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Processing of lignocellulosic polymer wastes using microwave irradiation

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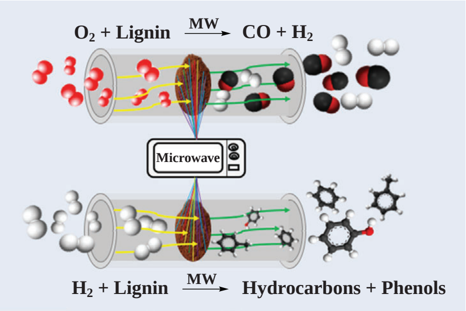
Lignin and mixed lignocellulosic natural polymer wastes have been accumulated in landfills over the past hundred years. These wastes should be processed to produce added-value chemicals and materials. This mini-review presents a brief literature survey related to state-of-the-art methods developed recently by the world research community to solve the problem of rational conversion of lignocellulosic polymer wastes, including production of hydrogen, synthesis gas, phenols, and monomers. The focus is made on microwave and plasma technologies used for lignocellulosic wastes processing.



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1. Introduction

The main problems of the conversion of lignocellulosic wastes are related to the poor solubility and irregular and non-uniform composition and structure of this natural polymer. Lignin, unlike cellulose, is hardly soluble even in ionic liquids that tend to dissolve cellulose and hemicellulose. Nevertheless, processing of lignocellulosic wastes became recently a global challenge[1–7] because of the accumulation of such wastes in huge amounts ranging from 100 to 250 million tons based on different estimated, mostly in the areas of developed forestry and paper industry. The environmental aspect of the problem is not less important as far as municipal solid wastes containing a large pool of polysaccharides (basically, cellulose) should be utilized and recycled.

Since the composition of lignocellulosic wastes is not uniform, there is no single product that can be produced selectively from this waste, except for hydrogen, and typically a mixture of gaseous, liquid and solid compounds is formed. In this concern, the conversion into gas products (synthesis gas, hydrogen, methane) may be most remarkable from the point of view of the increasing interest to hydrogen as an energy carrier. This short review is focused on novel energy-efficient and green approaches to lignin and lignocellulosics conversion, with catalysis being considered as the most powerful tool in this application. We will not consider the biochemical (enzymatic) conversion and depolymerization of lignin-containing materials. Also, we are not going to discuss the methods of production of carbon materials by carbonization of these natural polymers, although this is a very perspective field of activities,[8,9] as well as the use of lingocellulosic wastes as fillers in concrete, tires *etc*., reducing agents in metallurgy or other industries that fall outside

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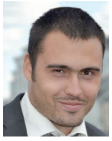

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the scope of this review. Instead, we will dwell upon the use of microwave and plasma treatment in biomass valorization. Finally, taking into account an avalanche-like growth of the literature on lignin processing in recent decade, the mini-review will mainly include results and approaches published in the last 5–10 years, while earlier publications and patents will be considered only if they provide valuable information.

2. Catalytic processes for conversion of lignin wastes

Examples on catalytic pyrolysis in comparison with non-catalytic processes are widely known in the literature.[10–14] Definitely, the use of catalysts brings some advantages like the decrease of the process temperature and reduction of energy expenses, an increase of the yield of desired liquid products and a decrease of the carbon footprint. The focus is made on the production of light products, mostly, gas mixtures, containing H_2, CH_4 and higher hydrocarbons. In general, the catalytic technology is characterized by the following advantages over the thermal (non-catalytic) technologies: a decrease of the operating temperature needed for the pyrolysis, reduction of the heat energy requirement, provision of favorable conditions for the industrial application of pyrolysis, production of final products of commercial significance.[15–18] The choice of catalysts includes zeolites and other commercial catalysts as well as materials that can also demonstrate the catalytic effect due to the presence of rather strong basic or acidic sites at the surface. It is worth to note that the catalysts for conversion of lignin wastes not necessarily should have a high surface area, since the processes in any case occur at the external surface of the catalyst grains or, in some cases, they can proceed in the macropores.

In many cases, co-processing of different wastes is discussed, for instance, a mixture of industrial polymer wastes with biomass components (wood, saw dust, switchgrass, *etc*.) is used with the application of cracking catalysts, for instance HZSM-5 zeolite.[19–22] Mixtures of polymers with lignocellulosics were also explored, in this case, catalytic hydrothermal processing of polypropylene with lignocellulose was realized.[23] Hydrothermal liquefaction catalysts were applied, including Fe, $FeSO_4$, $MgSO_4$, $ZnSO_4$, ZSM-5 zeolite, Y zeolite, amorphous aluminosilicate, and Na_2CO_3; the conversion of polymers reached a maximum of 38% with the use of amorphous aluminosilicate.

More complex municipal mixed plastic waste processing using thermal and catalytic technologies is discussed by Rajendran *et al*.[24] Comparison of different types of catalysts showed that HZSM-5 zeolite is the best catalyst in terms of the yield of liquid products (Table 1), although the difference in the performance of various catalysts is not so significant.[25–27]

Table 1 Comparison of different catalysts in the conversion of municipal mixed polymer wastes, the yields (wt%) of corresponding products are indicated.[24]

Products	Catalyst						
	HUSY	HZSM-5	H-MOR	Y zeolite	HNZ	Silica sand	Cement
Liquid	89.5	94.8	88.3	84.2	65.4	40	82
Gaseous	3.75	2.3	4.5	11.6	19.0	51	18
Solid residue	6.75	3.9	7.2	4.2	15.6	9	0
Coke	3.45	1.25	3.2	0	0	0	0

3. Catalytic conversion of lignin wastes based on the use of microwave irradiation

For the sake of cutting the energy expenses and/or increasing the overall efficiency of the processes, diverse sources of radiation (microwave or ultrasound, irradiation by UV light, low-temperature plasma) can be used in chemical processes, including catalytic reactions occurring in the course of lignocellulosic waste conversion. The effects caused by the microwaves, *i.e*. electromagnetic waves with the frequency ranging from 200 MHz to 300 GHz, are of particular interest. The advantage of microwave activation is the transfer of energy *via* radiation rather than heat transfer or convection. The interaction of microwave radiation with a substance (weather it is organic or inorganic or hybrid material) depends on the electrophysical properties of the substance (tangent of dielectric loss, *i.e*. the ratio of rational and imaginary parts of the dielectric constant) and may include absorption, reflection and transmission of the radiation. This ensures fast supply of energy into the volume of materials that are transparent to microwave radiation. The most pronounced effects of the appearance of temperature gradients and creation of non-equilibrium conditions are found when the reaction medium or material (a catalyst) consists of several phases with different microwave radiation absorption ability. The microwave treatment allows one to decrease the reaction time, to increase yields and selectivities, and to decrease energy and reagent consumption. The numerous examples that will be given and discussed below in this review demonstrate the advantages of the microwave processing in comparison with the conventional thermal treatment.

