.13	3.65	-	[50]
Olive waste	UK	52.8	6.5	39.1	1.6	-	5.9	80.1	19.9	7.6	20.1	[37]
Palm kernel cake	China	49.04	5.93	34.10	2.46	0.29	2.88	75.83	15.99	5.30	-	[51]
Jatropha seeds cake	China	45.3	6.2	43.8	4.5	0.2	-	73.5	18.2	7.3	-	[49]
Bagasse	China	46.4	6.7	45.8	0.7	0.4	-	87.4	9.7	2.9	-	[49]
Sugarcane	India	43.2	6.2	43.2	0.4	0.8	10	76	9.6	4.4	17.2	[41]
Sugarcane	UK	44.34	5.92	49.17	0.57	0	5.33	83.39	7.79	3.49	-	[50]
Sugarcane	Brazil	43.79	5.16	38.90	0.29	-	7.32	74.86	13.27	4.55	17.81	[46]
Sugarcane trash	Brazil	44.7	5.8	48.97	0.45	0.08	9.92	81.55	6.90	11.57	17.74 (16.50)	[52]
Cherry pulp	Turkey	50.80	6.79	39.66	2.67	-	6.42	72.02	19.70	1.86	19.82	[53]
Straw												
Wheat straw	Ukraine	39.90 ± 0.15	5.75 ± 0.02	41.97 ± 0.07	0.65 ± 0.08	0.13 ± 0.05	6.84	-	-	11.59 ± 0.76	16.12 ± 0.19	[37]
Wheat straw	UK	40.58	4.84	53.84	0.74	0	5.19	64.24	15.60	14.97	-	[50]
Wheat straw	China	45.94	5.83	39.08	0.56	0.45	2.50	72.36	18.00	5.64	-	[51]
Rice straw	China	42.66	5.68	37.37	1.03	0.44	1.51	69.09	18.09	11.31	-	[51]
Cotton stalk	India	46.8	6.4	46.8	0.3	0.2	8.9	71	16.6	3.5	19.2	[41]
Cotton stalk	UK	43.10	6.24	49.07	1.59	0	7.33	69.54	19.47	3.67	-	[50]
Rice Husk	UK	37.60	5.26	55.45	1.69	0	8.02	61.43	12.53	18.02	-	[50]
Nut husk and shells												
Sunflower husks	Ukraine	45.82 ± 0.08	6.32 ± 0.02	38.31 ± 0.08	2.61 ± 0.05	0.14 ± 0.02	6.1	-	-	6.81 ± 0.51	19.31 ± 0.13	[38]
Almond nut husk	India	48.8	5.79	43.45	1.95	0.1	7.43 ± 0.1	74.05 ± 0.2	15.55 ± 0.3	2.48 ± 0.05	18.21 ± 0.9	[41]
Peanut shell	China	49.7	5.8	43.7	0.6	0.1	-	84.1	14.5	1.4	-	[49]
Palm kernel shell	Malaysia	48.82	5.68	45.08	0.42	-	13.65	75.32	20.81	3.87	14.88 (14.75)	[54]
Walnut shells	Ukraine	43.41 ± 0.17	5.66 ± 0.06	48.44 ± 0.08	1.98 ± 0.06	0.11 ± 0.03	4.1	-	-	0.41 ± 0.11	16.79 ± 0.08	[38]
Coconut shell	UK	48.32	5.26	46.14	0.29	0	7.16	68.58	22.00	2.26	-	[50]
Other												
Cellulose	UK	41.61	5.63	52.64	0.11	0	4.74	84.16	9.85	1.25	-	[50]
Natural rubber	Malaysia	83.63	11.97	2.71	1.58	0.12	1.71	89.98	4.71	3.60	45	[55]
Spent coffee grounds	China	55.98	6.73	31.07	2.0	0.31	2.66	80.44	15.65	1.25	-	[51]
Brewer's spent grain	Brazil	42.2	7.2	37.6	3.6	1.1	3.97	83.3	9.51	3.22	21.6	[56]
Microalgae	China	52.07	7.15	21.65	8.57	0.62	-	72.37	22.16	5.46	24.19	[57]
Microalgae	China	49.6	7.0	25.4	8.2	0.5	10	81	16	9	-	[57]
Microalgae	Russia	61.3	6.4	22.5	8.8	1.1	3.0	-	-	5.1	25.04	[58]

There are certain conditions to be met when choosing the type of biomass for pyrolysis and gasification, which provide maximum efficiency of the processes. Based on data [6,26,59], the list of factors determining the choice of biomass type has been prepared (Table 5).

Table 5. Factors in choosing biomass type for pyrolysis and gasification.

Biomass Properties	Factors	Favorable Conditions for Pyrolysis and Gasification
Moisture content	There are two kinds of biomass moisture: inherent (the content of moisture in biomass not affected by the weather conditions), and external (the content of moisture in biomass considering the weather conditions).	A high content of moisture enhances pyrolysis and gasification.
Heating value	There are higher and lower heating values. The higher heating value is the maximum amount of energy potentially derived from this biomass source. It includes the content of energy released during the fuel combustion in the air, as well as latent heat in the water steam. The lower heating value is the minimum amount of energy released from biomass conversion.	The higher the heating value, the more rapid is pyrolysis and gasification.
Proportion of bound carbon and volatiles	The content of volatiles in the solid fuel, part of the fuel that is released as gas when it is heated. The content of bound carbon is a mass remaining after the release of volatiles, excluding the content of ash and moisture. The content of volatiles and bound carbon account for the rate of ignition and then gasification or oxidation. The elemental analysis, including the values of O, H, C, N, and S, indicates that a higher percentage of oxygen as compared with carbon reduces the heat of combustion of the fuel due to lower energy.	A high content of volatiles and carbon combined with a low content of oxygen.
Content of ash	The chemical degradation of a biomass-derived fuel as a result of thermochemical or biochemical processes produces a solid residue which is actually ash. The content of ash in biomass affects both the cost of processing and the total cost of biomass energy conversion. Depending on the ash content, the available energy of the fuel proportionally decreases. After combustion, ash can form slag, a liquid phase (at a high temperature), which impairs the performance of the facility and increases operating costs.	Low ash content.
Content of alkali metals	Alkali metals (Na, K, Mg, P, and Ca) in biomass lead to the formation of a sticky mobile liquid phase (slag) which may obstruct the flue gas path.	Lower content of alkali metals.
Cellulose/lignin ratio	Cellulose decomposes at lower temperatures than lignin does. Therefore, the total conversion of the carbon-containing plant matter in the form of cellulose is higher than that of plants with a higher proportion of lignin.	High content of cellulose and low content of lignin.

