

Review

Development of Heterogeneous Catalysts for Thermo-Chemical Conversion of Lignocellulosic Biomass

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Abstract: Lignocellulosic biomass is one of the most attractive renewable resources that can be used for the production of biofuels and valuable chemicals. However, problems associated with the low efficiency of its conversion and poor selectivity to desired products remain. Therefore, in recent years researchers have focused on the design of highly active and stable catalysts, enabling an increase in the effectiveness of lignocellulosic biomass processing. This work is devoted to the presentation of the latest trends in the studies of the heterogeneous catalysts used in thermo-chemical conversion of such feedstock. The systems applied for the production of both bio-oil and hydrogen-rich gas are discussed. Zeolites, mesoporous materials, metal oxides, supported metal catalysts, and modifications of their structure are described. Moreover, the impact of the physicochemical properties of the presented catalyst on their catalytic performance in the mentioned processes is demonstrated.

Keywords: heterogeneous catalysts; lignocellulosic biomass; high temperature conversion; bio-oil; hydrogen-rich gas; pyrolysis; nickel

1. Introduction

Thermo-chemical conversion of lignocellulosic biomass is one of the most promising methods for the production of various chemicals and bio-oil to replace fuels obtained from the processing of fossil resources [1]. The formed products can be divided into gaseous and liquid fractions. The gaseous phase contains mainly hydrogen, carbon oxide, carbon dioxide, and methane. The liquid fraction is consisted of a large number of compounds—oxygenates and hydrocarbons (carboxylic acids, aldehydes, ketones, alcohols, esters, aliphatics, paraffins, aromatics, and multifunctional compounds). After upgrading, bio-oil can be used as a transportation fuel. On the other hand, the gas phase is considered a source of hydrogen or syngas, which can be further converted into synthetic hydrocarbon fuels, methanol, lubricants, or lower olefins, being intermediates for the production of plastics, cosmetics, or drugs.

The advantages of an application of lignocellulosic feedstock are generally associated with the global availability of biomass, its relatively low price, and limited impact on the environment. However, the thermal decomposition of lignocelluloses is a complex process consisting of a large number of consecutive reactions. In spite of the fact that the composition of the formed products can be controlled by several factors (such as the final temperature of the process, residence time, or heating rate of biomass) to some extent, it is very difficult to obtain the desired chemical compounds at a high yield [2]. Due to that, the obtained bio-oil or gaseous mixture cannot directly replace fuels produced using conventional methods.

However, the literature has demonstrated that the selectivity of the reactions occurring during thermal conversion of lignocellulosic biomass can be considerably enhanced by the application of

heterogeneous catalysts [3–5]. Therefore, in recent years researchers have focused on the development of stable and highly efficient systems for thermo-chemical conversion of lignocellulosic biomass [6]. The studies were mainly devoted to the determination of optimal composition, surface properties, preparation method, or pretreatment conditions of the investigated catalysts. Taking that into account, we decided to discuss the latest achievements in this field.

2. The Role of Catalysts in Bio-Oil Production

Bio-oil is a mixture of a wide range of organic compounds and water formed during the high-temperature treatment of lignocellulosic biomass. As described above, this process, called pyrolysis, proceeds in several steps (Figure 1). In the first of them, thermal decomposition of biomass components (usually in the range of 200–300 °C) is observed. This results in the formation of primary products—mainly lignocelluloses-derived oxygenates (due to depolymerization, dehydration, or elimination reactions). In the next part of the process (usually performed at temperatures above 400–500 °C), primary products are submitted to further cracking, reforming, dehydration, decarboxylation, decarbonylation, or oligomerization [7]. These reactions lead to the production of secondary products containing hydrocarbons and their derivatives. It is observed that the thermal decomposition of lignocellulosic material allows for removal of only a portion of the oxygen atoms from the feedstock. Therefore, an application of the catalysts enhancing the conversion of oxygenates into more valuable products is essential [8]. A decrease in the amount of oxygenates is usually associated with a growth in the yield of aromatics and permanent gases in the final product [9].

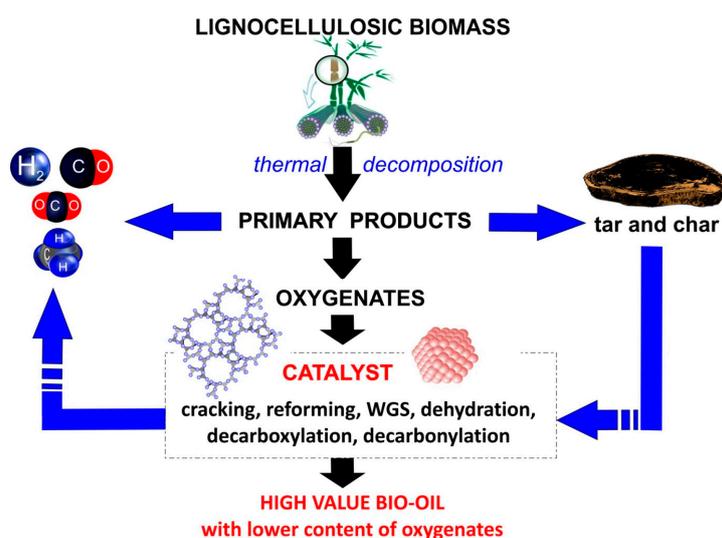


Figure 1. Role of the catalyst in high-temperature treatment of lignocellulosic biomass.

The literature data show that nowadays one of the most popular processes of bio-oil production from lignocellulosic biomass is catalytic upgrading of pyrolysis vapors, which consists of the initial decomposition of the raw material and further upgrading of the formed intermediates with the use of a solid catalyst [10]. However, several review papers demonstrated that bio-oil can also be produced by hydrolysis or co-pyrolysis with plastics or other kinds of feedstock like municipal, food, or garden waste [11–13].

The most important parameters impacting the catalyst performance in the discussed process are the acidity, surface area, and porosity of the catalyst. In the case of metal/support systems, the type and crystalline structure of the support, the size of metal crystallites and their location, interactions between an active phase, and the support and presence of dopants may be also crucial. An efficient catalyst should provide not only high conversion of the feedstock and selectivity of occurred reactions, but also should minimize the amount of arising tar and char, thereby protecting its own surface against

deactivation by the formation of a carbon deposit (which is one of the main drawbacks of catalytic systems used in thermo-chemical treatment of lignocellulosic biomass).

The investigations aimed at the enhancement of the quality of the produced bio-oil are strictly connected with the development of new catalytic systems based on zeolites, mesoporous silicas, metal oxides, supported metal catalysts, and modification of the properties of mentioned materials with the use of alkali or transition metals (Figure 2). In the next part of this review paper, recent trends in the studies devoted to the application of different groups of heterogeneous catalysts to the production of higher-value bio-oil will be presented.

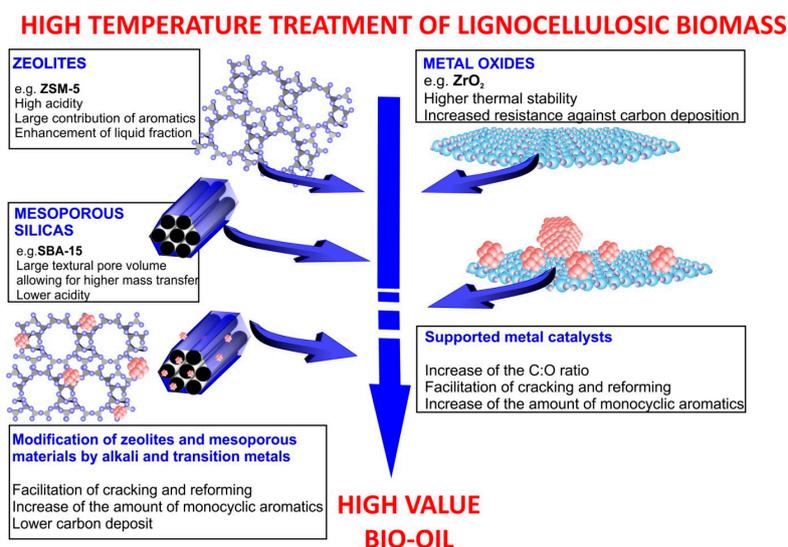


Figure 2. Types of materials used as catalysts for the production of high-value bio-oil from lignocellulosic feedstock.

2.1. Application of Zeolites and Mesoporous Materials

The literature data demonstrate that one of the most promising catalysts that can be used for the production of bio-oil from lignocellulosic feedstock is ZSM-5 (Zeolite Socony Mobil-5) (Table 1) [14]. The presence of such a material enhances the formation of a liquid fraction containing a mixture of organic compounds with reduced oxygen content and a larger contribution of aromatics. It was observed that the selectivity of the described process and the composition of the obtained bio-oil (including the amount of aromatic compounds) can be controlled by the modification of physicochemical properties of the used zeolites, such as the structure of the material and its crystallinity, porosity, acidity, and elemental composition.

Zheng et al. [15] showed that during the production of bio-oil by fast pyrolysis of pine, corncob, straw, reference cellulose, hemicelluloses, and lignin samples, the highest yield of aromatics was obtained in the presence of the ZSM-5 catalyst with the largest volume of micropores, highest amount of weaker acid sites, and highest Brönsted to Lewis acid sites ratio. An application of the mentioned material led to the formation of a mixture consisting of 38.4% and 25.4% of aromatic compounds in the case of pine and cellulose, respectively. The authors of the described work suggested that the production of aromatics was facilitated by weaker Brönsted acid sites, while medium and strong acid sites are involved in the formation of coke. Moreover, it was indicated that a decrease in the yield of aromatics observed for ZSM-5 nanocrystals (with a size of about 50 nm) may be connected with hindering the contact of reactants with a sufficient amount of acid sites due to the insufficient length of zeolite channels.