Microwave technologies can be used for *in situ* activation of catalytic processes. Noteworthy that lignin and cellulose poorly absorb microwave energy; therefore, either a catalyst or MW-absorbing material (SiC, carbon materials) introduced into the reaction zone can be heated. The dielectric polarization contributes to a large extent to the mechanism of the microwave action due to the presence of water and other polar compounds in the feed or polar functional groups in lignocellulosic material. The second mechanism involves free charges excited in solids and contributes to heating because of the Ohmic loss; this mechanism is characteristic of conductive or semiconductive catalysts. So, in the case of lignin conversion, all the mechanisms can be realized if the system contains polar molecules and solid catalysts containing supported metals or transition metal oxides or carbon materials. Obviously, microwave radiation cannot initiate chemical reactions by breaking chemical bonds, because the energy of microwave photons is low.

Literature data demonstrate that, under microwave activation conditions, higher reaction rates are observed than in thermally activated processes, and thus the yields of final products increase. Let us discuss most illustrative examples of the use of microwave activation in the conversion of lignocellulosic wastes. It should be noted that the distribution of gas, liquid and solid products obtained under microwave activation conditions does not differ dramatically from the distributions presented in Table 1 for zeolite or cement catalysts, with the exception that such distributions can be obtained at conversions close to 90% or higher under milder conditions in terms of the operating temperature and thus at the reduced energy spent for processing.

Several reviews of the methods for the utilization of polymer wastes with the use of microwave technologies were published.[28,29] Microwave technology demonstrated advantages over the thermal pyrolysis.[30] This technology increases the rate of reactions by rapid energy-efficient heating, increased production speed and lower production costs.[31,32]

Currently, the choice of an appropriate catalyst for a heterogeneous catalytic process of lignocellulosic waste valorization that is ideally suitable for activation in microwave fields is not quite obvious. The selection is complicated because the catalyst should, first, have substantial catalytic activity and, secondly, possess certain electrophysical properties (dielectric loss and conductivity). To obtain a maximum positive effect of microwave radiation on a catalytic system, comparatively inert components strongly interacting with electromagnetic fields may be introduced into catalysts. So, zeolites that are known to catalyze the pyrolysis of lignocellulosics are not MW-absorbing materials; therefore, other catalytic materials should be developed to better reveal the advantages of the microwave effects.

The advantages of microwave technologies can be used more effectively if the catalytically and electromagnetically active catalyst components are placed on a substrate transparent to microwave fields. This is done to form superheated regions (hot spots) only in the volume or on the surface of the active catalyst phase, which decreases the temperature of the catalyst. Thus, the microwave-assisted process is quite non-equilibrium, and the temperature varies along the catalyst grain, with the inert support being heated due to heat dissipation from hot spots. This offers the possibility of suppressing side reactions and decreasing energy expenses for heating inert materials that do not directly participate in the catalytic process.

Bifunctional catalysis, in which different stages of the process occur on different catalytic components, should be considered specifically. A typical example is transformation of an organic substrate (like lignin) on metal nanoparticles supported on acid or basic carriers. A metallic component (as a rule, a Pt family metal) activates the initial molecule *via* breaking bonds and/or charge transfer (dehydrogenation, hydrogenolysis), whereas carbon skeleton transformations (depolymerization, alkylation, isomerization) occur on acid/basic centers. Microwave radiation that creates temperature gradients in a heterogeneous system whose components differently interact with electromagnetic fields can then cause substantial changes in the reaction rates of the entire process and its different stages and may change the distribution of reaction products.

The advantages of the use of microwave activation of heterogeneous catalytic reactions of lignocellulosic waste valorization compared with thermal activation become obvious when fast heating or cooling and pulsed energy supply are required. The techniques of MW-initiated pyrolysis were reviewed by Motasemi *et al*.[33] A very important advantage of the MW technology is that it does not require any pretreatment of the raw materials. In the case of the use of heterogeneous catalysts, the most important advantage of microwave activation is the controlled formation of hot spots in the catalyst, where the active sites responsible for the conversion (depolymerization, cracking, *etc*.) are located. Thus, the use of microwave heating is reported to show beneficial features with respect to fast heating, higher pyrolysis rate achieved at a low operating temperature, enhanced heat distribution, compared to conventional heat treatment.[34] In addition, the activation could break the heavier hydrocarbon components of waste into lighter hydrocarbon components *via* chain-end scission mechanism that normally occurred during microwave pyrolysis.[35] This pyrolysis technique also allows direct heating and processing of moist feedstocks,[36–38] thereby excluding the necessity of pretreatment steps like drying. Nevertheless, as the first step, ultrafast fractionation of lignocellulosic biomass by using microwave-assisted deep eutectic solvent pretreatment can be achieved.[39,40] Noteworthy that the microwave conversion of cellulose and hemicellulose proceeds *via* the same mechanism and these substrates behave very similar to each other under the microwave processing conditions.[41]

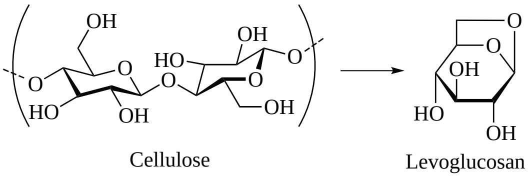
4. Synthesis of platform chemicals from lignocellulose under microwave conditions

The MW-stimulated fast conversion of carbohydrates into 5-hydroxymethylfurfural (a platform chemical) catalyzed by mesoporous TiO_2 nanoparticles was also studied.[42] The high surface area and the presence of Lewis acid sites were shown to be beneficial for ensuring the high activity in this process. Noteworthy that the commercial (non-mesoporous) sample of TiO_2 is poorly active in this reaction. The higher value of the tangent of dielectric loss, $\tan\delta$, for the solvent (dimethylsolfoxide) ensured a high yield in organic media compared to water. The catalyst manifests good recyclability.

Hydrolysis of xylan, as well as the conversion of D-xylose and D-lyxose and furfural production with molybdate as a catalyst were demonstrated to be more efficient under MW-irradiation.[43] The MW-irradiation allowed one to shorten the reaction time 400 times as compared to the thermal regime. The MW-stimulated hydrolysis of polysaccharides was also performed onto polyoxometallates as catalysts.[44] Polyoxometalates are MW-absorbing materials, which is favorable in the hydrolysis of corn starch and crystalline cellulose. Phosphotungstic and silicotungstic acids revealed high activity and good recyclability, unlike phosphomolybdic acid. The energy consumption in hydrolysis can be reduced by 17–23% using MW conditions.