4. Factors Influencing Pyrolysis and Gasification Efficiency

A list of factors affecting the efficiency of pyrolysis and gasification has been drawn up by reviewing the literature from the recent years.

4.1. Effect of Biomass Composition

Cellulose, hemicellulose, and lignin are the main biomass components. Biomass pyrolysis process can be divided into four temperature ranges: under 220 °C (moisture evaporation), 220–315 °C (primarily hemicellulose decomposition), 315–400 °C (cellulose decomposition), and over 400 °C (lignin decomposition). According to [60], lignin does not decompose completely until the temperature reaches 700 °C. It has also been established that the pyrolysis of wood biomass with a high content of lignin is generally an endothermic

reaction, whereas the pyrolysis of grass biomass with a lower lignin content involves an exothermic reaction [60]. Moreover, it is believed that the amount of lignin is the main factor conditioning the pyrolytic decomposition rate, emission of gaseous products and their composition. A higher lignin content accounts for slower decomposition, lower emission of the gaseous product, and a higher temperature at which volatiles are released. It has been established [61] that grass biomass with a higher cellulose and hemicellulose content takes less time to decompose and yields more gaseous products than wood biomass with a higher content of lignin.

Table 6 shows a list of selected biomass containing different proportion of cellulose, hemicellulose and lignin substrate.

Table 6. Lignin, cellulose, and hemicellulose content in biomass.

Feedstock	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Ref.
Rice straw	30	25	12	[6]
Bagasse	38	39	20	[6]
Oat straw	31–37	27–39	16–19	[59]
Beech wood	21.9	45.8	31.8	[59]
Oak	43.2	21.9	35.4	[59]
Sawdust	22.16	32.63	37.23	[59]
Leaves	4	15.5	80.5	[59]
Straw	28.90	36.70	34.4	[59]
Wood	25–30	35–50	20–30	[62]
Wheat straw	15–20	33–40	20–25	[62]
Rice husk	14.3	31.3	24.3	[63]
Coconut shell	28.7	36.3	25.1	[63]
Corn stalks	17.5	42.7	23.6	[63]
Millet husk	14	33.3	26.9	[63]
Olive husk	28.0	18.5	18.5	[64]

The content of cellulose, hemicellulose, and lignin in the composition of biomass has a significant effect on its gasification and pyrolysis characteristics. Pang et al. [65] present research findings for the thermal decomposition of three types of biomass with different ratios of the main components. It has been established that the higher the level of cellulose in biomass, the higher the yield of the liquid pyrolysis product. The amount of pyrolysis gas depends largely on the proportion of hemicellulose, whereas the share of char in the total amount of pyrolysis products is conditioned by the content of lignin.

Sahoo et al. [66] determined the dependence of the composition and heat of combustion of pyrolysis gas on the type of biomass in use. The research findings suggest that the heat of combustion of syngas obtained from the pyrolysis of biomass with a high content of cellulose and hemicellulose is lower than that from the pyrolysis of lignin-rich biomass. This is explained by the fact that the main product of cellulose and hemicellulose decomposition is CO₂, while lignin decomposes during heating into H₂ and CH₄.

The TGA results for cellulose, hemicellulose, and lignin are presented by Kirubakaran et al. [63]. The research was conducted at temperatures 20–720 °C, under a N₂-saturated atmosphere. The thermal decomposition of hemicellulose, cellulose, and lignin starts at 220 °C, 250 °C, and 500 °C, respectively. It has also been established that the maximum share of char in the solid pyrolysis product composition corresponds to lignin (55% of the initial mass), whereas the minimum share belongs to cellulose (8% of the initial mass).

Zhang et al. [67] explored the gasification of three types of biomass (corn stover, radiata pine wood, and rice husk). They studied the effect of the type of biomass on the gas and tar characteristics in gasification, with steam as a gasification agent in a dual fluidized bed gasifier. It was established that differences in biomass composition (in particular, in the content of cellulose, hemicellulose, and lignin) were the key factors for the formation of gas, tars, and their component composition. Corn stover was shown to be rich in cellulose, and rice husk contained a high percentage of hemicellulose, while pine contained a lot of

lignin. This explained a higher content of H_2 and CH_4 in gas, when pine was gasified, and a higher content of CO in the gasification of rice husk. The gasification of corn stover was characterized by an increased content of CO_2 , C_2H_4 , and C_2H_6 .

In this research, we also recorded the concentrations of the main components of the gas produced from the pyrolysis of different types of biomass and its mixtures. The experiments were conducted in a laboratory reactor with a temperature of 500 °C, with air as the pyrolysis medium. The fuel sample was introduced through an aperture on the reactor. After the sample was in the reactor, the aperture was closed hermetically with a valve, into which a modular gas analyzer probe was fitted. The composition of flue gases was recorded by the Test 1 gas analyzer (Boner-VT, Novosibirsk, Russia). The gas mixture went through the modular probe of the gas analyzer to its sensors, which determined the flue gas concentrations. A standard kit of the Test 1 gas analyzer includes six electrochemical sensors (O_2 , CO, NO, NO_2 , SO_2 , and H_2S). It is additionally fitted with optical sensors for CO_2 and CH_4 , as well as a polarographic sensor for H_2 . A detailed description of the experimental setup and the research method was presented in our previous studies [27]. The effect of the type of biomass on the gas composition was investigated.

It was established (Figure 2) that the pyrolysis of leaves featured the maximum concentrations of CO_2 . Leaves contain much more hemicellulose than any other biomass under study, which accounts for high CO_2 concentrations. However, the CO concentrations for them are minimum (11.6%), as they contain less cellulose than the other biomass types. The concentrations of CO for straw are 12% higher, due to a high content of cellulose. The pyrolysis of sawdust produced more H_2 , which may be connected with the proportion of hydrogen in sawdust (maximum for three biomass types) and the amount of lignin within it. It was also shown that producing mixtures based on the components under study had a positive effect on all the gas-air mixture components. For instance, the emissions of CO_2 from the mixture pyrolysis decreased by 28%, whereas those of CO increased by 10%, depending on the mixture composition. The concentrations of H_2 in the joint pyrolysis of three biomass components grew by 18–22%, as compared with the pyrolysis of leaves and sawdust. This indicates synergistic effects from the preparation of biomass fuel mixtures. It was established [59,68] that the ratio of components in the gas mixture was determined not only by the quantity of cellulose, hemicellulose, and lignin in biomass, but also by the interaction between them.