In spite of the ability to enhance the selectivity of the formation of aromatics, ZSM-5 is not capable of efficient conversion of heavier oxygenates (intermediates of biomass pyrolysis process) due to their

larger size in comparison to the size of the pores of the used catalyst. The larger molecules cannot penetrate the internal structure of ZSM-5, which leads to a reduction in the reaction yield. Taking that into account, Li et al. [16] decided to modify the ZSM-5 structure by desilication with a sodium hydroxide solution. The activity tests performed in the fast pyrolysis of beech wood revealed that an application of desilicated catalyst resulted in the formation of a larger amount of aromatic compounds (30.2%) in comparison to unmodified material (26.2%). Moreover, a slight decrease in the production of carbon deposit was observed for desilicated ZSM-5 (39.9% instead of 41.2%). On the one hand, the acidity measurements confirmed a decrease in Brønsted acid sites' density during desilication process. However, those sites that remained were more accessible for the reactants due to the formation of mesopores and this effect was predominant. Due to that, the cracking of larger oxygenates into smaller molecules was more effective. It could also facilitate the removal of accumulating coke to some degree.

The impact of the physicochemical properties of the ZSM-5 catalyst on the yield of the aromatics produced in fast pyrolysis of biomass was also proved by Hoff et al. [17]. It was shown that the amount of aromatic compounds formed in the presence of the catalyst depended mostly on the crystallinity and accessibility of framework aluminum sites.

On the other hand, Engtrakul et al. [18] demonstrated the influence of ZSM-5 acidity on the selectivity of aromatic products of upgrading of pine pyrolysis vapors. The obtained results indicated that the increase in the acidity of zeolite results in a reduction of alkylated aromatics and growth in the yield of unsubstituted and polycyclic compounds. This phenomenon is related to changes in the rate of cyclization and alkylation reactions. It was noted that cyclization is favored by a higher density of acid sites.

The studies associated with the application of ZSM-5 are also focused on the determination of its catalytic performance in the decomposition of different feedstock or co-pyrolysis processes [12,19–23]. Fisher et al. [19] investigated the effect of the use of ZSM-5 catalyst on the course of fast pyrolysis of spent coffee grounds. The experiments were performed in both a fixed bed reactor and a pyroprobe. The obtained data revealed that irrespective of the type of reactor, the presence of zeolite resulted in the formation of a considerably larger amount of aromatic hydrocarbons in comparison to a non-catalyzed process. It is worth noting that in the case of the experiment conducted in a pyroprobe the contribution of the aromatic fraction was the highest among the liquid products. Moreover, the formation of a larger amount of aromatics was accompanied by a slight increase in the carbon oxide yield, probably due to the enhancement of the decarbonylation reaction. Other studies devoted to the co-pyrolysis of lignocellulosic biomass with food waste (consisting of rice, vegetables, fruits, meat, or oil) or plastics (low-density polyethylene) [20,21] confirmed that this is a promising method for the production of bio-oil.

One of the main drawbacks of the use of ZSM-5 in fast pyrolysis of lignocellulosic biomass is the possibility of its deactivation during the process. The main mechanism of deactivation is associated with carbon deposit formation and blockage of the pores of the catalyst. In spite of the fact that the deactivation by coking is reversible, the regeneration of the catalyst at relatively high temperatures (usually 650 °C–700 °C) can be dangerous to the stability of its structure (especially due to the possibility of local overheating, related to the exothermic nature of the process of carbon removal in the oxygen atmosphere). A further reason for the decrease in the efficiency of ZSM-5 is hydrothermal deactivation, consisting of a decrease in density of acid sites due to removal of aluminum species from the catalyst associated with the presence of water vapor (formed during high-temperature decomposition of lignocellulose) in the elevated temperature. The third phenomenon connected with a drop in the catalytic activity of ZSM-5 concerned an adsorption of various inorganic contaminants on the surface of zeolite (including metals originating from the lignocellulosic feedstock). Stefanidis et al. [24] investigated the changes in the performance of ZSM-5 submitted to hydrothermal deactivation and contamination by selected metals. The obtained results revealed that potassium accumulated on the catalyst very selectively and was deposited evenly in the bulk, while calcium and magnesium were observed only on the outer surface of the catalyst particles. It was supposed that

the migration of metals from the biomass might lead to a deterioration of the activity of ZSM-5 by introduction of basic sites into its structure.

In order to enhance the activity of HZSM-5 zeolite in microwave-assisted catalytic fast pyrolysis of corn stover to bio-oil, and taking into account the negative impact of coke formation on the catalytic performance of the material, Zhang et al. [25] decided to modify its surface by chemical vapor deposition with tetraethyl orthosilicate (TEOS). It was demonstrated that the formation of a layer of SiO₂ on the surface of HZSM-5 led to a decrease in the density of external acid sites and a reduction of the coking rate. Due to that, an increase in the aromatic compounds content was observed in comparison to the reaction conducted with the use of unmodified material. The maximal relative content of aromatics (about 38%–39%) was noted for the sample containing 3.7% of SiO₂. Further growth in the concentration of silicon dioxide (up to 5.9% of SiO₂) resulted in a drop in the aromatics production, but their content was still a bit higher (36%–37%) than in the case of parent HZSM-5 (about 33%). On the other hand, the modification of HZSM-5 also led to a decrease in the amount of liquid fraction.

A comparison of the catalytic performance of HZSM-5 with other catalytic materials (such as sulfated zirconia, aluminosilicate mesoporous molecular sieves (Al-MSU-S exhibiting a foam-like mesopore structure and Al-MSU-S exhibiting wormhole mesopores) and a bauxite waste) in fast pyrolysis of poplar revealed that an application of HZSM-5 allowed for the production of a high amount of condensables containing the largest content of aromatics [26]. The high selectivity of HZSM-5 towards aromatics was associated with the presence of desired pore window size, internal space of pores, and steric hindrance resulting in the limitation of carbon deposition. On the other hand, the properties of mesoporous catalysts studied in this work, such as mesoporosity, high pore volume, and acidity, facilitated the cracking of intermediates of thermal decomposition of lignocellulosic feedstock, which led to the production of a higher amount of permanent gases and coke. The structure of Al-MSU-S catalysts contributed to the elimination of diffusion resistance and increased deoxygenation activity. However, the lack of micropores and the presence of larger pores resulted in a decrease in the selectivity to aromatic compounds. Sulfated zirconia was also not selective to aromatics and led to the formation of a larger amount of carbon deposit. However, the authors of described work [26] suggested that an introduction of sulfated zirconia on the surface of MCM-41 mesoporous material may contribute to the improvement of its deoxygenation activity and resistance to coking. The second part of the study [26] was devoted to the investigation of the influence of the Si:Al ratio in HZSM-5 material on the yield of aromatic products. It was demonstrated that samples with a lower silicon:aluminum ratio possessed a higher density of Brønsted acid sites and produced more aromatics. However, it was also noted that the use of the material with a Si:Al ratio of 23 led to the formation of a greater amount of C6-C7 compounds, while the presence HZSM-5 with Si:Al ratio 30 facilitated the production of C8-C9 molecules.

The catalytic performance of HZSM-5 (in flash pyrolysis of woody biomass (LIGNOCEL) conducted in a continuous bench scale reactor) was also evaluated by Imran et al. [27]. In this case an activity of the mentioned zeolite was compared with the efficiency of the H-Y sample. The obtained results indicated that an application of HZSM-5 allowed for a more efficient decrease in the contribution of acid fraction and production of a considerably higher amount of phenolic compounds in comparison to the H-Y zeolite. However, the authors noted that in spite of the high contribution of desirable compounds in the mixture of products, the use of both catalysts may lead to a decrease in the yield of bio-oil due to the production of permanent gases and coke. It can be controlled by the modification of the properties of the used catalysts, associated with the choice of optimal density and strength of acid sites in the zeolite structure.

Table 1. Application of zeolites and mesoporous materials to high-temperature conversion of lignocellulosic biomass.

No.	Catalyst	Feedstock	Products and Remarks Regarding Influence of Catalyst	Conditions of Pyrolysis Process	Reference
1	ZSM-5	Cellulose, hemicelluloses, lignin	Carbon yields of aromatics from cellulose, hemicelluloses and lignin were 28.8%, 19.4 and 7.4%, respectively.	Micro-furnace pyrolyzer equipped with an autoshot sampler at 400 °C–800 °C, analysis of products by GCMS (Gas Chromatograph coupled with Mass Spectrometer)	[7]
2	ZSM-5	Pine, corncob and straw cellulose, hemicellulose and lignin	Fast pyrolysis, the highest yield of aromatics (38.4% for cellulose and 25.4% for pine) was obtained in the presence of catalyst.	Py-GCMS, residence time and heating rate were fixed to 600 °C, 50 s and 20,000 °C/s, catalyst to feedstock weight ratio = 9	[15]
3	desilicated ZSM-5	Beech wood	Fast pyrolysis, desilicated ZSM-5 more active towards production of aromatics than unmodified material (26.2% and 30.2%, respectively) and slightly limits coke formation (from 41.2% to 39.9%).	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 650 °C, 60 s and 20,000 °C/s, catalyst to feedstock weight ratio = 10	[16]
4	ZSM-5	Cellulose	32% of aromatics in the presence of ZSM-5 with optimized structure	Micro-pyrolyzer (equipped with an autoshot sampler) at 700 °C, catalyst to biomass weight ratio = 20, analysis of products by GCMS	[17]
5	ZSM-5	Spent coffee grounds	Considerable increase in the amount of aromatic hydrocarbons in comparison to non-catalyzed process	(a) Py-GCMS and (b) fixed bed reactor (a)—maximal temperature, residence time and heating rate were fixed to 490 °C–590 °C, 10 s and 2000 °C/s, catalyst to feedstock weight ratio = 1 (b)—temperature—490 °C–590 °C, residence time in thermal bed 1.5 s and 2.5 s in catalytic bed, catalyst to feedstock weight ratio = 1	[19]
6	ZSM-5	Corn stalk and food waste	Co-pyrolysis, relative content of aromatics about 30%	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 500 °C–700 °C, 20 s and 20,000 °C/s, catalyst to feedstock weight ratio = 1	[20]
7	HZSM-5	Citrus unshiu peel	Ex situ catalytic pyrolysis, yield of aromatics about 7%	Tandem micro-reactor consisting of two sequential furnaces coupled to GCMS, pyrolysis—500 °C, upgrading—400 °C–600 °C, catalyst to feedstock weight ratio = 1	[22]

Table 1. Cont.