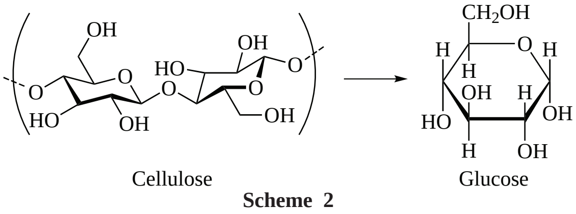
Valuable chemicals can be prepared from cellulose selectively under MW-irradiation.[45] MW-depolymerization afforded liquid products from cellulose in 87% yield with acid catalysts. The selectivities to glucose or levulinic acid were 50 and 69%, respectively. MW-depolymerization of cellulose resulting in 55% glucose (20 min) was reported.[46]

MW-pyrolysis of cellulose at 200–280 °C was also studied.[47] The maximum yield of bio-oil (45%) was observed with amorphous cellulose as a starting material at 260 °C. Water present in the feed enhanced the yield by 7–8%. The introduction of activated carbon as a MW-absorbing material increased the yield of gas products. Levoglucosan was produced with a high yield by pyrolysis of amorphous cellulose at 260 °C, *i.e*. at a much lower temperature than the thermal process occurring at $T > 400$ °C (Scheme 1).



Scheme 1

Microcrystalline cellulose is transformed with the yield of 100% into glucose under MW-treatment with NaOH as a catalyst (Scheme 2).[48]



Scheme 2

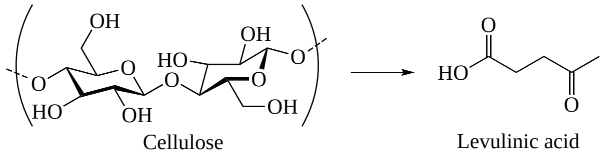
Lactic acid (LA) production from normal corn starch, high-amylose corn starch, and waxy corn starch dissolved in water using microwave heating was reported.[49] In the microwave mode, the LA yield (53–55%) for waxy corn starch in the shorter reaction time (0–5 min) was much higher compared to conventional heating. The microwave heating in the presence of either Brønsted acid (H_2SO_4) or Lewis acid ($CrCl_3$ or $AlCl_3$) was also used for the conversion of biomass, including carbohydrate-rich potato peel waste and sporocarps of the fungus *Cortinarius* *armillatus* to LA. The maximum LA yield of 62% was achieved at 180 °C, 15 min.[50]

5. Use of ionic liquids and deep eutectic solvents in microwave-assisted lignocellulosics processing

Ionic liquids in combination with microwave radiation provide an alternative approach to lignin and cellulose processing. Ionic liquids are expected to become significantly more economically attractive in case of their wider industrial application and efficient re-use in the future.[51,52]

In this context, the microwave-assisted synthesis of 5-hydroxymethylfurfural (5-HMF) from cellulose is an illustrative example. This approach results in the yield of 5-HMF reaching 62% in 2 min using ionic liquids as the reaction medium. The $Zr(O)Cl_2/CrCl_3$ catalyst in 1-butyl-3-methylimidazolium ionic liquid is active in the synthesis of 5-HMF from cellulose and lignocellulosic biomass using the microwave-assisted method.[53]

Levulinic acid can be produced from cellulose selectively with the yield approaching 55% when the MW-reaction is performed in SO_3H-functionalized ionic liquids (Scheme 3).[54]



Scheme 3

MW-assisted conversion of cellulose directly into 5-HMF, *i.e*. the platform chemical, can proceed in ionic liquids with $CrCl_3$ or $ZrCl_4$ as a catalyst.[55,56] The yields are as high as 60%.

Ionic liquids that exhibit good MW absorption ability may be used not only as a MW-absorbing media, but also as catalysts in the conversion of cellulose into 5-HMF.[57] Tetramethylguanidine-based ionic liquid with the BF_4 anion provides the yield of 5-HMF close to 30%.

The combination of deep eutectic solvents and microwave irradiation had a significant synergetic effect on efficiently cleaving the lignin–carbohydrate composite.[58] Cellulose from sunflower stalks was converted to value-added components in deep eutectic solvents.[59] With choline chloride and oxalic acid mixture under microwave irradiation, 99% carbon efficiency was found at 180 °C in 1 min. 5-Hydroxymethylfurfural (4%), levulinic acid (76%), furfural (5.5%), and formic acid (about 15%) were found among the products.[60] Comparison of the conductive heating with microwave heating for the pretreatment of waste biomass in deep eutectic solvents has been performed.[61] Cellulose esterification by alkyl chlorides under MW-conditions was studied.[62]

A number of publications are focused on MW-pretreatment of cellulose before the fermentation to decrease the degree of polymerization, *i.e*. for partial depolymerization.[63,64] The rate of cellulose hydrolysis increased 50 times after the microwave pretreatment in ionic liquids. Acid and alkaline hydrolysis with additional microwave-assisted processing was also described.[65] A design of a MW reactor for lignocellulose bio-waste hydrolysis was proposed.[66]

In spite of the poor MW absorption ability, H-forms of zeolites were quite efficient in MW-assisted cellulose hydrolysis when they are used in combination with ionic liquids.[67] A comparison of H-forms of zeolites with sulfated ion-exchange resin used together with ionic liquids demonstrated the higher efficiency of the zeolites in this application (Scheme 4).

A lignocellulosic raw material was partially depolymerized in cholinium ionic liquid under the microwave irradiation (110 °C, 20 min) to improve the enzymatic hydrolysis.[68]

6. Microwave-assisted lignin and cellulose pyrolysis and depolymerization

Lignin is a cross-linked polymer formed by phenolic and aliphatic fragments; therefore, it is more difficult to depolimerize this raw material. Nonetheless, the use of MW-irradiation was found to be efficient for lignin pyrolysis into phenolic moieties and fuel components. Bio-oil can be produced by microwave pyrolysis (1.5–2.7 kW) of kraft lignin.[69] The temperatures determined under the MW conditions were as high as 900–1240 K. The yields of the bio-oil, gas products, and char reached 20, 27, and 40%, respectively. Depolymerization of different types of lignin using a two-dimensional CuO/BCN catalyst (CBN stands for carbon-modified boron nitride) was studied by Cao *et al*.[70] Microwave-assisted lignin conversion was demonstrated to enhance the yields of aromatic monomers. The yields of bio-oils reached 70 wt% in 10 min.

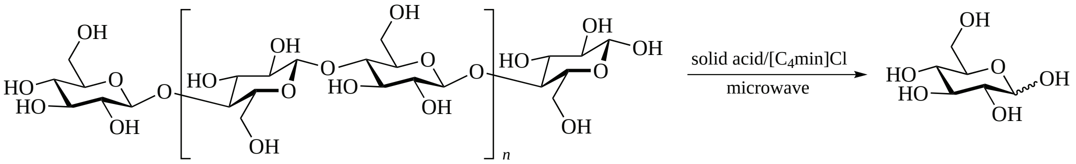
Hydrolysis of cellulose under microwave conditions was found to be very efficient in the presence of an ion-exchange resin.[71]

Hydrogenolysis of organosolv lignin from olive tree prunings was explored under microwave heating using a number of hydrogen donor solvents (without using H_2 for hydrogenolysis).[72,73] The activity of metallic (Ni, Ru, Pd, Pt) catalysts supported on mesoporous carrier with acidic properties (Al-SBA-15) was studied and the catalyst 10% Ni/Al-SBA-15 with tetralin as a hydrogen donor demonstrated improved bio-oil yields up to 17 wt%, the liquid contained phenolic compounds, including mesitol and syringaldehyde, and a small amount of esters.