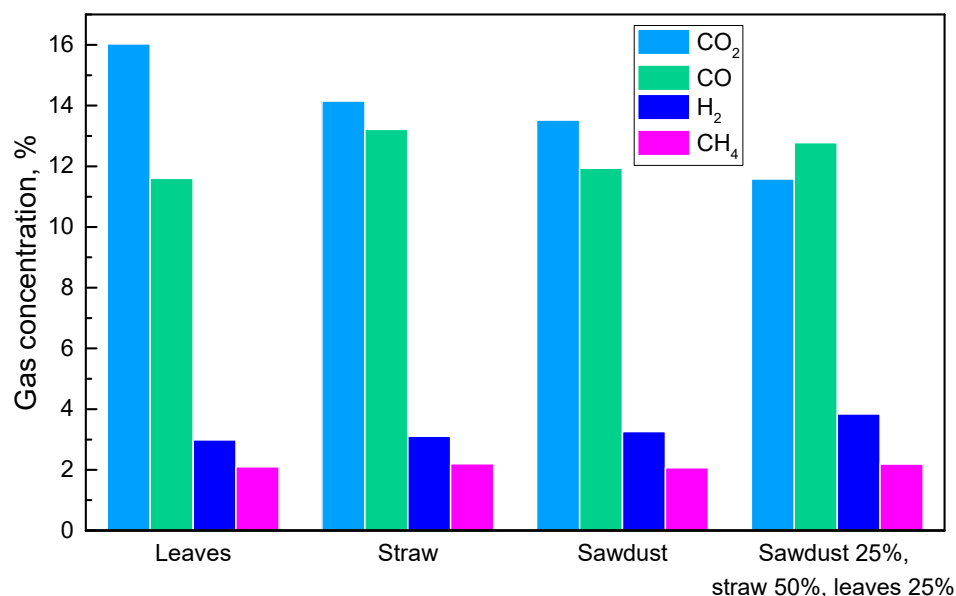


Figure 2. Gas composition during pyrolysis of different types of biomass.

4.2. Effect of Biomass Particle Size

The particle-size distribution of raw biomass affects the residence time of particles, their attrition rate, and entrainment in the reactor [31]. It was established [69] that the particle size of biomass affected the pyrolysis and gasification product yield. Smaller particles with a size of 0.15–0.5 mm enhanced the total gas release, with high concentrations of H_2 . At the same time, the amount of char and tar decreased. With 1–5-mm particles, the temperature gradient inside the particle increased. Consequently, the temperature inside particles could be lower than that on their surface, thus leading to a higher yield of char and tars and reducing the proportion of gas [69]. It was established [69] that the thermal decomposition of large biomass particles contributed to the emission of CH_4 , C_2H_4 , and CO. The heat of combustion was maximum in the pyrolysis of particles with a size of 3–5 mm [69].

The effect of particle size and biomass properties on the characteristics of pyrolysis in a fixed-bed reactor was researched by Sahoo et al. [66]. The experiments for the thermal decomposition of rice husk, straw, and sugarcane bagasse in a N_2 medium were conducted at a temperature of 350–500 °C. The analysis of pyrolysis products revealed that larger biomass particles (over 600 μm) yielded a greater amount of solid and gaseous pyrolysis products. The pyrolysis of particles with a size of 200–400 μm produced the maximum amount of bio-oil. This was explained by the fact that the heat exchange between small particles occurred faster, which accelerated thermal decomposition and contributed to bio-oil production [66].

Mohammed et al. [70] investigated the pyrolysis of biomass with a particle size between 300 and 1000 μm . According to the findings, the yield of a gaseous pyrolysis product decreased with an increase in the biomass particle size. Another important finding was that using finer particles led to a higher H_2 , CO, and CH_4 release, whereas the pyrolysis of larger particles produced more CO_2 . The smaller the particle size, the larger the area of biomass contact with a pyrolyzing gas medium, which leads to faster chemical reactions. However, Ahmad et al. [71] concluded that the factor of the particle size had a less significant effect than the other parameters. Thus, for instance, the effect of the particle size on gasification decreased at a higher temperature [71].

Coconut shell and palm kernel shell gasification was investigated in [72]. Yahaya et al. considered the effect of biomass particle size and reactor temperature on the gas composition, and the mass yield of gasification products in general. Three particle size ranges were chosen: 1–3 mm, 4–7 mm, and 8–11 mm; three temperatures were considered: 700, 800, and 900 °C. These particle sizes correspond to recommended industrial ranges for downdraft gasifiers (≤ 10 mm) [72]. The highest H_2 , CO, and CH_4 concentrations were recorded when smaller particles were gasified. The authors attributed this trend to the tar cracking and reforming reactions, the water–gas shift reaction, the Boudouard reaction, and the exothermic water–gas shift reaction [72]. The concentrations of CO_2 rose slightly as the particle size increased. They also showed that the mass flow rate of gas decreased with the growth of the biomass particle size. By contrast, the mass flow rate of char and tar increased when larger particles were gasified. This result is explained by a lower temperature gradient inside smaller particles, and a larger reaction surface area, which accelerates the reactions during gasification as compared with larger particles [72]. Similar trends were obtained with a temperature increase from 700 °C to 900 °C for all particle sizes. However, the authors claim that temperature has a more considerable effect on gasification reactions than the particle size does [72].

In this research, we also analyzed the influence of biomass particle size on the quantitative characteristics of gas (Figure 3).