No.	Catalyst	Feedstock	Products and Remarks Regarding Influence of Catalyst	Conditions of Pyrolysis Process	Reference
8	HZSM-5	Beech wood, cellulose, microalgae	The relative yield of total BTX (benzene, toluene, xylene) was the highest for beech wood among studied feedstocks	Tandem micro-reactor consisting of two sequential furnaces coupled to GCMS, temperature 400 °C–600 °C, catalyst to feedstock weight ratio = 5–20	[23]
9	ZSM-5	Beech wood	Investigations of the influence of various metals contamination on the efficiency of in situ catalytic pyrolysis of biomass	Bubbling fluidized bed pyrolysis reactor, temperature 500 °C, catalyst 150 g, biomass 100 g (fed to the reactor at a rate of 5 g/min)	[24]
10	HZSM-5	Corn stover	Microwave-assisted catalytic fast pyrolysis conducted with the presence of HZSM-5 (H form of Zeolite Socony Mobil-5) modified by chemical vapor deposition with TEOS (tetraethyl orthosilicate), relative content of aromatics 38%–39%	Microwave oven containing semi-continuous biomass feeder, temperature 500 °C, HZSM-5 was mixed with SiC particles (used as the microwave absorbent)	[25]
11	HZSM-5, sulfated zirconia, Al-MSU-S aluminosilicate and bauxite waste	Poplar	High selectivity of HZSM-5 towards aromatics, in the case of mesoporous catalysts their mesoporosity, high pore volume and acidity facilitated cracking of pyrolysis intermediates which led to the production of higher amount of permanent gases and coke	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 650 °C, 20 s and 1000 °C/s, catalyst to feedstock weight ratio = 5	[26]
12	HZSM-5, H-Y	Woody biomass (LIGNOCEL)	Flash pyrolysis, HZSM-5 allowed for the more efficient decrease in the contribution of acid fraction and production of considerably higher amount of phenolics in comparison to H-Y	Continuous bench scale unit, temperature 450 °C–550 °C, residence time 2–4 s, catalyst to feedstock weight ratio = 0.1–0.5	[27]
13	waste FCC catalyst and H-Y	Wild reed	H-Y zeolite allows for the formation of higher amount of aromatics and a decrease in the content of oxygenates in comparison to regenerated FCC catalyst	Batch-type reactor, temperature 500 °C, residence time 14–20 s, catalyst to feedstock weight ratio = 1–10	[28]
14	Al-MCM-41, Al-SBA-15 Al-MSU-J and HZSM-5	Lignin	Al-MCM-41 (Mobil Composition of Matter No. 41) possessing large pore volume and allowing for enhanced mass transfer enabled formation of similar amount of aromatics to that obtained in the case of H-ZSM-5 having noticeably higher acidity	650 °C at heating rate 20,000 °C/s, reaction time 20 s, catalyst to feedstock weight ratio = 4	[29]

On the other hand, Yoo et al. [28] compared the activity of waste FCC (fluidized catalytic cracking) catalyst in the pyrolysis of wild reed with the performance of the H-Y zeolite. The FCC catalyst was regenerated before use in the pyrolysis process by washing with acetone or calcination in air at 550 °C. The authors of this work [28] suggested that an activated waste FCC catalyst possessed comparable activity in the studied reaction to the H-Y sample, taking into account the production of furans, phenolics, and aromatics. However, a deeper analysis of the obtained results demonstrates that the presence of the H-Y zeolite allows for the formation of higher amount of aromatics and a decrease in the content of oxygenates in comparison to the activated FCC catalyst.

Taking into account the influence of both the acidity and the porosity of the catalyst on its activity in the fast pyrolysis process, Custodis et al. [29] focused on the studies of the catalytic performance of a series of mesoporous aluminosilicates (Al-MCM-41, Al-SBA(Santa Barbara Amorphous)-15, and Al-MSU-J) in the thermal decomposition of lignin. It is known that the presence of acidic sites facilitates the conversion of lignocellulosic feedstock due to cracking, dehydration, deoxygenation, aromatization, delakylation, and isomerization reactions. Owing to that, the formation of bio-oil can be observed. However, some portion of the intermediates of thermal treatment of lignin may be too large to penetrate the pores of the catalysts and cannot be decomposed into smaller molecules, which decreases the efficiency of the entire process. Therefore, the pore structure of the catalysts is also of high importance for the formation of desired products. As in the case with zeolites, the shape of the pores, pore size, grain size, and accessibility of the acid sites present in the structure of the mesoporous materials have a strong impact on the efficiency of the pyrolysis process. It was shown that an Al-MCM-41 material in the form of nanosized grains possessing large textural pore volume and allowing for enhanced mass transfer enabled the formation of a similar amount of aromatic hydrocarbons in the described process to that obtained in the case of the H-ZSM-5 zeolite having noticeably higher acidity (0.10 and 0.53 mmol NH₃/g, respectively—evaluated on the basis of temperature-programmed desorption of ammonia).

An analysis of the results of the studies presented above indicated that, besides the use of different mesoporous materials, an application of ZSM-5 zeolite allowed for the most efficient conversion of lignocellulosic feedstock into aromatics. The physicochemical properties of such a catalyst favor the formation of liquid products, which is important in the case of bio-oil production. However, it is worth noting that the high acidity of ZSM-5 can also contribute to catalyst deactivation by coking.

2.2. Modification of Zeolites and Mesoporous Materials by the Addition of Metals

The application of zeolites and mesoporous materials to the thermal decomposition of lignocellulosic biomass seems to be a promising solution, but researchers are also making efforts to further improve the quality of the produced bio-oil through the modification of the mentioned catalysts by the introduction of various kinds of dopants (Table 2).

The first group of studies has focused on the investigation of the influence of the addition of selected transition metals (iron, zirconium, and cobalt) to the HZSM-5 structure on the composition of the liquid mixture formed in the catalytic upgrading of biomass (pine sawdust) fast pyrolysis vapors [30]. The obtained results revealed that an introduction of metals into the zeolite structure (via a wet impregnation method using aqueous solutions of the corresponding nitrate salts) resulted in a decrease in the bio-oil yield and an increase in the amount of gaseous fraction and deposited carbon due to the promotion of cracking and reforming reactions. The formation of the highest amount of gas and coke was observed in the case of Co/HZSM-5 catalysts. In spite of the fact that the use of Zr/HZSM-5 and Fe/HZSM-5 allowed for production of higher yield of liquids, its content was lower than that noted for an unmodified HZSM-5 sample. However, Zr/HZSM-5 and Fe/HZSM-5 catalysts promoted the formation of aromatic hydrocarbons. The content of aromatics observed for these two materials was noticeably higher (43%–45%) in comparison to that obtained in the presence of Co/HZSM-5 and unmodified HZSM-5 (23% and 33%, respectively). The authors of this work indicated that Zr/HZSM-5 favors an intermolecular hydrogen-transfer reaction, leading to the formation of

benzene and its derivatives. On the other hand, Fe/HZSM-5 can promote the addition of benzene rings, resulting in the formation of a larger amount of naphthalene and its derivatives.

Similar investigations aimed at a comparison of the catalytic performance of Fe/HZSM-5 and an unmodified zeolite were performed by Mullen and Boateng [31]. In this case the Fe-modified catalyst was prepared by the ion exchange method and its activity was tested in the pyrolysis of cellulose, cellobiose, lignin, and switchgrass. It was shown that an addition of iron to the catalyst structure impacted the chemical pathways of the decomposition of the used feedstock. The Fe/HZSM-5 catalyst favored the formation of benzene and naphthalene and inhibited the production of p-xylene, ethylbenzene, and trimethylbenzene in comparison to unmodified HZSM-5. It suggested that the presence of Fe promoted the aromatization of primary products to naphthalenes rather than the alkylation of initially formed benzene. The authors also noted that this phenomenon was the opposite what was described by Cheng et al. [32] for a gallium-modified HZSM-5 material, where the increase in the efficiency of alkylation reaction was observed in the presence of metallic dopant.

On the other hand, Sun et al. [33] indicated that an application of Fe/ZSM-5 to the fast pyrolysis of wood sawdust conducted using Py-GC/MS increased the efficiency of the production of monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and decreased the amount of the formed polycyclic aromatic hydrocarbons (such as naphthalenes, phenanthrenes, or anthracenes) in comparison to the ZSM-5 material. They also suggested that the drop in the yield of the polymerization of monocyclic compounds and the decrease in the amount of polycyclic aromatics observed in the case of the Fe-ZSM-5 material suppressed the formation of coke, which is the main reason for catalyst deactivation.