Efficient attempts to enhance lignin conversion with carbon as a MW-absorbing agent were reported.[74–76] Phenols, guaiacols, hydrocarbons, and esters making up to 71–87% of bio-oil were identified in the reaction mixture. Long-chain fatty acid esters (42.2% in bio-oil) were also produced with Zn powder as a catalyst. The use of MoS_2 with a very high microwave absorptivity (185 °C min^{-1}) showed very high yields of liquid products (34 wt%) and phenolic compounds (32 wt%).

Microwave-assisted catalytic pyrolysis of biomass (cellulose) to produce phenol-rich bio-oil was described by Wang *et al*.[77] Fe/HZSM-5, Ni/HZSM-5 and Fe–Ni/HZSM-5 zeolites were used as catalysts. Fe/HZSM-5 showed the enhancement of the yields of bio-oil by 11.4% and a decrease of the coke formation by 24% compared to unmodified HZSM-5 zeolite. The Fe–Ni/HZSM-5 system demonstrated the highest selectivity to phenols (20.86%) in the bio-oil.

Hierarchical ZSM-5/MCM-41 catalysts were also applied in biomass valorization, in particular, *via* microwave-assisted co-pyrolysis of lignin and waste oil to produce aromatic



Scheme 4

hydrocarbons.[78] The MCM-41 material was used as a shell and the ZSM-5 zeolite was applied as a core. The optimum reaction conditions were as follows: temperature 400 °C, the waste-to-catalyst ratio of 10 : 1 and the ratio of lignin to oil of 2 : 1. The conversion reached 76%, the share of aromatics was 50% and the selectivity to monocyclic aromatic hydrocarbons reached 43%.

Numerous examples of the application of microwave treatment in hydrolysis of cellulosic wastes for plant raw material processing were described.[79]

7. Production of hydrogen, synthesis gas and bio-oil

One more example is related to the conversion of bio-wastes in production of hydrogen under microwave conditions.[80] Thus, microwave-assisted pyrolysis of biomass in the presence of microwave absorbing materials provides significant advantages over the thermal processing.[81]

The influence of the nature of the microwave absorbing material (diverse biochars) and microwave input power on biomass (pine sawdust) pyrolysis and product yields are studied.[82–84] The liquid products of microwave pyrolysis of pine sawdust contain predominantly phenols.

In this concern, it is interesting to compare the potential efficiency of lignin conversion into hydrogen and one of the added-value products in terms of the highest H_2 productivity and the lowest carbon footprint. This can be done using the data reported in the review by B. Weckhuysen *et al*.[85] by recalculating the productivities to H_2 and CO_2 (Table 2).

It is seen from Table 2 that the most beneficial products that provide the highest H_2 productivity and the lowest yield of CO_2 are benzene and phenol, whereas other aromatics, as well as vanillin and other derivatives of phenols are less suitable.

Gasification of palm shell char using CO_2 was found to be enhanced by MW-activation.[86] The Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) was determined to be the major reaction pathway. The use of a Fe catalyst supported onto the char allowed one to reach the CO_2 conversion of 99% within 60 min of the reaction.

Synthesis gas is a valuable product that can be produced from biomass (sewage sludges, coffee hulls), it can be used downstream for production of methanol or hydrocarbons.[87] Microwave heating was characterized by enhanced syngas yields compared to thermal conversion. The microwave process was shown to be less time and energy consuming in comparison to the thermal process.

Xie *et al*. reported the enhanced syngas production from biomass under MW-conditions with Fe, Co and Ni on Al_2O_3 as catalysts.[88] Ni/Al_2O_3 demonstrated the highest activity in syngas production with the synthesis gas yield reaching 80%. The presence of water vapor enhanced the syngas yield due to the occurrence of the steam reforming reaction.

Another work disclosed the syngas generation from municipal solid waste treatment.[89] The yield of syngas in the MW-assisted process is rather high. A gas mixture with a significant H_2 content (50–55 vol%) was obtained, and a positive effect of the moisture on synthesis gas production is found and explained by gasification of the char formed.

Table 2 Theoretical yields of added-values products from lignin (averaged composition), the productivities to H_2 and CO_2 and the molar H_2/CO_2 ratios.

Product	Theoretical yield from lignin (%)	Productivity of H_2/mol per 1 mol of product	Productivity of CO_2/mol per 1 mol of product	H_2/CO_2 molar ratio
Benzene	40	7.07	4.71	1.5
Toluene	47	3.44	3.02	1.14
Xylene	54	0.74	1.73	0.43
Phenol	48	6.72	3.91	1.72

Hydrogen can be also produced from banyan leaves in the MW-plasma under atmospheric pressure.[90] The applied microwave power was proportional to the rate of production of hydrogen, hydrogen productivity per gram of banyan leaves, and amount of hydrogen formed with respect to the H-atom content of converted banyan leaves. Increasing the microwave power leads to an increase of H_2 and decrease of CO_2 concentrations in the products due to the water–gas shift reaction: $CO_2 + H_2 = CO + H_2O$.

There are quite many publications focused on production of biofuels (bio-oil) from biomass under the MW conditions, including the review by Yin.[91] Fuel can be produced by MW-pyrolysis of a packaging waste[92] represented as a composite of paper, polyethylene, and aluminum. The use of different MW-absorbing solids like chopped tire, carbon, iron powder turned out to be efficient. Paper was converted into bio-oil composed from alcohols, aldehydes, acids, and anhydrosugars. Since the microwave regime provides very mild conditions and the reaction temperatures were quite low, both types of wastes were subject to very gentle depolymerization and dehydration (in the case of paper (cellulose), without severe reconstruction of the carbon chains. Even the yield of aldehydes that are most reactive among the products was rather high. Paper (cellulose) and polyethylene can be depolymerized much easier than lignin.

8. MW-pyrolysis of real biowastes and mixtures

Co-pyrolysis of polymer wastes with biomass components has also been studied in some works, for instance the conversion of polyethylene terephthalate with biomass components.[93] Bio-oil basically contains a complex mixture of C_6–C_{14} hydrocarbons and some ethers, including phenolic and furanic products. The duration of pyrolysis, microwave power, and particle size may affect the pyrolysis characteristics in the case of a blend of biomass and polymer waste.[94] In most cases, the decrease of the particle size results in the higher efficiency of the pyrolysis process due to the better contact of the active phase of a catalyst with the polymer molecules of both types (biopolymers and synthetic polymers).