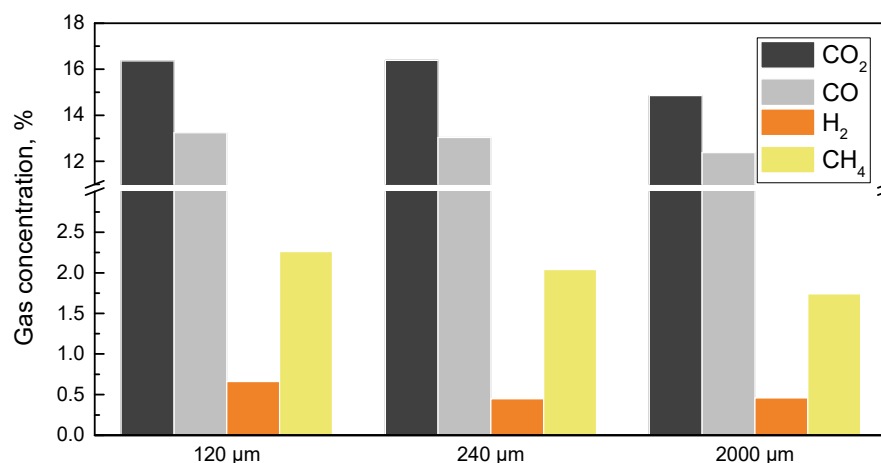


Figure 3. Gas component concentrations in the pyrolysis of biomass (sawdust 25%, straw 50%, leaves 25%) with different particle sizes at a pyrolysis temperature of 500 °C.

It was established that the pyrolysis of finer particles resulted in higher concentrations of all the main gas mixture components. Finer particles meant a larger reaction surface area per a unit of mass, which improved the heat and mass exchange between them. Efficient heat transfer enhanced the efficiency of biomass pyrolysis reactions. Larger particles were more resistant to heat transfer, which led to incomplete pyrolysis, and produced more residual char. Thus, when the particle size decreased from 2000 μm to 120 μm, the average concentrations of CO, H₂, and CH₄ varied from 12.38 to 13.24%, from 0.46 to 0.66%, and from 1.74 to 2.26%, respectively.

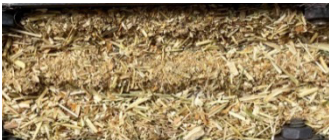
4.3. Effect of Biomass Structure

Kirubakaran et al. [63] explored the way biomass structure affected pyrolysis characteristics. It was shown [63] that the reaction surface area of highly porous biomass was larger, which facilitated the reagent/product diffusion. The temperature was constant both inside the particle and on its surface. As a result, the pyrolysis and gasification reactions proceeded simultaneously in all the biomass layers. This resulted in a homogeneous composition of gaseous products. Less porous biomass particles featured quite a significant temperature gradient between their near-surface layer and deeper layer. A non-uniform temperature caused the drying, pyrolysis, and gasification stages to proceed at different time points, thus generating a heterogeneous gas composition [63]. Sibiya et al. [73] explored the effect of pre-treatment methods on gasification properties during grass pyrolysis. The pre-treatment methods were dry torrefaction, wet torrefaction, and leaching (chemical). It was experimentally established that wet torrefaction improved the gasification efficiency, as compared with dry torrefaction and leaching. This was explained by an increase in the pore size of torrefied char, which later led to the emergence of more active sites for conversion or reaction [73].

To study this factor, we changed the surface structure of biomass (sawdust 25%, straw 50%, leaves 25%) in our experiments: a perforated structure was created, and a biomass sample was divided into vertical and horizontal segments (see the images of surface structure in Table 7).

The experiments revealed (Table 5) that when the surface was perforated, the average concentrations of oxygen in the reaction zone decreased, as compared with the level surface. At the same time, the yield of CO₂, CO, H₂, and CH₄ increased. This indicated enhanced pyrolysis. Making a lot of holes in the biomass sample surface increased the intensity of diffusion of the pyrolyzing agent into the layer, thus promoting biomass decomposition and gas release. The identified positive effect produced by a special surface structure did not exceed 10%.

Table 7. Gas component concentrations in the pyrolysis of biomass (sawdust 25%, straw 50%, leaves 25%) with different surface structures at a pyrolysis temperature of 500 °C.

Surface Structure	CO ₂ , %	CO, %	H ₂ , %	CH ₄ , %
Level layer	14.56	12.38	0.46	1.74
Perforated area				
	15.40	12.94	0.50	1.97
Segments				
	14.76	12.52	0.41	1.52
Channels				
	15.03	12.78	0.47	1.54

4.4. Effect of Temperature

It was established that higher temperatures of biomass gasification reduced the production of char and heavy tar, but increased the concentrations of gaseous H₂ and total gas yield. Increased H₂ production is conditioned by the reaction of thermal cracking of tar, which also reduces its concentration [71,74,75]. According to Le Chatelier's principle, an increased temperature facilitates the yield of endothermic reaction products and reagents in exothermic reactions. Therefore, an increase in temperature enhances the endothermic reactions of conversion of hydrocarbons. A higher temperature usually contributes to the formation of a greater amount of hydrogen and gas release. However, it does not always positively affect the calorific value of gas [76].

Ismail et al. [77] showed the effect of temperature on the pyrolysis gas composition. It was established that raising the pyrolysis temperature to 500–700 °C increased the amount of the gaseous product. Moreover, the temperature growth was accompanied by a higher proportion of CO and a lower amount of CO₂ in the pyrolysis gas composition.

Chai et al. [78] presented experimental research findings for the pyrolysis of sawdust and plastic waste. The temperature inside a fixed bed reactor was varied in the range of 600–800 °C. It was established [78] that the layer temperature increase led to a higher production of pyrolysis gas in general, and H₂ in particular. A similar conclusion was made by Li et al. [79]. When the temperature of microwave pyrolysis of straw was varied from 500 to 900 °C, the volume of the gaseous pyrolysis product increased by 33%. When convective heating was used, it increased by 20%.

Li et al. [80] illustrated the mechanisms of sulfur and nitrogen oxide formation from the joint pyrolysis of coal and biomass in a tube furnace. In the experiments, the temperature in the combustion chamber changed in the range of 300–900 °C, the atmosphere was pure N₂. The analysis of pyrolysis products revealed that the temperature increase to 600 °C led to higher sulfur oxide emissions. With a further temperature growth, the concentration of SO₂ decreased due to the presence of alkali and alkaline earth metals in biomass. These reacted to produce sulfites and sulfates. NO_x, CO, and CH₄ concentrations increased as the temperature grew in the analyzed range.

In this research, we also investigated the effect of thermal conditions on the concentrations of gaseous substances produced by pyrolysis. The temperature range under study

was 300–700 °C. According to the data obtained, the production of CO₂, H₂, and CH₄ rose with the pyrolysis temperature increase. The most considerable growth was recorded when the temperature exceeded 500 °C. This effect stems from faster semicoke pyrolysis and decomposition of volatiles. The average concentrations of H₂ and CH₄ increased by 60–95% and 40–97%, respectively. In the temperature range of 300–500 °C, the CO concentrations were found to rise too. However, when the temperature grew from 500 to 700 °C, the average concentrations of carbon monoxide fell by 4–17% (Figure 4). The latter can be attributed to enhanced reactions of carbon conversion and CO reduction. The established trend is in good agreement with other research findings, e.g., [81–83].