The next group of studies focused on the evaluation of the catalytic performance of ZSM-5 materials containing nickel. Veses et al. [34] compared the activity of the zeolite modified by Ni and other metals (Mg, Cu, Ga, and Sn) in the upgrading of biomass-derived pyrolysis vapors. The obtained results confirmed that an application of Ni-ZSM-5 and Ga-ZSM-5 materials was most promising and led to the formation of the highest amount of aromatic hydrocarbons. Similar findings were reported by Yung et al. [35]. The performed experiments indicated that the modification of ZSM-5 by nickel resulted in an increase in the contribution of aromatics and enhanced the conversion of oxygenates in relation to the unmodified material. The observed difference was more distinct with increasing Ni content. The authors suggested that the upgrading effect was associated with the ability of nickel to promote deoxygenation, decarboxylation, and the transition-metal-assisted hydrogen transfer reaction.

Melligan et al. [36,37] applied Ni-modified ZSM-5 and mesoporous MCM-41 materials to the upgrading of biomass pyrolysis vapors. The upgrading process conducted in the Py-GC/MS unit was performed in the presence of hydrogen. It was demonstrated that the addition of H₂ enhanced the performance of the catalyst and led to a notable improvement in the quality of the produced bio-oil. However, it was also connected with a reduction in the yield of condensable products. The activity measurements demonstrated that, besides an increase in the amount of hydrocarbons, a growth in the yield of lighter phenols can also be observed in the presence of metallic catalysts. It was indicated that the presence of Ni could lead to the decomposition of heavier phenols and the formation of smaller molecules. Moreover, it was shown that Ni supported on ZSM-5 was more effective in the production of aromatics in comparison to the Ni/MCM-41 sample, probably due to the presence of a higher amount of Brønsted acid sites in the first case.

The literature data showed that heterogeneous catalysts are also used in co-pyrolysis processes where biomass is subjected to thermal decomposition with plastics. An example of such investigations was described by Yao et al. [38]. In this case, co-feeding of lignocellulosic biomass (pine wood) with a waste polymer—low-density polyethylene (LDPE)—was applied. In spite of the fact that the unmodified ZSM-5 material is not able to effectively convert alkanes to olefins (which is a limiting step of alkane aromatization), it was observed that, owing to the addition of P and Ni to the zeolite structure, an increase in the catalyst activity for the conversion of alkanes to olefins may be achieved. This is associated with the structure of the acid sites of the ZSM-5 (the modification of this material by P

and Ni leads to a decrease in the amount of Brønsted acid sites and an increase in the content of Lewis acid sites). The increased amount of olefins produced results in the formation of an enhanced fraction of valuable aromatics. Moreover, the modification of ZSM-5 by phosphorus and nickel increased the hydrothermal stability of the catalyst and its resistance to carbon deposit formation.

The upgrading of bio-oil originating from biomass pyrolysis is not only conducted in the presence of the modified ZSM-5 materials. Widayatno et al. [39] applied to this process a Cu-modified β -zeolite catalyst (containing up to 3% metal). The performed investigations revealed that the presence of copper also promoted the production of hydrocarbons; however, it was impossible to avoid coke formation during the upgrading process. The studies of the mechanism of the reactions occurring in the presence of copper indicated that Cu species can replace proton sites on the surface of the zeolite. In addition, a synergy effect between remaining proton sites and metal species is observed. The proton sites facilitate the dehydration or decarboxylation of oxygenates, while Cu promotes decarbonylation. That is why the presence of copper species increases the yield of formed carbon oxide. This phenomenon can also be observed for other catalytic systems containing transition metals.

The high selectivity to hydrocarbons during the investigation of the catalytic upgrading of bio-oil performed with the use of Cu/MCM-41 and Cu/KIT-6 (KIT: Korea Advanced Institute of Science and Technology) catalysts was also observed by Karnjanakom et al. [40]. It was found that catalysts prepared by the cyclodextrin-assisted co-impregnation method were more active than the materials synthesized via impregnation. In contrast to the previous work [39], a relatively high amount of Cu was incorporated into the structure of mesoporous materials (the highest efficiency of the hydrocarbons production was achieved for the samples containing 20% of Cu). In spite of a slightly lower acidity and surface area, the Cu/KIT-6 catalyst was more active in the formation of monocyclic aromatic compounds than the Cu/MCM-41 sample. It was probably associated with considerably larger pores in the case of the first material, decreasing the diffusion resistance for larger reaction intermediates.

Other studies concerning an application of modified zeolites and mesoporous materials to pyrolysis process also confirmed that the introduction of metals (such as V or Mo) into the catalyst structure increases the yield of valuable compounds in the obtained mixture [41–43]. On the other hand, the investigations performed by Mahadevan et al. [44] indicated that contamination of the catalyst surface by alkali or alkaline earth metals (especially Na, K, or Ca) present in biomass feedstock resulted in a reduction in the amount of aromatic hydrocarbons and olefins, with a simultaneous increase in the yield of permanent gases and char.

Table 2. Modification of zeolites and mesoporous materials used in high-temperature conversion of lignocellulosic biomass.

No.	Catalyst	Feedstock	Products and Remarks Regarding Influence of Catalyst	Conditions of Pyrolysis Process	Reference
1	HZSM-5 modified by Fe, Zr and Co	Pine sawdust	Zr/HZSM-5 and Fe/HZSM-5 catalysts promoted formation of aromatic hydrocarbons, the content of aromatics observed for these two materials was noticeably higher (43%–45%) in comparison to that obtained in the presence of Co/HZSM-5 and unmodified HZSM-5 (23% and 33%, respectively).	Two-stage fixed-bed pyrolysis system with continuous feeding, temperature 550 °C, catalyst to feedstock weight ratio = 0.5	[30]
2	HZSM-5 modified by Fe	Cellulose, cellobiose, lignin, and switchgrass	Fe/HZSM-5 catalyst favored formation of benzene and naphthalene and inhibited production of p-xylene, ethylbenzene and trimethylbenzene in comparison to unmodified zeolite.	Py-GCMS, maximal temperature and residence time were fixed to 500 °C, 30 s, catalyst to feedstock weight ratio = 5–10	[31]
3	Fe/ZSM-5	Wood sawdust	Fe/ZSM-5 increased efficiency of the production of monocyclic aromatic hydrocarbons and decreased the amount of the formed polycyclic aromatic hydrocarbons in comparison to ZSM-5.	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 600 °C, 25 s and 20,000 °C/s, catalyst to feedstock weight ratio = 10	[33]

Table 2. Cont.

No.	Catalyst	Feedstock	Products and Remarks Regarding Influence of Catalyst	Conditions of Pyrolysis Process	Reference
4	ZSM-5 modified by Ni, Mg, Cu < Ga and Sn	Woody biomass	Ni-ZSM-5 and Ga-ZSM-5 materials led to the formation of the highest amount of aromatics.	Fixed bed reactor, temperature 450 °C	[34]
5	Ni/ZSM-5	Pine	Modification of ZSM-5 by Ni resulted in the increase in the amount of aromatics and enhanced conversion of oxygenates in comparison to unmodified material.	Bench-scale, semi-batch reactor system, temperature 500 °C, 35.5 mg of biomass per 2.5 min was inserted into the pyrolysis zone containing 500 mg of catalyst	[35]
6	Ni/ZSM-5	Miscanthus	Hydropyrolysis, both hydrogen pressure and the presence of catalyst led to the increase in the amount of saturated hydrocarbons.	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 600 °C, 20 s and 20,000 °C/s, catalyst to feedstock weight ratio = 3.3	[36]
7	ZSM-5, Ni/ZSM-5, MCM-41, Ni/MCM-41	Miscanthus, scots pine, mahogany	Fast pyrolysis of biomass pyrolysis vapors, the presence of catalysts increased content of aromatics and lighter phenols.	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 600 °C, 20 s and 20,000 °C/s, catalyst to feedstock weight ratio = 3.3	[37]
8	ZSM-5 modified by Ni/P	Pine and low-density polyethylene	Co-pyrolysis, modification of zeolite results in the production of increased amount of olefins and valuable aromatics. Moreover, increased hydrothermal stability of the catalyst and resistance against carbon deposit formation is observed.	Py-GCMS, maximal temperature, residence time and heating rate were fixed to 650 °C, 60 s, catalyst to feedstock weight ratio = 15	[38]
9	B-zeolite modified by Cu	Japanese knotweed	Introduction of copper promoted selectivity to hydrocarbons.	Down-draft fixed bed reactor, temperature 600 °C, heating rate 80 °C/min, duration 30 min, catalyst to feedstock weight ratio = 3.3	[39]
10	Cu/MCM-41 and Cu/KIT-6	Cedar wood	Catalysts prepared by cyclodextrin-assisted co-impregnation method were more active than the materials synthesized via impregnation. Cu/KIT-6 catalyst was more active in the formation of monocyclic aromatic compounds than Cu/MCM-41 sample.	Fixed bed reactor, reaction temperature, reaction time, and heating rate were fixed at 565 °C, 4 min, and 1000 °C/min, catalyst to feedstock weight ratio = 6	[40]
11	V-MCM-41	Commercial cellulose, xylan kraft lignin and levoglucosan	Ex-situ catalytic pyrolysis, H-V-MCM-41 showed highest catalytic activity for the production of valuable furanic compounds.	Py-GCMS for 3 min at 500 °C, catalyst to feedstock weight ratio = 1	[41]
12	Mo/KIT-5	Pine, lignin and cellulose	Fast pyrolysis, catalyst highly selective for the production of furans.	Horizontal quartz annular flow reactor, temperature 500 °C	[42]

The presented literature data demonstrate that an introduction of metals on the surface of zeolites or mesoporous silicas (i.e., by impregnation or ion-exchange methods) leads to an increase in the value of the bio-oil produced. The presence of transition metals facilitates the formation of a higher content of monocyclic aromatic hydrocarbons (such as benzene, toluene, ethylbenzene, etc.) at the expense of larger aromatics. It is connected with the facilitation of cracking and reforming reactions by metallic active sites, among others. Unfortunately, that positive effect is accompanied by a decrease in the content of liquid fraction and the formation of a higher amount of gaseous products.