Corn stover wastes were treated in the catalytic MW-assisted pyrolysis process (microwave power of 500 W, treatment time 30 min).[95] The use of metal oxides as catalysts improved the efficiency and reduced the formation of polyaromatic hydrocarbons, which are known to be ecotoxicants. The occurrence of the Fischer–Tropsch reaction resulted in an increase of the yield of liquid products and a decrease of the yield of gas products.

Mixtures of biowastes with vegetable oil or other natural raw materials (triolein, soybean oil, microalgae biomass of *Nannochloropsis*, castor and jatropha seeds), cooked oil or microalgae can be converted into biodiesel using MW treatment.[96] Strontium oxide was used as an efficient catalyst.

MW-pyrolysis of wheat straw was studied at 500 °C.[97,98] The yield of solid products decreased when the applied microwave power increased, unlike the yield of gas products, such as CO and H_2. The minimal yield of CO_2 as a by-product was found with CaO as an additive. CuO and Fe_3O_4 tend to catalyze the formation of liquid products. Pyrolysis occurs most intensively when activated carbon is used as a MW-absorbing material added to the mixture, with the maximum content of H_2 in the gas mixture exceeding 35%.

Sugarcane bagasse is an abundant by-product of sugar production and can serve as a benign raw material for MW pyrolysis.[99] Metal oxides catalyze the conversion of sugarcane bagasse, and the required reaction temperature decreased when such catalysts are used. NiO or CaO increased the production of H_2.

Cotton can be effectively converted into cellulose esters under MW heating in a *N*,*N*-dimethylacetamide/lithium chloride mixture with 4-(*N*,*N*-dimethylamino)pyridine as a catalyst.[100]

There are only a few reports on the effect of the nature of the catalyst, though this issue may be equally important as the optimization of the microwave regime. Strictly speaking, the efficiency of heating depends significantly not only on the nature and chemical composition of the MW-absorbing material, but also on its phase composition, particle size and morphology.[101] One of such papers[102] describes the effect of catalysts, including CaO, $CaCO_3$, NiO, Ni_2O_3, γ-Al_2O_3 and TiO_2, on the efficiency of sewage sludge pyrolysis. Wet sewage sludge was used, so the dipolar polarization mechanism predominated in the MW process. The realization of this mechanism becomes possible in the presence of water molecules and carbohydrate molecules that contain polar functional groups. The products included char, water and water-soluble compounds, oil and non-condensable gas. Different catalysts demonstrated different behavior resulting in a dramatic difference in the product distribution. The catalysts tested can be arranged in the following order for the reaction temperature rise: $Ni_2O_3 \approx \gamma\text{-}Al_2O_3 > TiO_2 > NiO > CaCO_3$. Ni-containing catalysts exhibited the highest activity towards the decomposition of organic compounds in the sludge as well as enhanced the yields of bio-oil and gas products. The use of CaO was beneficial for the formation of H_2-enriched syngas, whereas CO-enriched syngas was produced on Ni-catalysts. γ-Al_2O_3 and TiO_2 catalyzed the decomposition of organic compounds in the sludge, but the composition of gas products was about the same.

The upscaling of the pyrolysis technique is one of the major barriers for the commercialization of the MW pyrolysis. The microwave-assisted technology is an effective method to reduce the pyrolysis reaction time and increase the yields of value-added products from diverse feedstocks. A very important advantage of the MW technology is that it does not require any pretreatment or shredding of the raw materials.

9. Microwave processes under supercritical conditions

Recently processes under supercritical (SC) conditions became industrially attractive and gained importance. Conversion of organic wastes is one of the examples in this area.[103,104] The use of supercritical media is considered nowadays as a benign method of performing the chemical processes, because it allows one to increase dramatically the productivity (space-time yield) of the processes. The combination of the supercritical and microwave technologies would probably result in a synergy and additional benefits, though the use of the microwave technology is limited in terms of the pressure applied. Such a combined MW+SC approach was discussed for trans-esterification of algal biomass in supercritical ethanol.[105] The lipid-rich, dry algae (*Nannochloropsis salina*) was converted successfully into fatty acid ethyl esters. A short reaction time, reduction of energy consumption and high conversion are the benefits of the integrated approach. SiC was used as an inert additive absorbing MW energy.

A similar process was performed in supercritical methanol, where the MW approach was compared to the SC-approach.[106] The microwave approach improved the efficiency of extraction of algae, reduced extractive-trans-esterification time and increased the yield. The supercritical method gives purified extracts, and reduces energy consumption.

10. Catalytic conversion of lignin wastes based on the use of plasma

Under certain conditions (applied microwave power, material's dielectric loss characteristics, pressure and composition of gas present in the system), microwave irradiation is transformed into microwave plasma. Other types of plasma may be used, except for the microwave plasma, including corona discharge, ark discharge, glow discharge, or dielectric barrier discharge plasma, *etc*. Each type of plasma demonstrates certain advantages and drawbacks in comparison with conventional thermal processes and in comparison with other types of plasma, but this is not the focus of this mini-review to give a comprehensive analysis of the different types of plasma applied in lignocellulosic wastes processing. We will limit our discussion by some examples of the use of microwave plasma. Thus, an alternative example of pyrolytic recycling is plasma treatment: diverse organic polymeric waste is degraded by plasma into a harmless slag and syngas. This method has already been applied on a large scale in Japan.[107] Under controlled conditions, plasma processing may result in enhanced yield of liquid products.

In the case when the MW treatment is performed under reduced pressures, microwave plasma can be produced. A few studies were focused on the conversion of biomass in the MW plasma.[108] Hydrogen can be produced with a high yield from rice straw by MW-plasma-pyrolysis.[109] The concentrations of hydrogen in the gas mixture reached 48–56% at the highest conversion of 67.5%.

Deposition of iron or nickel salts on kraft lignin at a very low metal concentration (0.1 wt%) makes it possible to increase the conversion of lignin to hydrogen gas with the degree of hydrogen extraction reaching 90% based on the hydrogen present in the composition of the lignin sample.[110–115] The process is considered to occur under plasma conditions.

Low-temperature plasma was studied in the application to lignin depolymerization in ethanol to produce derivatives of aromatics and dicarboxylic acids.[116] The use of the Fenton reaction (in the presence of Fe_2O_3 and H_2O_2) creates oxidative conditions so that the lignin yield increases from 42.6 to 66.0%.

One more example of the use of plasma is related to liquefaction of lignocellulosic biomass (sawdust, corncob and rice straw).[117] A higher energy yield of the liquid fraction was achieved in the plasma treatment of sawdust, as a result of the higher content of lignin and lower ash content in this material compared to other lignocellulosic materials. Lignocellulosic biomass liquefaction by plasma electrolysis under acidic conditions has been reported by Xi *et al*.[118] Sulfuric acid, *p*-toluenesulfonic acid, and their sodium salts were used as catalysts in sawdust liquefaction. Sulfuric acid turned out to be the optimal system with glycerol as a solvent. The liquefaction yield achieved 83.5% after 25 min with sodium *p*-toluenesulfonate as a catalyst.