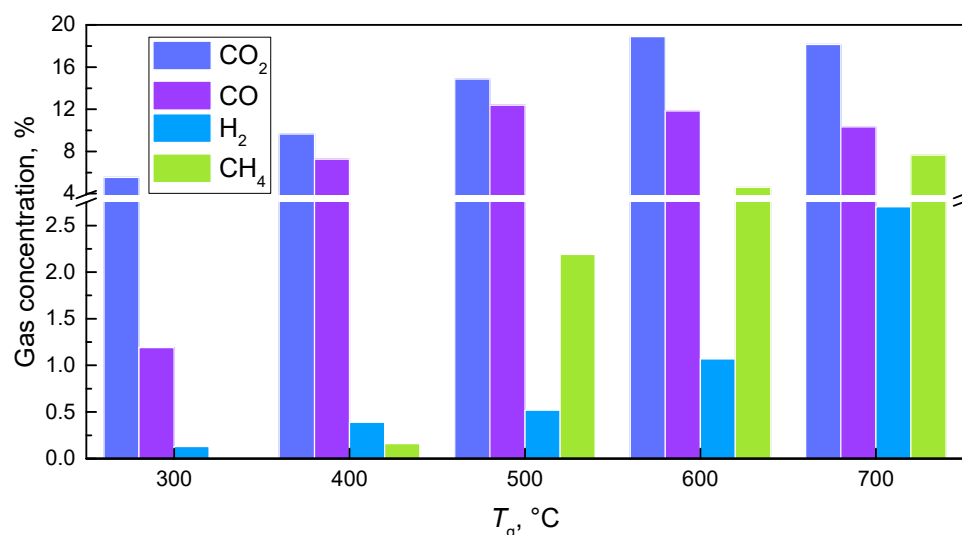


Figure 4. Gas component concentrations in the pyrolysis of biomass (sawdust 25%, straw 50%, leaves 25%) when varying the temperature in the reactor.

4.5. Effect of Gasifying Agent

Extensive research is currently conducted for biomass gasification in different media, such as air, oxygen, steam, or a mixture of these components. Lv et al. [84] compared air and steam to discover that steam gasification was more efficient than air gasification for maximizing hydrogen production. The amount of H₂ and CO in gaseous products also increased when an air-steam mixture was a gasifying medium [84].

The steam/biomass (S/B) ratio affected gasification characteristics, too. In the research [84], an increase in the steam to biomass ratio from 0 to 1.33 maximized the total yield of gas and hydrogen. However, with an increase in the S/B ratio from 1.33 to 2.67, the total gas and hydrogen yield started falling. These findings show good congruence with the data from [85]. Chang et al. studied gasification effects of α -cellulose at 800 °C, when varying the S/B ratio from 0 to 1.5 [85]. H₂ yield rose significantly, with an increase in the S/B ratio from 0 to 1. However, with a further increase in the S/B ratio from 1 to 1.5, the amount of hydrogen decreased. The lowest heat of combustion for producer gas was obtained at an S/B ratio of 1.5.

In air gasification, an identical ratio of air to biomass (excess air) can affect the quality of the resulting gas. In the study [70], the ratio was increased from 0.15 to 0.35. This reduced the semicoke and tar yield. At the same time, the total gas production increased. The concentration of H₂ reached its maximum at a component ratio of about 0.25. This was followed by a reduction, when the ratio grew to 0.35. The concentration of CO₂ significantly increased, whereas the yields of CH₄ and CO decreased [70].

Parthasarathy et al. [86] compared the characteristics of gas produced when using different gasifying agents: air, oxygen, and steam. It was shown that in oxygen and steam gasification, the concentrations of H_2 were 2.7 times as high as those in the air medium. The calorific value of gas and the economic efficiency of the process were higher than in steam gasification. The quality of the resulting gas and the energy consumed were found to depend greatly on the steam/biomass ratio [86]. An increase in this ratio led to a higher gas yield with higher H_2 and CO_2 concentrations in it. At the same time, the release of CH_4 and CO decreased. This trend is congruent with Le Chatelier's principle. An increase in the steam to biomass ratio affects the reactions by reducing the steam concentration during gasification. Thus, a high concentration of steam facilitates gasification and conversion of methane by generating a lot of H_2 [71].

However, too much steam in the gas generator may negatively affect energy production, as the system loses great energy on heating the steam. Excessive steam in the gas generator may also reduce the reaction temperature, thus impairing the gas quality [87].

The research findings [71] indicate that excess air generally contributes to lower char and tar yield, lower heat of combustion, and lower CO level, though higher CO_2 concentrations. The gas quality becomes less appealing as the ratio of components (air/fuel) is increased: there are more oxidation reactions that lead to growing CO_2 concentrations and reduce combustible gas production. With the excess air too high, the concentrations of H_2 and CO may decrease. A higher excess air factor leads to exothermic oxidation reactions producing more heat during gasification. This may somewhat improve the product quality (tar destruction) [71].

Wongsiriamnuay et al. [88] studied the effect of a gasifying agent on the composition of biomass-derived syngas. The experiments conducted in a fluidized bed reactor indicate that the total volume of syngas obtained in a steam-air medium in the furnace increases, as do the concentrations of CO and H_2 .

Another possible gasifying medium is flue gas. Elshokary et al. [89], for instance, compared the compositions of two syngases obtained from biomass gasification in an air medium with CO_2 excess. The content of hydrogen and sulfur oxide in syngas obtained using flue gas was 8% and 4% higher, respectively.

Zhang et al. [90] investigated the effect of a pyrolyzing medium in a fluidized bed reactor on the characteristics of thermal decomposition of biomass. N_2 , CO_2 , CO, CH_4 , and H_2 were used as pyrolyzing media. The temperature of the boiling layer in pyrolysis was 550 °C. It was experimentally established that a gas atmosphere reduced the proportion of the respective gas in the resulting pyrolysis product [90]. For example, in the thermal decomposition of biomass in a CO medium, the resulting syngas has the highest CO_2 and the lowest CO content, as compared with the gases in the other media. CH_4 in pyrolysis gas was highest when the thermal decomposition of biomass was implemented in a CO_2 medium, whereas the highest yield of H_2 corresponded to the pyrolysis in CH_4 .