2.3. Application of Metal Oxides and Supported Catalysts

The results of previous experiments suggest that, owing to the application of various metal oxides and the introduction of noble or transition metals on their surface, it is possible to increase the C/O ratio of the bio-oil produced during the pyrolysis process [45]. Therefore, researchers began to study the effect of the presence of such catalysts on the composition of liquid products of the thermal treatment of biomass (Table 3).

Nguyen et al. [46] noted that the use of a $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ system in the upgrading of bio-oil allowed for a decrease in the oxygen content and enhancement in the caloric value of the obtained mixture. Unfortunately, an increase in the amount of carbonyls responsible for the instability of the fuel was also observed. In order to improve the composition of the obtained bio-oil, they proposed the introduction of platinum on the surface of the $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ support. Pt is known for its activity in hydrogenation reactions. In spite of that, the presence of a $\text{Pt}/\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ catalyst did not improve the quality of the liquid fraction coming from biomass decomposition. Probably, it was connected with the agglomeration of platinum species and a decrease in the surface area of this catalyst. Due to that, a dual-bed system was designed. It consisted of two separate units containing $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$. This modification resulted in the noticeable improvement of the quality of the obtained products.

Table 3. Application of metal oxides and supported catalysts to high-temperature conversion of lignocellulosic biomass.

No.	Catalyst	Feedstock	Products and Remarks Regarding Influence of Catalyst	Conditions of Pyrolysis Process	Reference
1	$\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$	Pine	Hydropyrolysis—dual-bed system consisting of two separate units containing $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ and $\text{Pt}/\text{Al}_2\text{O}_3$ allowed for a noticeable improvement in the quality of bio-oil	Horizontal quartz annular flow reactor consists of two beds, the catalysts in this study were applied using single-bed and dual-bed modes, temperature $500\text{ }^\circ\text{C}$, vapor residence time 2 s, catalyst to feedstock weight ratio = 0.5	[46]
2	Cu, Fe and Zn supported on Al_2O_3 and SiO_2	Ultrasonically pretreated cedar	The highest yield of hydrocarbons was achieved in the presence of $\text{Zn}/\text{Al}_2\text{O}_3$, the largest fraction of aromatic hydrocarbon was produced with the use of $\text{Fe}/\text{Al}_2\text{O}_3$	Fixed bed reactor, reaction temperature, reaction time and heating rate were fixed at $500\text{ }^\circ\text{C}$, 30 min and $20\text{ }^\circ\text{C}/\text{min}$, catalyst to feedstock weight ratio = 3.3	[47]
3	Cu and Fe supported on mesoporous rod-like Al_2O_3	Sunflower stalks	Application of mesoporous Al_2O_3 with a larger pore size resulted in the formation of more polycyclic aromatic hydrocarbons	Fixed bed reactor, reaction temperature, reaction time and heating rate were fixed at $565\text{ }^\circ\text{C}$, 4 min and $1000\text{ }^\circ\text{C}/\text{min}$, catalyst to feedstock weight ratio = 8	[48]
4	TiO_2 , CeO_2 , $\text{CeO}_x\text{-TiO}_2$, ZrO_2 and MgO	Sugar maple, cellulose	CeO_2 -based catalysts were the most effective in the production of a wide group ketones from oxygenated reaction intermediates	Py-GCMS, temperature $550\text{ }^\circ\text{C}$, residence time 20 s, catalyst to feedstock weight ratio = 8	[49]
5	Ni supported on Al_2O_3 , SiO_2 , MgO , CeO_2 , ZrO_2 and CaO-ZrO_2	Cellulose	Fast pyrolysis, $\text{Ni}/\text{Al}_2\text{O}_3$ and Ni/ZrO_2 favored formation of hydrocarbons, while Ni/CeO_2 and Ni/SiO_2 were less effective, the last two catalysts were not capable to the efficient decrease in the amount of carboxylic acids	Py-GCMS, maximal temperature, residence time and heating rate were fixed to $600\text{ }^\circ\text{C}$, 20 s and $2000\text{ }^\circ\text{C}/\text{s}$, catalyst to feedstock weight ratio = 5	[50]
6	Ni supported on CeO_2 , ZrO_2 and $\text{CeO}_2\text{-ZrO}_2$	Cellulose	Fast pyrolysis, introduction of ceria to the support structure resulted in the formation of larger amount of olefins and paraffins in comparison to the catalyst supported on monoxide zirconia. Simultaneously, the production of a higher yield of carboxylic acids was also observed.	Py-GCMS, temperature, residence time and heating rate were fixed to $400\text{ }^\circ\text{C}$ – $600\text{ }^\circ\text{C}$, 20 s and $2000\text{ }^\circ\text{C}/\text{s}$, catalyst to feedstock weight ratio = 5	[51]
7	Pt/C , Pd/C , ZSM-5, MCM-41	Wheat bran	Pt/C and Pd/C catalysts efficient in the removal of oxygen from the produced bio-oil and formation of aromatic hydrocarbons	Thermogravimetric analyzer coupled to FTIR spectrometer, dry biomass samples were heated to $700\text{ }^\circ\text{C}$ with heating rate of $100\text{ }^\circ\text{C}/\text{min}$, catalyst to feedstock weight ratio = 1	[52]

Aluminum oxide was also used as a support for Cu, Fe, and Zn catalysts used in the catalytic upgrading of ultrasonically pretreated cedar wood [47,48]. The obtained results revealed that synthesized catalysts facilitated the conversion of oxygenates to aromatic and aliphatic hydrocarbons. The highest yield of hydrocarbons was achieved in the presence of the $\text{Zn}/\text{Al}_2\text{O}_3$ sample. Moreover, in this case the lowest value of aromatics to aliphatic hydrocarbons ratio was observed. On the other

hand, the activity tests showed that the largest fraction of aromatic hydrocarbon was produced with the use of a Fe/Al₂O₃ catalyst. However, the Cu/Al₂O₃ system allowed for the production of the highest content of monocyclic aromatic hydrocarbons (such as benzene, toluene, and xylene), while the catalyst containing Zn enhanced the formation of indene or naphthalene. Further measurements indicated that the introduction of the abovementioned metals on the surface of alumina allowed for more efficient production of hydrocarbons in comparison to the same catalysts supported on silica. It is connected with the differences in acidity of both kinds of oxides, which was noticeably higher for Al₂O₃.

The catalytic performance of different metal oxides, such as TiO₂, CeO₂, CeO_x-TiO₂, ZrO₂, and MgO, was tested in the conversion of biomass pyrolysis vapors into the ketonic-rich liquid fraction that can be used as the precursor of hydrocarbon fuel [49]. It was demonstrated that CeO₂-based catalysts were most effective at the production of a wide group of ketones from oxygenated reaction intermediates.

On the other hand, the investigations conducted in our laboratory were focused on the characterization of the efficiency of a Ni-based catalyst supported on Al₂O₃, SiO₂, MgO, CeO₂, and ZrO₂ in fast pyrolysis of cellulose [50]. The performed experiments aimed at a determination of the influence of different factors (such as type and structure of the support, kind of preparation method, presence of the interactions between an active phase and the support, size of nickel crystallites, etc.) on the composition of the products arising. Moreover, the pyrolysis of cellulose was conducted in the presence of unsupported NiO particles. The chromatographic data showed that an application of unsupported nickel oxide resulted in the formation of larger amount of hydrocarbons and esters with a simultaneous drop in the concentration of alcohols, aldehydes, and carboxylic acids as compared to non-catalytic process. Of course, an introduction of nickel on the surface of the support enhanced the efficiency of the production of desired pyrolysis products. It was shown that Ni/Al₂O₃ and Ni/ZrO₂ catalysts favored formation of hydrocarbons to the greatest extent. Ni/CeO₂ and Ni/SiO₂ were less effective in the production of valuable compounds. In addition, catalysts supported on ceria and silica were not capable of efficiently decreasing the amount of carboxylic acids. The comparison of the activity of Ni catalysts supported on zirconia prepared with the use of different methods showed that the support structure (phase composition, surface area, and pore structure) and its thermal stability considerably impact the composition of the products of the bio-oil upgrading process. Further experiments devoted to the investigations of Ni/CeO₂-ZrO₂ catalysts demonstrated that the introduction of ceria into the support structure resulted in the formation of a larger amount of olefins and paraffins in comparison to the catalyst supported on monoxide zirconia [51]. However, in this case the production of a higher yield of carboxylic acids was also observed.

The last group of studies on the thermal decomposition of biomass was devoted to the analysis of the influence of catalysts containing noble-metals, such as platinum and palladium [52]. In this case, pyrolysis of wheat bran was investigated with the use of a thermogravimetric analyzer coupled with a Fourier transform infrared spectrometer (TGA-FTIR). The obtained results confirmed that Pt/C and Pd/C systems were more efficient at the removal of oxygen from the produced bio-oil than the investigated zeolites. This was connected to their higher activity in the deoxygenation of carbonyl, carboxyl, and hydroxyl groups in comparison to the reference ZSM-5 and MCM-41 materials. Moreover, the presence of noble-metals resulted in the formation of a higher amount of aromatics, while silica-based materials favored the production of olefins and aliphatic hydrocarbons. Furthermore, it was demonstrated that catalysts consisting of noble-metals allowed for more efficient reduction of carboxylic acids, ketones, and aldehydes than ZSM-5 and MCM-41.