Pulsed corona discharge was also studied as an alternative method for lignin processing.[119] Kraft lignin and birch lignin under treatment in a low oxygen content atmosphere produced mainly aldehydes.

11. Conclusions

Thus, the new approaches to lignocellulosics conversion into added-value products include the use of microwave[120,121] or plasma activation,[122] application of supercritical fluids or ionic liquids for depolymerization. The future perspectives are related to the realization of nano-effects in lignocellulosics conversion. The influence of the particle size and morphology has not been studied for any of the catalytic systems used in the conversion of this waste. Also, the optimization of the microwave parameters such as a dependence of the performance on the operating microwave frequency (1–10 GHz) is far from the final understanding. The role of each of the three possible mechanisms (dipolar polarization, conductivity mechanism, inter-phase polarization) of microwave activation is also not quite clear. Obviously, benefits of each mechanism should be revealed and used to enhance the efficiency of lignin waste processing, to further decrease the energy consumption and to improve the selectivity/activity pattern. Other approaches (not covered by this mini-review are based on the use of additives to conventional FCC catalysts, additives of radical-producing moieties (like phenols), or solvents, or olefins to the feed during the pyrolysis process (non-catalytic and catalytic). A combination of the above approaches can show a synergy. Other reactions of lignin and cellulose that have not been studied yet under microwave or plasma conditions, such as steam or dry reforming resulting in synthesis gas production,[123,124] also deserve attention.