Similar results were obtained by Habibollahzade et al. [91]. It was established that gasification in a CO_2 medium yielded the lowest proportion of carbon dioxide in syngas. The reason for that is that a gasifier consumes more CO_2 than the thermal decomposition of biomass produces.

In that research, different pyrolyzing media under identical heating conditions (500 °C) were also compared: atmospheric air, a steam-air mixture, and flue gases. The comparison results are presented in Figure 5. It was established that in a steam medium, the yields of H_2 and CH_4 increased by 27 and 66%, respectively, as compared with pyrolysis in the air. However, the CO concentrations fell by 40%. The process developing in a flue gas medium was also characterized by an increase in hydrogen, methane, and carbon monoxide concentrations by 17%, 42%, and 10%, respectively, as compared with the air atmosphere.

4.6. Effect of Catalysts

The quality of pyrolysis and gasification products, in particular bio-oil and oil, can be improved by using different additives (catalysts). These make it possible to reduce moisture content, remove oxygen (deoxygenation), and crack heavy aromatic compounds to produce smaller structures [13].

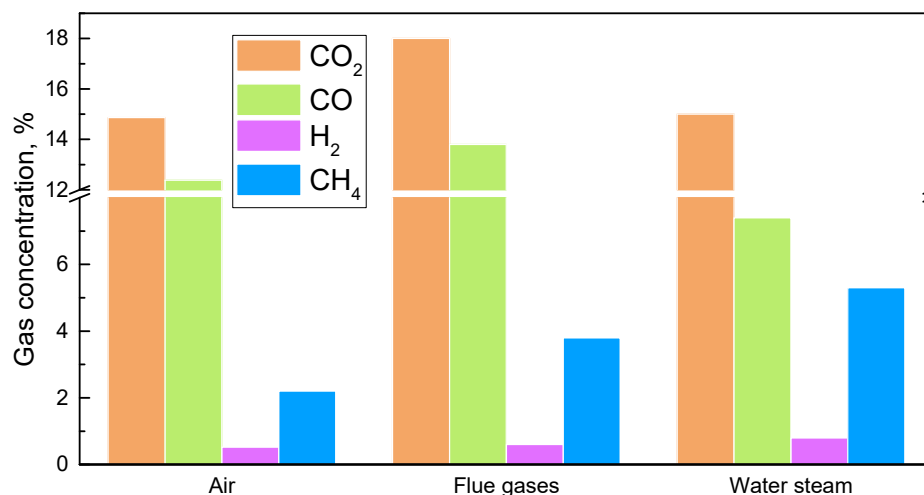


Figure 5. Gas component concentrations in the pyrolysis of biomass (sawdust 25%, straw 50%, leaves 25%) in different atmospheres at a pyrolysis temperature of 500 °C.

Zeolites with different porous structures are often used for the catalytic pyrolysis of biomass and to improve bio-oil quality. HZSM-5 zeolites are common catalysts of catalytic cracking. According to [92], this type of zeolite is characterized by limited deactivation of the coke residue and high thermal stability. Samolada et al. [93] used HZSM-5 zeolites as biomass pyrolysis catalysts to discover that they reduced the concentrations of liquid products and increased the amount of produced gas. Applying catalysts caused the cracking of tars. This reduced their molecular mass and increased the gas proportion.

Lin et al. [94] used CaO as a catalyst of white pine biomass pyrolysis. It was experimentally established that the content of oxygen in bio-oil, as well as the content of formic and acetic acids, were lower than those in an identical experiment without a catalyst.

Florentino-Madiedo et al. [95] studied the effect of four additives (paraffin, molasses, coal-tar, and coal-tar sludge) on the characteristics of bituminous coal and pine sawdust pyrolysis. In this study, 40 g fuel briquettes were fed into the combustion chamber, pre-heated to 1000 °C, and filled with N₂ with a flow rate of 100 mL/min. The analysis of the gas obtained as a result of pyrolysis showed that the pellets containing paraffin featured the lowest CO and CO₂ concentrations, yet the highest CH₄ amount. Maximum CO₂ yield was typical of the fuel with molasse, although the latter is carbon-neutral. The level of CH₄ in the pyrolysis gas of the pellets with molasse is comparable with the values obtained for the fuel with paraffin.

The effect of adding copper and nickel on biomass pyrolysis in a solar reactor was investigated by Zeng et al. [96]. The pyrolysis temperature was varied in the range of 600–1600 °C, argon was fed into the combustion chamber with a flow rate of 9 L/min. The experiments with temperature variations showed that at a higher temperature, the release of gaseous pyrolysis products increased, whereas the proportion of solid and liquid components decreased. A threshold temperature at which copper and nickel particles started interacting with biomass was 1000 °C [96]. Thus, at 1200 °C, the gas yield from the decomposition of the fuel with copper and nickel additives was 14.76% and 34.37% higher, respectively, than that from pure biomass. Zeng et al. state [96] that adding nickel increases the release of H₂ and CO by 22% and 23%, respectively, as compared with pure biomass.

The share of CO₂ in the fuel with nickel is lower than that in biomass without additives within the whole range of temperatures under study.

The characteristics of straw pyrolysis with different catalysts were explored in [79]. Nickel and iron were used as additives. Pyrolysis experiments were conducted at 500–900 °C using a microwave reactor and a TG-MS analyzer. The lowest nitrogen oxide emissions were recorded from the pyrolysis of straw with nickel. This is attributed to the ability of Ni to actively participate in the decomposition of NH₃ into H₂ and N₂. Moreover, adding Ni to biomass increases the amount of the pyrolysis gas by 143% [79].

One of the major challenges of biomass gasification is the formation of tars and methane, as well as catalyst deactivation. Tars can disable the process equipment. They are a complex mixture of condensed hydrogen compounds, consisting of one to five aromatic ring compounds, alongside other acid-containing hydrocarbons and polycyclic aromatic hydrocarbons (PAH). Therefore, the main purpose of catalysts used for biomass gasification is efficient tar conversion. According to the data [97], the following criteria are applied when choosing catalysts for gasification: (i) high tar removal efficiency; (ii) deactivation resistance; (iii) high strength; and (iv) low cost.

Dolomites, aluminum oxide, olivines, and alkali metal salts are used as catalysts for biomass gasification [13]. Dolomites are cheap natural minerals consisting of a mixture of magnesium and calcium carbonates that decompose to oxides at high temperatures. These minerals can also contain aluminum and iron oxides, which increase the catalytic activity of the material [97].