The investigations focusing on the application of metal oxides as catalysts for the high-temperature conversion of lignocellulosic biomass are not as promising as the studies associated with the use of zeolites. However, it was proven that an introduction of both noble and transition metals on their surface can considerably increase the value of the formed bio-oil. The experiments performed pointed

out that not only the kind of metal and its support, but also the catalyst preparation method can considerably influence the composition of the formed liquid mixture.

2.4. Bio-Oil Upgrading via Hydrodeoxygenation (HDO)

The necessity of upgrading biomass pyrolysis products results from the fact that they differ considerably in terms of properties and composition compared to the fuel obtained from crude oil. This variety is connected with the presence of a high content of oxygen-containing compounds (such as carboxylic acids, ketones, aldehydes, alcohols, esters, etc.). One of the methods of pyrolysis oil conversion into valuable products (such as hydrocarbons) is hydrodeoxygenation. According to the literature data [53,54], during the HDO process, oxygen can be eliminated from the pyrolysis products in various ways: hydrogenation of C–C and C–O bonds, dehydration of C–OH groups, C–C bond cleavage by retro-aldol condensation, and decarboxylation or hydrogenolysis of C–O–C groups. The reaction is usually conducted at a lower temperature than in the case of pyrolysis (usually between 200 and 400 °C) and under higher pressure (10–70 atm) [53].

The deoxygenation process can be performed after the condensation of pyrolysis vapors into a liquid phase or passing the vapors over the catalyst with subsequent condensation of the upgraded mixture into liquid [55]. The presence of the catalyst considerably increases the efficiency of oxygen removal and the formation of hydrocarbons. Noble metals (Pt, Pd, Ru), nickel and bimetallic (NiMo, CoMo) systems are most commonly used in HDO process [53]. On the other hand, alumina, silica, carbon, or zirconia are the most popular supports applied in the mentioned reaction. It is worth noting that traditional refinery catalysts, such as zeolites or silica-alumina-based materials, were also investigated in vapor-phase deoxygenation. Furthermore, Robinson et al. [56] in their review paper described the bifunctional catalysts for the upgrading of biomass-derived oxygenates (i.e., supported metal and bimetallic catalysts as well as transition-metal oxides, sulfides, carbides, nitrides, or phosphides) possessing active sites enabling both hydrogenation and C–O scission.

In order to increase the efficiency of the process, the hydrodeoxygenation of pyrolysis oil can be carried out in two reactor system. The first low-temperature step aims at a reduction of some part of the reactive alkene, phenolic, aromatic, and carbonyl groups, which are responsible for intense coke formation. Owing to the reduction of the amount of unstable bio-oil components in the next stage of the process, a lower amount of hydrogen is consumed and more valuable products can be formed. Taking that into account, Routray et al. [57] applied a two-zone, continuous flow trickle bed reactor to the hydrodeoxygenation of bio-oil derived from white oak wood. The obtained results showed that the use of Ru/C catalyst in the first step (130 °C) allowed for the conversion of the bio-oil components into alcohols, such as propylene glycol, ethylene glycol, and sorbitol. Furthermore, an addition of Pt/ZrP bifunctional catalyst to the next, higher temperature step (300 °C–400 °C) favored the production of monoaromatics, naphthalenes, and naphthenes. It was suggested that platinum was responsible for the hydrogenation and dehydrogenation reactions, while ZrP facilitated C–O bond cleavage in the hydrogenolysis reaction.

The two-step hydrodeoxygenation process was also applied by Pucher et al. [58] for the upgrading of pyrolysis oil produced from spruce wood pellets in the pilot-scale bioCRACK plant at the OMV refinery in Vienna. It was demonstrated that the performance of HDO in the two-step procedure (at 250 °C, 85 atm and 400 °C, 150–170 atm, respectively) and the application of a Raney Ni catalyst resulted in the formation of an upgraded product with properties very similar to those observed for diesel fuel. The amount of oxygen in bio-oil after HDO dropped from about 65 wt % for pyrolysis oil to not more than 2 wt % for the upgraded mixture, while the carbon amount increased from 26 wt % to 85 wt %, respectively. The density, viscosity, and lower calorific value were also similar to those noticed for diesel fuel.

Besides the investigations focused on the hydrodeoxygenation of the pyrolysis oil originated from real biomass samples, a large group of studies is devoted to the HDO of model substrates, such as

phenolic compounds [59–62], acetone [63], anisole [64], levulinic acid [65], and angelica lactone [66]. The presented results emphasize the importance of the use of catalyst.

Nelson et al. [59] investigated the hydrodeoxygenation of phenols over a ruthenium catalyst. They proposed a new mechanism of the reaction occurring with the use of titania as Ru support. According to them, the catalytic performance of Ru/TiO₂ can be associated with titania's ability to act as a conjugated acid/base pair. Therefore, H₂O molecules adsorbed on the catalyst surface can accept and donate protons across the interface between support and metal and lower the C–O scission barrier. This favors the conversion of phenols to benzene. On the other hand, Xu et al. [60] used a Ru/ZrO₂-La(OH)₃ catalyst for the hydrodeoxygenation of lignin-derived phenols to alkyl cyclohexanols. It was demonstrated that zirconium and lanthanum formed a mixed phase, making the support stable with well-dispersed ruthenium on its surface. The authors suggested that the conversion of guaiacol to cyclohexanol can occur in two ways—demethoxylation followed by hydrogenation, or saturation of the aromatic ring through hydrogenation and then demethoxylation through direct hydrogenolysis.

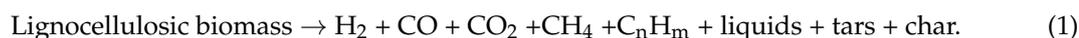
The investigation of the hydrodeoxygenation of phenol over a Pd/ZrO₂ catalyst showed that the zirconia structure plays an important role in the process [61]. It was observed that the Pd/t-ZrO₂ sample possessed the highest activity for HDO reaction and selectivity to benzene. This was connected with differences in the density of acid sites present on the surface of monoclinic-ZrO₂ and tetragonal-ZrO₂ phase, which was higher in the second case. The acidity of the catalyst affected the reaction pathway. The higher acidity of Pd/t-ZrO₂ favored the dehydration of cyclohexanol to cyclohexene, followed by benzene formation. A Pd/m-ZrO₂ catalyst with a lower density of acid sites exhibited low dehydration activity. Therefore, in this case the benzene molecules were formed in an alternative way, involving the tautomerization of phenol to cyclohexadienone intermediate.

The influence of the support on the activity of a noble-metal-based catalyst in the hydrodeoxygenation of guaiacol was also confirmed by Hellinger et al. [62]. It was demonstrated that acidic supports of Pt, such as H-MFI (mobil five) zeolites, provided the highest activity, while the order of the reactivity of metal oxide supports was Pt/SiO₂ > Pt/Al₂O₃ ≈ Pt/ZrO₂ > Pt/TiO₂.

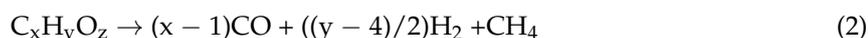
The next studies focused on the hydrodeoxygenation of levulinic acid or angelica lactone dimers/trimers to highly branched alkanes [65,66]. In this case, Ni-based materials were used as catalysts. It was confirmed that catalytic HDO of the abovementioned compounds led to a decrease in the content of compounds containing oxygen and selective formation of hydrocarbons. The literature data show that not only nickel- but also molybdenum-based catalysts can be applied in the HDO process. Sullivan and Bhan [63] showed that a bifunctional molybdenum carbide catalyst can be successfully used in the hydrodeoxygenation of acetone. In this case, acetone molecules were firstly hydrogenated to isopropyl alcohol and then the arising intermediate was dehydrated to propylene over Brönsted acid sites. Furthermore, propylene could be sequentially hydrogenated to form propane.

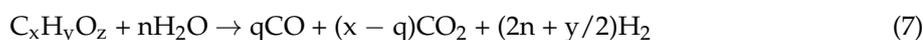
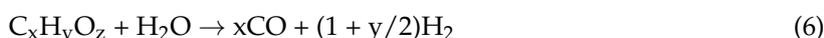
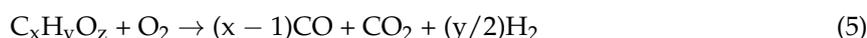
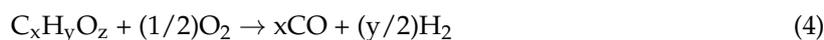
3. Catalysts for the Production of a Hydrogen-Rich Gas from Lignocellulosic Biomass

The literature data show that, besides of the production of bio-oil, lignocellulosic feedstock can also be used for the formation of hydrogen-rich gas [67–69]. Generally, the process of high-temperature conversion of lignocellulosic biomass can be presented as follows:



However, it should be noted that the formation of gaseous products proceeds in several steps, consisting of thermal decomposition of lignocelluloses, cracking, partial oxidation, steam and dry reforming, water–gas shift, and methanation, among others. The exemplary primary and secondary reactions (adapted from [70,71]) are demonstrated below:





It can be observed that the gaseous mixture obtained in the thermal treatment of lignocellulosic biomass mainly contains hydrogen, carbon oxide, carbon dioxide, and methane. These compounds are usually accompanied by a lower amount of light hydrocarbons remaining in the gas phase. It turned out that the hydrogen content in the formed gaseous mixture can be increased by the application of heterogeneous catalysts. Therefore, the next part of this chapter will be devoted to the presentation of the latest achievements in this field. Figure 3 demonstrates the exemplary processes used for the enhancement of H₂ production from lignocellulosic feedstock.