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References

1 Z. Jiang and C. Hu, *J. Energy Chem*., 2016, **25**, 947.
2 R. Roy, M. S. Rahman and D. E. Raynie, *Curr. Res. Green Sustainable Chem*., 2020, **3**, 100035.
3 S. De, S. Dutta and B. Saha, *Catal. Sci. Technol*., 2016, **6**, 7364.
4 H. Li, Y. Liang, P. Li and C. He, *J. Bioresour. Bioprod*., 2020, **5**, 163.
5 U. De Corato, I. De Bari, E. Viola and M. Pugliese, *Renewable Sustainable Energy Rev*., 2018, **88**, 326.
6 J. Becker and C. Wittmann, *Biotechnol. Adv*., 2019, **37**, 107360.
7 R. Abejón, *ChemEngineering*, 2018, **2**, 7.
8 S. Chen, Z. Liu, S. Jiang and H. Hou, *Sci. Total Environ*., 2020, **710**, 136250.
9 D. Yao, H. Li, Y. Dai and C.-H. Wang, *Chem. Eng. J*., 2021, **408**, 127268.
10 J. Walendziewski and M. Steininger, *Catal. Today*, 2001, **65**, 323.
11 F. J. Passamonti and U. Sedran, *Appl. Catal., B*, 2012, **125**, 499.
12 R. Miandad, M. A. Barakat, A. S. Aburiazaiza, M. Rehan and A. S. Nizami, *Process Saf. Environ. Prot.*, 2016, **102**, 822.
13 S. H. Shah, Z. M. Khan, I. A. Raja, Q. Mahmood, Z. A. Bhatti, J. Khan, A. Farooq, N. Rashid and D. Wu, *J. Hazard. Mater*., 2010, **179**, 15.
14 M. Stelmachowski and K. Slowiński, *Chem. Process Eng.*, 2012, **33**, 185.
15 R. Miandad, M. Rehan, M. A. Barakat, A. S. Aburiazaiza, H. Khan, I. M. I. Ismail, J. Dhavamani, J. Gardy, A. Hassanpour and A.-S. Nizami, *Front. Energy Res*., 2019, **7**, 1.
16 G. Elordi, M. Olazar, G. Lopez, M. Amutio, M. Artetxe, R. Aguado and J. Bilbao, *J. Anal. Appl. Pyrolysis*, 2009, **85**, 345.
17 T. Maharana, Y. S. Negi and B. Mohanty, *Polym. Plast. Technol. Eng*., 2007, **46**, 729.
18 D. P. Serrano, J. A. Melero, G. Morales, J. Iglesias and P. Pizarro, *Catal. Rev. Sci. Eng*., 2018, **60**, 1.
19 Z. Wang, K. G. Burra, T. Lei and A. K. Gupta, *Prog. Energy Combust. Sci*., 2021, **84**, 100899.
20 C. A. Mullen, C. Dorado and A. A. Boateng, *J. Anal. Appl. Pyrolysis*, 2018, **129**, 195.
21 L. Zhang, Z. Bao, S. Xia, Q. Lu and K. B. Walters, *Catalysts*, 2018, **8**, 659.
22 C. Vasile and M. A. Brebu, *Cellul. Chem. Technol*., 2006, **40**, 489.
23 S. Hongthong, H. S. Leese and C. J. Chuck, *ACS Omega*, 2020, **5**, 20586.
24 K. M. Rajendran, V. Chintala, A. Sharma, S. Pal, J. K Pandey and P. Ghodke, *Mater. Today Commun.*, 2020, **24**, 100982.
25 Y.-H. Lin and H.-Y. Yen, *Polym. Degrad. Stab*., 2005, **89**, 101.
26 R. Bagri and P. T. Williams, *J. Anal. Appl. Pyrolysis*, 2002, **3**, 29.
27 J. J. Park, K. Park, J.-S. Kim, S. Maken, H. Song, H. Shin, J.-W. Park and M.-J. Choi, *Energy Fuels*, 2003, **17**, 1576.
28 T. J. Appleton, R. I. Colder, S. W. Kingman, I. S. Lowndes and A. G. Read, *Appl. Energy*, 2005, **81**, 85.
29 D. A. Jones, T. P. Lelyveld, S. D. Mavrofidis, S. W. Kingman and N. J. Miles, *Resour., Conserv. Recycl*., 2002, **34**, 75.
30 B. Kunwar, H. N. Cheng, S. R. Chandrashekaran, B. K. Sharma, B. K. S. Bidhya Kunwar, H. N. Cheng and S. R. Chandrashekaran, *Renewable Sustainable Energy Rev*., 2016, **54**, 421.
31 S. S. Lam and H. A. Chase, *Energies*, 2012, **5**, 4209.
32 A. Undri, S. Meini, L. Rosi, M. Frediani and P. Frediani, *J. Anal. Appl. Pyrolysis*, 2013, **103**, 149.
33 F. Motasemi and M. T. Afzal, *Renewable Sustainable Energy Rev*., 2013, **28**, 317.
34 D. Cyranoski, *Nature*, 2006, **444**, 262.
35 F. Motasemi and A. G. Gerber, *Fuel*, 2018, **211**, 649.
36 J. Yang, J. Rizkiana, W. B. Widayatno, S. Karnjanakom, M. Kaewpanha, X. Hao, A. Abudula and G. Q. Guan, *Energy Convers. Manage*., 2016, **120**, 422.
37 W. A. W. Mahari, C. T. Chong, W. H. Lam, T. N. S. T. Anuar, N. L. Ma, M. D. Ibrahim and S. S. Lam, *Energy Convers. Manage*., 2018, **171**, 1292.
38 D. V. Suriapparao and R. Vinu, *J. Anal. Appl. Pyrolysis*, 2015, **113**, 701.
39 Z. Chen and C. Wan, *Bioresour. Technol*., 2018, **250**, 532.
40 V. Rigual, J. C. Domíngue, M. V. Alonso and T. M. Santos, *Biomass Bioenergy*, 2018, **117**, 190.
41 J. Robinson, E. Binner, D. B. Vallejo, N. D. Perez, K. Al Mughairi, J. Ryan, B. Shepherd, M. Adam, V. Budarin, J. Fan, M. Gronnow and F. Peneranda-Foix, *Chem. Eng. J*., 2022, **430**, 132975.
42 S. Dutta, S. De, A. K. Patra and M. Sasidharan, *Appl. Catal., A*, 2011, **409–410**, 133.
43 Z. Hricovíniová, *Carbohydr. Polym*., 2013, **98**, 1416.
44 S. Tsubaki, K. Oono, T. Ueda, A. Onda, K. Yanagisawa, T. Mitani and J. Azuma, *Bioresour. Technol*., 2013, **144**, 67.
45 S. Hassanzadeh, N. Aminlashgari and M. Hakkarainen, *Carbohydr. Polym*., 2014, **112**, 448.
46 S. Shaveta, N. Bansal and P. Singh, *Tetrahedron Lett*., 2014, **55**, 2467.
47 A. Al Shra'ah and R. Helleur, *J. Anal. Appl. Pyrolysis*, 2014, **105**, 91.
48 H. Peng, H. Chen, Y. Qu and L. Hongqiang, *Appl. Energy*, 2014, **117**, 142.
49 A. Mukherjee and M. J. Dumont, *Ind. Eng. Chem. Res*., 2016, **55**, 8941.
50 Y. Dong, K. Lappalainen, A. Markkola, A. Rusanen, P. Wäli, N. Vogeler, A. L. Ruotsalainen, J. Kärkkäinen, U. Lassi and M. Niemelä, *Biomass Convers. Biorefin.*, 2018, **8**, 965.
51 H. G. Joglekar, I. Rahman and B. D. Kulkarni, *Chem. Eng. Technol*., 2007, **30**, 819.
52 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev*., 2008, **37**, 123.
53 S. Dutta, S. De, I. Alam, M. M. Abu-Omar and B. Saha, *J. Catal*., 2012, **288**, 8.
54 H. Ren, Y. Zhou and L. Liu, *Bioresour. Technol*., 2013, **129**, 616.
55 C. Li, Z. Zhang and Z. K. Zhao, *Tetrahedron Lett*., 2009, **50**, 5403.
56 B. Liu, Z. Zhang and Z. K. Zhao, *Chem. Eng. J*., 2013, **215–216**, 517.
57 Y. Qu, Q. Wei, H. Li, P. Oleskowicz-Popiel, C. Huang and J. Xu, *Bioresour. Technol*., 2014, **162**, 358.
58 R. Liu, Z. Chen, H. Ren and E. Duan, *BioResources*, 2017, **12**, 5407.
59 M. Sert, A. Arslanoglu and L. Ballice, *Renewable Energy*, 2018, **118**, 993.
60 P. D. Muley, J. K. Mobley, X. Tong, B. Novak, J. Stevens, D. Moldovan, J. Shi and D. Boldor, *Energy Convers. Manage*., 2019, **196**, 1080.
61 N. Kumar, P. D. Muley, D. Boldor, G. G. Coty IV and J. G. Lynam, *Ind. Crop. Prod*., 2019, **142**, 111865.
62 C. Satgé, B. Verneuil, P. Branland and R. Granet, *Carbohydr. Polym*., 2002, **49**, 373.
63 V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth and D. J. Macquarrie, *Bioresour. Technol*., 2010, **101**, 3776.
64 S. H. Ha, N. L. Mai, G. An and Y.-M. Koo, *Bioresour. Technol*., 2011, **102**, 1214.
65 V. Kumar and T. Satyanarayana, *Bioresour. Technol*., 2015, **179**, 382.
66 A. Orozco, M. Ahmad, D. Rooney and G. Walker, *Process Saf. Environ. Prot.*, 2007, **85**, 446.
67 Z. Zhang and Z. K. Zhao, *Carbohydr. Res.*, 2009, **344**, 2069.
68 K. Ninomiya, T. Yamauchi, C. Ogino, N. Shimizu and K. Takahashi, *Biochem. Eng. J*., 2014, **90**, 90.
69 S. Farag, D. Fu, P. G. Jessop and J. Chaouki, *J. Anal. Appl. Pyrolysis*, 2014, **109**, 249.
70 Y. Cao, S. S. Chen, D. C. W. Tsang, J. H. Clark, V. L. Budarin, C. Hu, K. C.-W. Wu and S. Zhang, *Green Chem.*, 2020, **22**, 725.
71 X. Qi, M. Watanabe, T. M. Aida and J. R. L. Smith, *Green Chem*., 2008, **10**, 799.
72 A. Toledano, L. Serrano, J. Labidi, A. Pineda, A. M. Balu and R. Luque, *ChemCatChem*, 2013, **5**, 977.
73 A. Toledano, L. Serrano, A. Pineda, A. A. Romero, R. Luque and J. Labidi, *Appl. Catal., B*, 2014, **145**, 43.
74 W. Wang, Z. Ma, X. Zhao, S. Liu, L. Cai, S. Q. Shi and Y. Ni, *ACS Sustainable Chem. Eng*., 2020, **8**, 16086.
75 Q. Bu, H. Lei, L. Wang and Y. Wei, *Bioresour. Technol*., 2014, **162**, 142.
76 Q. Bu, H. Lei, S. Ren, L. Wang, Q. Zhang, J. Tang and R. Ruan, *Bioresour. Technol*., 2012, **108**, 274.
77 W. Wang, M. Wang, J. Huang, N. Tang, Z. Dang, Y. Shi and M. Zhaohe, *J. Energy Inst*., 2019, **92**, 1997.
78 R. Zou, Y. Wang, L. Jiang, Z. Yu, Y. Zhao, Q. Wu. L. Dai, L. Ke, Y. Liu and R. Ruan, *Bioresour. Technol*., 2019, **289**, 121609.