Lv et al. [84] used calcined dolomite as a catalyst. The catalyst to biomass ratios were 0:1, 1:1, and 1.5:1. An increase in temperature and the catalyst to biomass ratio led to rising H₂ and CO yields, though falling CH₄ and CO₂ concentrations. The heat of combustion, efficiency of carbon conversion, and the gas yield increased due to higher H₂ and CO concentrations. The catalyst also enhanced the reaction of decomposition of tar, thus reducing its yield. The absorption of CO₂ by calcium oxide was greatly dependent on the partial pressure of CO₂ in the flow at a given gasification temperature. When the equilibrium temperature, corresponding to the partial pressure of CO₂, was higher than the gasification temperature, CO₂ was absorbed, and the sorbent transformed into CaCO₃. However, if the equilibrium temperature was lower than the gasification temperature, CaCO₃ was desorbed to produce the initial CaO. Calcium oxide acts both as a sorbent and a catalyst, since tars and hydrocarbons decompose in the presence of CaO, producing additional hydrogen. The catalyst also increased the gas yield due to secondary cracking of tar in vapors and in hydrocarbons, such as CH₄ and C_nH_m.

The research by Matsuoka et al. [98] revealed that catalysts based on aluminum and iron oxides reduced the amount of tars produced from the gasification of woodchips at 500–700 °C. Catalysts promoted the steam reforming of tars with the production of syngas. Adding iron facilitated hydrogen formation. This was related to the interaction of steam with reduced iron.

Nickel catalysts are often considered for biomass and bio-oil gasification due to their fairly low cost and high activity. Ahmad et al. [71] used nickel catalysts to increase hydrogen concentrations and improve tar decomposition. Glycerol was gasified in a reactor with a motionless layer in the presence of a catalyst (Ni/Al₂O₃). It was established that increasing the amount of catalyst from 0 to 0.8% led to a steady growth of H₂ in gas. Zhang et al. [99] also explored the catalytic destruction of tar. They proved the effectiveness (more than 99%) of three catalysts based on nickel for the elimination of heavy tars. Hydrogen concentrations rose by 6–11%. Another issue under discussion [100,101] is the ability of nickel-based catalysts to reverse the ammonia reaction, thus reducing the emission of NO_x in biomass gasification [100,101].

The results of the literature review are summed up in Table 8.

Table 8. Review of data on biomass pyrolysis and gasification.

Type of Biomass	Particle Size	Biomass Structure	Catalyst	Pyrolysis/ Gasification Air	Gas Concentration	Temperature	Ref.
Corn straw, biomass	125–250 µm	Level layer	Without catalysts	N ₂	SO ₂ : 1.25–1.75 mg/g; CH ₄ : 2–44 mg/g; CO: 12–85 mg/g	300–900 °C	[80]
Biomass	-	Level layer	-	O ₂ (entrained flow)	H ₂ : 15–20%; CO: 40–60%; CO ₂ : 10–15%; CH ₄ : 0–1%; N ₂ : 0–1%	1000 °C	[102]
	-	Level layer	-	O ₂ (fluidized bed)	H ₂ : 20–30%; CO: 20–30%; CO ₂ : 25–40%; CH ₄ : 5–10%; N ₂ : 0–1%		
	-	Level layer	-	Steam	H ₂ : 30–45%; CO: 20–25%; CO ₂ : 20–25%; CH ₄ : 6–12%; N ₂ : 0–1%		
Herb residue	20–40 µm	Level layer	Ni, Fe	Microwave pyrolysis in argon	H ₂ : 30–37%; CO: 45–55%; CO ₂ : 10–15%; CH ₄ : 5–8%	500–800 °C	[79]
				TG in argon	H ₂ : 15–27%; CO: 30–60%; CO ₂ : 8–25%; CH ₄ : 13–18%		
Willow wood	500–1000 µm	Pressurized level layer (pellets)	Cu Ni	Argon	H ₂ : 0.5–12 mol/kg; CO: 1.7–13 mol/kg; CO ₂ : 0.45–1.2 mol/kg; CH ₄ : 0.2–1.75 mol/kg	600–1600 °C	[96]
Bamboo	100–250 µm	Level layer	Dolomite	Air	H ₂ : 6.6–8.16%; CO: 23.5–30.6%; CO ₂ : 59–63%; CH ₄ : 4–5%	400–500 °C	[88]
Agricultural wastes	210–250 µm	Level layer	Without catalysts	Air	H ₂ : 10–15%; CO: 20–28%; CO ₂ : 40–50%; CH ₄ : 8–10%	700 °C	[103]
Corn stover	pellets of 10–15 mm long and 6 mm in diameter	Pressurized level layer (pellets)	Without catalysts	Water steam	H ₂ : 23–26%; CO: 28–29%; CO ₂ : 26–30%; CH ₄ : 10–11%; C ₂ H ₄ : 7–8%; C ₂ H ₆ : 0.7–1.4%	700–800 °C	[67]
Rice husk					H ₂ : 22–28%; CO: 36–37%; CO ₂ : 18–23%; CH ₄ : 11–12%; C ₂ H ₄ : 4–5%; C ₂ H ₆ : 0.5–1%		
Pine					H ₂ : 25–31%; CO: 35–36%; CO ₂ : 16–22%; CH ₄ : 12–13%; C ₂ H ₄ : 3–4%; C ₂ H ₆ : 0.6–1%		
Wood pellet	5–20 mm size	Pressurized level layer (pellets)	Without catalysts	Air	H ₂ : 10–12%; CO: 9–13%; CO ₂ : 4–5%; CH ₄ : 1–2%	900 °C	[89]
	20–50 mm	Pressurized level layer (pellets)		CO ₂	H ₂ : 16–19%; CO: 14–19%; CO ₂ : 8–10%; CH ₄ : 2–4%		
Corn cob	1000–2000 µm	Level layer	Without catalysts	N ₂	H ₂ : 0%; CO: 6.1%; CO ₂ : 8.6%; CH ₄ : 0.7%	550 °C	[90]
				CO ₂	H ₂ : 0.3%; CO: 6.1%; CO ₂ : 7.7%; CH ₄ : 0.8%		
				CO	H ₂ : 0%; CO: 5.8%; CO ₂ : 14.3%; CH ₄ : 0.9%		
				CH ₄	H ₂ : 0.7%; CO: 4%; CO ₂ : 6%; CH ₄ : 0.3%		
				H ₂	H ₂ : 0%; CO: 4.2%; CO ₂ : 8.5%; CH ₄ : 0.5%		
Biomass	-	-	-	Air	H ₂ : 19.20%; CO: 18.30%; CO ₂ : 11.09%; CH ₄ : 0.89%; N ₂ : 39.75%; H ₂ O: 10.77%	800 °C	[91]
	-	-	-	O ₂	H ₂ : 33.31%; CO: 32.63%; CO ₂ : 15.76%; CH ₄ : 2.68%; N ₂ : 0.74%; H ₂ O: 14.87%		
	-	-	-	CO ₂	H ₂ : 23.51%; CO: 43.79%; CO ₂ : 21.83%; CH ₄ : 0.03%; N ₂ : 0%; H ₂ O: 10.84%		
	-	-	-	Steam	H ₂ : 39.13%; CO: 18.45%; CO ₂ : 13.08%; CH ₄ : 3.70%; N ₂ : 0%; H ₂ O: 25.65%		
Pine sawdust	0.30–0.45 mm	Level layer	Limestone	Steam	H ₂ : 35%; CO: 36%; CO ₂ : 17%; CH ₄ : 6%; C ₂ H ₄ : 4%	800 °C	[104]
			Olivine		H ₂ : 35%; CO: 34%; CO ₂ : 22%; CH ₄ : 4%; C ₂ H ₄ : 2%		
			Dolomite		H ₂ : 42%; CO: 30%; CO ₂ : 16%; CH ₄ : 10%; C ₂ H ₄ : 1%		
Empty fruit bunch	300–1000 µm	Level layer	Without catalysts	Air	H ₂ : 10.27–38.02%; CO: 21.87–36.36%; CO ₂ : 10–65%; CH ₄ : 5.84–14.72%	700–1000 °C	[70]
Pine sawdust	75–1200 µm	Level layer	Dolomite	Steam	H ₂ : 40–51.2%; CO: 15–22.4%; CO ₂ : 12–40%; CH ₄ : 2–5%	900 °C	[69]
Coconut shell	1–11 mm	Level layer	Without catalysts	Air	H ₂ : 8.2–14.6%; CO: 13.0–17.4%; CO ₂ : 14.7–16.7%; CH ₄ : 2.82–4.23%	700–900 °C	[72]