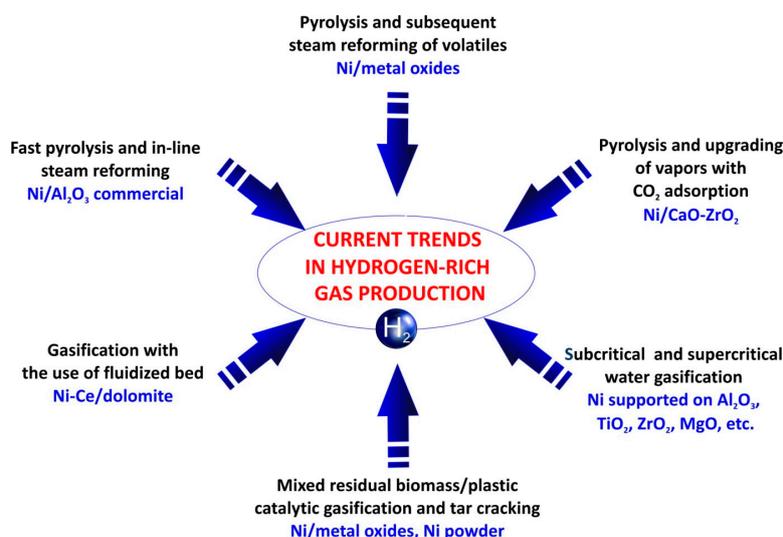


Figure 3. Exemplary processes and catalysts used for the enhancement of hydrogen production from lignocellulosic feedstock.

The literature shows that nickel-based systems are still the most popular catalysts for the conversion of lignocellulosic biomass (or products of its decomposition) to hydrogen-rich gas (Table 4). The investigations performed by Cheah et al. [72] focusing on the gasification of white oak submitted to thermal pretreatment (torrefaction) confirmed that the presence of Ni facilitates the production of H₂ and reduces the formation of CH₄ and tars due to the increase in the efficiency of the reforming reaction occurring during the conversion of lignocellulosic feedstock.

It can be seen that some of the investigations connected with the production of hydrogen-rich gas are devoted to the design of a new reaction setup and the use of commercially available catalysts. Arregi et al. [73] studied the fast pyrolysis of pine sawdust, which was conducted in a conical spouted

bed reactor followed by in-line steam reforming of formed vapors in a fluidized bed reactor (in this case, a commercial nickel catalyst supported on alumina doped with calcium (G90LDP, Süd Chemie) was applied in the reforming step). It was demonstrated that an application of the aforementioned process allowed for efficient production of hydrogen (the highest H₂ yield was observed at 600 °C) and can be a promising alternative for direct steam gasification or reforming of bio-oil. The authors concluded that the separation of pyrolysis and reforming steps can be beneficial, taking into account the performance of the catalytic reforming reaction.

On the other hand, a commercial nickel powder catalyst (Sigma-Aldrich, Ni ≥ 99% trace metal basis, CAS number 7440-02-0) was also used for integrated catalytic gasification and tar cracking of mixed residual biomass (coconut shells) and high-density polyethylene (HDPE) [74]. It was reported that the application of such feedstock and conversion procedure allowed for enhanced syngas and hydrogen production.

The production of hydrogen-rich gas by pyrolysis-gasification of a biomass/plastic mixture becomes more and more popular. Kumagai et al. [75] used the Ni-Mg-Al-Ca system for the thermal conversion of wood sawdust mixed with polypropylene in a two-stage stainless tube reactor. The obtained results showed that the presence of the catalyst led to an increase in hydrogen content, highest for the material with the Ni:Mg:Al:Ca molar ratio 1:1:1:4. Calcium was responsible for the enhancement of in situ adsorption of carbon dioxide formed during the process and limitation of the growth of filamentous carbon on the surface of the catalyst.

Investigations of the influence of Ca content on the catalytic performance of Ni/CaAlO_x catalysts in the pyrolysis-steam reforming of biomass sawdust were conducted by Chen et al. [76]. It was demonstrated that, besides the increase in the production of hydrogen, the presence of calcium resulted in a growth in the selectivity of carbon oxide formation and a reduction in the carbon dioxide content. Moreover, the experiments showed that, owing to the change of Ca content in the catalyst structure, it is possible to control the ratio between hydrogen and carbon oxide in the formed gaseous mixture while keeping the amount of arising H₂ nearly the same.

This increase in hydrogen production and reduction of the catalyst deactivation rate were also observed in the case of the NiZnAlO_x system used in the pyrolysis and subsequent steam reforming reactions [77]. The H₂ yield more than doubled, while the amount of introduced nickel on the catalyst surface rose from 5% to 35%. Dong et al. [77] indicated that this was connected with the growth of the number of catalytically active sites (Ni⁰) on the support. According to the obtained results, the presence of zinc oxide could protect a catalyst against an agglomeration of nickel particles and the formation of a coke deposit.

The studies performed by our group mainly focused on the selection of an optimal support for Ni catalysts, enabling the most efficient production of hydrogen-rich gas during high-temperature treatment of biomass. The first part of the investigation indicated that zirconia was the most promising material among the investigated oxides (ZrO₂, Al₂O₃, SiO₂, CeO₂, TiO₂, and MgO) [78]. In the next step of the studies, an optimal method for the synthesis of a zirconia support allowing for the production of the highest amount of H₂ was developed [79]. It was demonstrated that the catalyst containing ZrO₂ prepared from ZrOCl₂ by precipitation with NaOH was the most active in the conversion of cellulose to gaseous products, especially hydrogen. Its high activity was connected with a higher stability in the reaction conditions (700 °C) and an increased ability of zirconium ions to migrate on the surface of nickel, among other factors.

Further investigations revealed that the modification of ZrO₂ structure by various dopants can noticeably increase the efficiency of the hydrogen production. In the first case, zirconia was modified by the addition of various amounts of cerium oxide (15%–30%) [80]. The literature data show that the presence of ZrO₂ enhances the activity of the Ni catalyst in the reforming reaction due to the fact that zirconia is able to accumulate water molecules and form OH groups on its own surface, thereby facilitating the formation of hydrogen [81]. Simultaneously, CeO₂ is able to limit the formation of coke on the catalyst surface and favor in situ removal of deposited carbon. This is associated

with the high oxygen storage/release capacity and thermal stability of this oxide. An analysis of the influence of the preparation method of the bi-oxide support indicated that the introduction of Ni on the surface of CeO₂-ZrO₂ synthesized by sol-gel or impregnation allowed for the production of the highest hydrogen yield.

In the next part of the studies, it was demonstrated that the incorporation of alkali and alkaline earth metals into the structure of Ni/ZrO₂ can also enhance its catalytic performance in the high-temperature conversion of cellulose to hydrogen-rich gas [82,83]. Similar to the previous investigations, the role of the dopant is to inhibit the growth of a carbon deposit. It is suggested that the presence of alkali metals allows for the formation of oxygen vacancies in the catalyst structure that are responsible for the formation of OH and O radicals, enabling the removal of the carbon accumulated on the catalyst surface. On the other hand, the mentioned dopants (especially calcium) facilitate the adsorption of CO₂ on the support. The adsorbed carbon dioxide can change the equilibrium of the reactions taking place during the cellulose conversion process and increase the production of H₂.

Our investigations were also focused on the application of selected mesoporous silicas (SBA-15, SBA-16, KIT-6, and MCM-41) as supports for Ni catalysts in the high-temperature treatment of cellulose [71]. The obtained results showed that the use of SBA-15 and KIT-6 and the introduction of nickel onto their surface results in an increase in the efficiency of H₂ production in comparison with the reference Ni/SiO₂ sample. The activity of the studied catalysts was associated not only with surface acidity, but also with pore size, pore volume, stability of the structure, and accessibility of nickel atoms on the surface and inside the pores of the catalyst. It was suggested that a bigger pore diameter of the supports favored penetration of their structure by larger intermediates formed in the first step of biomass pyrolysis process owing to the larger amount of H₂ that could be produced.

The next group of studies was devoted to the development of catalysts for supercritical water gasification of lignocellulosic biomass or its components. The literature data demonstrate that Ni-based systems are also most popular in this case [84–87]. In fact, promising results were obtained for catalysts containing noble metals as well [88]. However, nickel catalysts have a greater chance of being implemented on a larger scale due to their lower cost and comparable activity with Ru or Pt.

Biomass steam gasification and steam reforming of volatiles from pyrolysis of wood or biomass tar were also conducted with the use of Fe-based systems [89–91]. However, investigations of the use of iron catalysts in the abovementioned process have not been very popular so far.

The performed studies indicate that Ni-based materials are the most active catalysts for the high-temperature conversion of lignocellulosic feedstock to hydrogen-rich gas. However, there is still the issue of carbon deposit formation on their surface during the reaction. Coking can be limited by the choice of an optimal catalyst support. Our investigations demonstrated that the use of materials containing ZrO₂ may be an interesting option. The second solution is associated with the application of reaction systems consisting of several steps, allowing for the catalyst to be used in optimal conditions.

Table 4. Catalysts for the production of hydrogen-rich gas from lignocellulosic biomass.

No.	Catalyst	Feedstock	Process, Products and Remarks Regarding Influence of Catalyst	Reaction Conditions	Reference
1	Ni, Ni-Ce supported on olivine	White oak submitted to thermal pretreatment	Gasification with the use of fluidized bed, Ni facilitated the production H ₂ and reduced the formation of CH ₄ and tars.	Inconel 800 reactor operated at 800 °C, gas residence time at a fluidizing steam flow rate of 0.8 kg/h was calculated to be 8.6 s	[72]
2	Commercial Ni/Al ₂ O ₃	Pine sawdust	Fast pyrolysis followed by steam reforming process, highest H ₂ yield observed at 600 °C.	Conical spouted bed reactor followed by in-line steam reforming of formed vapors in a fluidized bed reactor (temperature 500 °C–700 °C), steam biomass ratio 2–5, space time 2–25 g _{cat} /min·g	[73]

Table 4. Cont.

No.	Catalyst	Feedstock	Process, Products and Remarks Regarding Influence of Catalyst	Reaction Conditions	Reference
3	Commercial Ni powder	Coconut shells mixed with HDPE	Integrated catalytic gasification and tar cracking, enhanced syngas and hydrogen production.	Bench scale setup consists of two cylindrical reactors with both the fluidized and fixed bed gasifiers, temperature of fluidized bed 650 °C–870 °C, temperature of fixed bed 600 °C	[74]
4	Ni-Mg-Al-Ca	Wood sawdust mixed with polypropylene	Ca addition responsible for enhancement of in situ adsorption of carbon dioxide and limitation of growth of filamentous carbon.	Two-stage stainless tube reactor, pyrolysis was carried out in the first stage and evolved volatiles were passed directly to the second stage reactor where steam gasification of pyrolysis gases took place, gasification and pyrolysis temperature 800 °C and 600 °C, respectively	[75]
5	Ni/CaAlO _x	Wood sawdust	Pyrolysis-steam reforming, presence of calcium resulted in growth of selectivity to carbon oxide and reduction of carbon dioxide content, change of Ca content allowed for control of ratio between hydrogen and carbon oxide in the formed gaseous mixture.	Fixed bed two-stage reaction system, the first stage involved pyrolysis of feedstock and pyrolysis gases were passed directly to the second stage where catalytic reforming took place, temperature of the first unit 500 °C and the second 800 °C	[76]
6	NiZnAlO _x	Wood sawdust	Pyrolysis and subsequent steam reforming reactions, H ₂ yield increased more than twice while amount of introduced Ni on the catalyst surface changed from 5% to 35%, presence of ZnO protect against the agglomeration of nickel particles and formation of coke deposit.	Two-stage fixed bed reactor, in the first reactor biomass was decomposed into pyrolysis vapors, which were passed to the second reactor for catalytic steam reforming, temperature of the first unit 535 °C and the second 800 °C	[77]
7	Ni supported on ZrO ₂ , Al ₂ O ₃ , SiO ₂ , CeO ₂ , TiO ₂ and MgO	Cellulose	Pyrolysis, zirconia the most promising material among the investigated oxides.	Stirred batch reactor at 700 °C for 4 h, 5 g of biomass and 0.2 g of catalyst were used	[78]
8	Ni supported on ZrO ₂ prepared by different methods	Cellulose	Pyrolysis, catalyst containing ZrO ₂ prepared from ZrOCl ₂ by precipitation with NaOH was the most active in the conversion of cellulose to gaseous products, especially hydrogen.	Stirred batch reactor at 700 °C for 4 h, 5 g of biomass and 0.2 g of catalyst were used	[79]
9	Ni/CeO ₂ -ZrO ₂	Cellulose	Pyrolysis, introduction of Ni on surface of CeO ₂ -ZrO ₂ synthesized by sol-gel or impregnation allowed for the production of the highest hydrogen yield.	Stirred batch reactor at 700 °C for 4 h, 5 g of biomass and 0.2 g of catalyst were used	[80]
10	Ni/Me _x O-ZrO ₂ (M e = Ca, Mg, Na and K)	Cellulose	Pyrolysis, alkali metals allows for the formation of oxygen vacancies responsible for the removal of the carbon deposit, enhanced adsorption of CO ₂ shifts an equilibrium of the reactions of thermal treatment of cellulose.	Stirred batch reactor at 700 °C for 4 h, 5 g of biomass and 0.2 g of catalyst were used	[82]
11	Ni/CaO-ZrO ₂	Cellulose and pretreated beech, birch, poplar and pine	Upgrading of pyrolysis vapors, higher resistance against coke formation, decrease in the production of permanent gases in the case of real biomass samples.	Quartz fixed bed two step reactor, biomass decomposition (500 °C) was separated from the catalyst bed (700 °C), 0.4 g of biomass and 0.1 g of the catalyst were used	[83]
12	Ni supported on SBA-15, SBA-16, KIT-6 and MCM-41	Cellulose	Pyrolysis, the use of Ni/SBA-15 and Ni/KIT-6 results in the increase in the efficiency in H ₂ production in comparison to Ni/SiO ₂ sample	Stirred batch reactor at 700 °C for 4 h, 5 g of biomass and 0.2 g of catalyst were used	[71]

Table 4. Cont.

No.	Catalyst	Feedstock	Process, Products and Remarks Regarding Influence of Catalyst	Reaction Conditions	Reference
13	Ni-Co/Mg-Al Ni supported on Al ₂ O ₃ , activated carbon, TiO ₂ , ZrO ₂ , MgO Ni/biomass Ru/C	Lignin, cellulose, wheat straw, timothy grass, canola meal pine wood, fruit pulp	Subcritical and supercritical water gasification of various kinds of lignocellulosic biomass	[70–72]—batch supercritical water reactor, temperature and pressure—650 °C, 260 atm, water to biomass mass ratio = 5 [73]—batch reactor, temperature 300 °C–500 °C, pressure 230–250 atm, residence time 15–45 min, water to biomass mass ratio = 5–10 [74]—batch reactor, temperature 400 °C–600 °C, reaction time up to 60 min	[84–88]
14	Fe-Zn/Al ₂ O ₃	Wood sawdust	Steam reforming of volatiles from pyrolysis of wood sawdust, hydrogen production increased with the increase of Zn content, catalysts showed high stability in the reaction conditions	Fixed bed two-stage reaction system, the first stage involved pyrolysis of feedstock and pyrolysis gases were passed directly to the second stage where catalytic steam reforming took place, temperature of the first unit 500 °C and the second 800 °C	[89]

4. Summary

Two different approaches to the high-temperature conversion of lignocellulosic biomass, leading to the formation of bio-oil and hydrogen-rich gas, were presented in this work. In both cases our considerations were focused on the application of heterogeneous catalysts. It was demonstrated that zeolites (especially ZSM-5), mesoporous materials, their modifications with transition metals (mainly Ni, but also Fe, Cu, V or Mo), metal oxides, and systems containing noble metals were used most often in the production of high-value bio-oil. On the other hand, the formation of gaseous products was mainly conducted in the presence of a nickel catalyst supported on metal oxides. Due to their physicochemical properties, ZrO₂, CeO₂, and CaO appeared the most attractive among them.

The presented studies demonstrated that an application of heterogeneous catalysts can considerably enhance the efficiency of both bio-oil and hydrogen-rich gas production from lignocellulosic feedstock. It was exhibited that the presence of catalysts led not only to a growth in the amount of the abovementioned fractions but also resulted in a noticeable upgrading of their composition. Owing to that, products with considerably higher value could be obtained.

5. Perspectives on the High-Temperature Conversion of Lignocellulosic Feedstock

Studies on the high-temperature conversion of lignocellulosic biomass have been significantly expanded in recent years. However, there are still contradictory opinions related to the profitability of the processing of such a feedstock. It is observed that the governments of a large number of countries wish to stimulate research on the development of lignocellulosic feedstock processing. On the other hand, there are many problems related with biomass conversion (such as high transportation costs, lack of reproducibility of the raw material, complex biomass decomposition, and, connected with that, unsatisfactory selectivity of the formation of valuable products).

Therefore, in order to increase the competitiveness of the high-temperature biomass conversion process, it is especially important to design highly active and selective catalysts enabling us to obtain a reasonable yield of desired chemicals. However, an optimal catalyst should not only be effective in the processing of lignocellulosic feedstock, but also thermally stable and resistant to coking.

The literature data show that nickel-based systems are most popular in the high-temperature conversion of lignocellulosic biomass to hydrogen-rich gas. However, due to their drawbacks connected with relatively fast coking rate and the unsatisfactory stability of the prepared materials, further improvement of their properties is necessary (i.e., by optimization of the composition or preparation method of the support of this metal). On the other hand, the production of high-value bio-oil is associated with the use of zeolites and various mesoporous materials. However, in this case

not only acidity but also other parameters of the catalysts, such as surface area, pore diameter, pore volume, and stability of the structure, should also be taken into consideration.

The second way to increase the efficiency of the high-temperature conversion of biomass is a novel multistep process consisting of separate pyrolysis and upgrading units. This should allow for more efficient utilization of the catalysts due to the limitation on their deactivation rate associated with the reduction of the contact of the catalyst with primary products of the decomposition of lignocellulosic feedstock. One example of such a process is the separation of pyrolysis and catalyst steam reforming stages during the production of hydrogen-rich gas or performing the upgrading step with adsorption of carbon dioxide.

Finally, it is worth mentioning that crucial prerequisites for the implementation of the high-temperature conversion of biomass on the industrial scale are: a decrease in the production cost enabling it to compete with fuels originating from crude oil, an improvement of the properties of bio-oil, and an increase in the selectivity of the reactions leading to the formation of the desired products. We believe that the design of highly active and stable catalysts will allow the processes of lignocellulosic biomass conversion to play a major role in future biorefinery schemes. The obtained products can be applied as high-quality fuel in air or maritime transport and as valuable intermediates in the chemical sector.

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