5. Mathematical Models of Pyrolysis and Gasification

The review of experimental data reveals that, in thermochemical biomass conversion, it is necessary to study the quantitative correlation between the end products of pyrolysis/gasification and biomass composition, as well as performance parameters. A

theoretical description of thermochemical biomass conversion is very complex and difficult. Modeling and optimization of thermochemical processes of using biomass as feedstock is a relevant problem for science and actual practice [105,106]. Obtaining a great mass of thermochemical data (standard enthalpy of formation, standard entropy, heat capacity, and exergy of biomass) is one of the most important and complex tasks when modeling biomass pyrolysis and gasification.

We can single out several markedly different models of biomass pyrolysis and gasification: thermodynamic equilibrium, kinetic, and artificial neural networks [105,107]. Each of these models features some pros and cons. Equilibrium models are important to predict the highest gasification or thermal efficiency which can be achieved for certain feedstock [108]. However, equilibrium model development often implies that the system is in a steady state [106]. Therefore, a kinetic model should be developed to evaluate the composition of gaseous pyrolysis and gasification products, as well as the effect of operational characteristics in any space and time point of the system (thermal mode of the reactor) [109]. Such models factor in the kinetic mechanisms and characteristics of the main reactions [105,110]. Kinetic models make it possible to evaluate the resulting gas composition under different operational conditions, which is important when designing pyrolysis and gasification facilities. The disadvantages of kinetic models include their high sensitivity to parameters determined empirically, which limits their flexibility and applicability to different process units [106].

Artificial intelligence algorithms are also employed in pyrolysis and gasification modeling. Neural network models improve the accuracy of predicting the composition of gas produced from pyrolysis and gasification. However, these algorithms rely on a great mass of experimental data and are compute intensive. That is why there are not many studies on developing neural network models, and their application to practical engineering tasks remains limited [106,107].

Thus, the development of universal predictive mathematical models of biomass pyrolysis and gasification requires in-depth experimental research into these processes.

6. Conclusions

Biomass is the most widespread and available renewable energy source. Biomass-derived fuel is of great potential. Most countries can involve this feedstock in the energy sector by using different products and waste from wood processing and agriculture, such as sawdust, woodchips, forest fuels, straw, husk, stalks and leaves, palm kernel waste, press cakes, and others. Pyrolysis and gasification are promising technologies of biomass processing. This research reviews numerous aspects affecting the end products of biomass pyrolysis and gasification, such as biomass composition, particle size of feedstock, surface structure of samples, temperature, pyrolysis, and gasification atmosphere, as well as use of catalysts. The following key findings in the field of biomass pyrolysis and gasification have been highlighted based on the analysis.

The yield of the main pyrolysis and gasification products depends on the content of hemicellulose, cellulose, and lignin. It has been established that the higher the content of cellulose in biomass, the higher the yield of the liquid pyrolysis product. The amount of pyrolysis gas depends largely on the proportion of hemicellulose, whereas the share of char in the total amount of pyrolysis products is conditioned by the content of lignin. Reducing the size of a biomass particle increases the gas release and the concentrations of hydrogen in it. This provides a larger surface area of reaction of the particle with a heated medium, thus accelerating heating and decomposition. Changing the surface structure of a biomass sample (making holes and channels) improves the efficiency of carbon conversion and facilitates gas release. However, such factors as particle size and surface structure have a less significant effect than the other parameters (temperature, catalyst addition, steam/biomass ratio). Hydrogen yield rises with a temperature increase due to enhanced gasification and tar cracking reactions. It has been shown that a steam medium is more effective for maximizing hydrogen yield than the air. Adding catalysts enhances the release

of hydrogen and improves the gas quality by reducing the amount of water, removing oxygen and cracking heavy aromatic structures.

The effect of different parameters on the properties and yield of gaseous pyrolysis and gasification products was discussed to optimize future research and process in general. This paper presents positive aspects of biomass pyrolysis and gasification as a high-potential economically viable technology. It has been shown that the processes are not confined to particular feedstock and end product. There are a lot of opportunities for involving different types of biomass waste to obtain various end products.

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