79 S. Zhu, Y. Wu, Z. Yu, X. Zhang, H. Li and M. Gao, *Bioresour. Technol*., 2006, **97**, 1964.

80 L. Guo, X. M. Li, X. Bo, Q. Yang, G.-M. Zeng, D.-X. Liao and J.-J. Liu, *Bioresour. Technol*., 2008, **99**, 3651.

81 F. Mushtaq, R. Mat and F. N. Ani, *Renewable Sustainable Energy Rev*., 2014, **39**, 555.

82 C. R. Ellison, R. Hoff, C. Mărculescu and D. Boldor, *Appl. Energy*, 2020, **259**, 114217.

83 J. L. Klinger, T. Westover, R. Emerson, L. Williams, S. Hernández, G. D. Monson and J. C. Ryan, *Appl. Energy*, 2018, **228**, 535.

84 Y. Wang, Z. Zeng, X. Tian, L. Dai, L. Jiang, S. Zhang, Q. Wu, P. Wen, G. Fu, Y. Liu and R. Ruan, *Bioresour. Technol.*, 2018, **269**, 162.

85 R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx and B. M. Weckhuysen, *Angew. Chem., Int. Ed*., 2016, **55**, 8164.

86 P. Lahijani, Z. A. Zainal, A. R. Mohamed and M. Mohammadi, *Bioresour. Technol*., 2014, **158**, 193.

87 Y. Fernández and J. A. Menéndez, *J. Anal. Appl. Pyrolysis*, 2011, **91**, 316.

88 Q. Xie, F. C. Borges, Y. Cheng, Y. Wan, Y. Li, X. Lin, Y. Liu, F. Hussain, P. Chen and R. Ruan, *Bioresour. Technol*., 2014, **156**, 291.

89 D. Beneroso, J. M. Bermúdez, A. Arenillas and J. A. Menéndez, *J. Anal. Appl. Pyrolysis*, 2014, **105**, 234.

90 Y.-C. Lin, T.-Y. Wu, S.-R. Jhang, P.-M. Yang and Y.-H. Hsiao, *Bioresour. Technol*., 2014, **161**, 304.

91 C. Yin, *Bioresour. Technol*., 2012, **120**, 273.

92 A. Undri, L. Rosi, M. Frediani and P. Frediani, *Fuel*, 2014, **133**, 7.

93 N. Caroko, H. Saptoadi and T. A. Rohmat, *J. Adv. Res. Fluid Mech. Therm. Sci*., 2020, **71**, 72.

94 W. A. Wan Mahari, C. T. Chong, C. K. Cheng, C. L. Lee, K. Hendrata, P. N. Y. Yek, N. L. Ma and S. S. Lam, *Energy*, 2018, **162**, 309.

95 Y.-F. Huang, W.-H. Kuan, C.-C. Chang and Y.-M. Tzou, *Bioresour. Technol*., 2013, **131**, 274.

96 M. Koberg and A. Gedanken, in *New and Future Developments in Catalysis*, ed. S. L. Suib, Elsevier, Amsterdam, 2013, pp. 209–227.

97 X. Zhao, M. Wang, H. Liu and C. Zhao, *J. Anal. Appl. Pyrolysis*, 2013, **100**, 49.

98 X. Zhao, W. Wang, H. Liu and C. Ma, *Bioresour. Technol.*, 2014, **158**, 278.

99 W.-H. Kuan, Y.-F. Huang, C.-C. Chang and S.-L. Lo, *Bioresour. Technol*., 2013, **146**, 324.

100 U. Ratanakamnuan, D. Atong and D. Aht-Ong, *Carbohydr. Polym*., 2012, **87**, 84.

101 *Microwaves in Catalysis: Methodology and Applications*, eds. S. Horikoshi and N. Serpone, Wiley-VCH, Weinheim, 2015.

102 Y. Yu, J. Yu, B. Sun and Z. Yan, *J. Anal. Appl. Pyrolysis*, 2014, **106**, 86.

103 M. Sugano, A. Komatsu, M. Yamamoto, M. Kumagai, T. Shimizu, K. Hirano and K. Mashimo, *J. Mater. Cycles Waste Manage.*, 2009, **11**, 27.

104 F. Cansell, S. Rey and P. Beslin, *Revue de l’Institut Francais du Petrole*, 1998, **53**, 71.

105 P. D. Patil, H. Reddy, T. Muppaneni, S. Ponnusamy, P. Cooke, T. Schuab and S. Deng, *J. Supercrit. Fluids*, 2013, **79**, 67.

106 P. D. Patil, V. G. Gude, A. Mannarswamy, P. Cooke, N. Nirmalakhandan, P. Lammers and S. Deng, *Fuel*, 2012, **97**, 822.

107 D. Zhao, X. Wang, J. B. Miller and G. W. Huber, *ChemSusChem*, 2020, **13**, 1764.

108 J. Vanneste, T. Ennaert, A. Vanhulsel and B. Sels, *ChemSusChem*, 2017, **10**, 14.

109 Y.-C. Lin, T.-Y. Wu, W.-Y. Liu and Y.-H. Hsiao, *Fuel*, 2014, **119**, 21.

110 P. A. Zharova, O. V. Arapova, G. I. Konstantinov, A. V. Chistyakov and M. V. Tsodikov, *J. Chem*., 2019, 1.

111 A. I. Netrusov, V. V. Teplyakov, M. V. Tsodikov, A. V. Chistyakov, P. A. Zharova and M. G. Shalygin, *Pet. Chem*., 2019, **59**, 11 (*Neftekhimiya*, 2019, **59**, 14).

112 M. V. Tsodikov, O. G. Ellert, S. A. Nikolaev, O. V. Arapova, O. V. Bukhtenko, Yu. V. Maksimov, D. I. Kirdyankin and A. Yu. Vasil’kov, *J. Nanopart. Res.*, 2018, **20**, 86.

113 M. V. Tsodikov, O. G. Ellert, O. V. Arapova, S. A. Nikolaev, A. V. Chistyakov and Y. V. Maksimov, *Chem. Eng. Trans*., 2018, **65**, 367.

114 M. Kobayashi, K. Konno, H. Okamura, T. Yamaguchi and K. Onoe, *J. Jpn. Inst. Energy*, 2005, **84**, 468.

115 M. V. Tsodikov, O. G. Ellert, S. A. Nikolaev, O. V. Arapova, G. I. Konstantinov, O. V. Bukhtenko and A. Y. Vasil’kov, *Chem. Eng. J*., 2017, **309**, 628.

116 R. Zhou, R. Zhou, S. Wang, U. G. Mihiri Ekanayake, Z. Fang, P. J. Cullen, K. Bazaka and K. Ostrikov, *Bioresour. Technol*., 2020, **318**, 123917.

117 D. Mei, S. Liu, S. Wang, R. Zhou, R. Zhou, Z. Fang, X. Zhang, P. J. Cullen and K. Ostrikov, *Renewable Energy*, 2020, **157**, 1061.

118 D. Xi, C. Jiang, R. Zhou, Z. Fang, X. Zhang, Y. Liu, B. Luan, Z. Feng, G. Chen, Z. Chen, Q. Liu and S.-Z. Yang, *Bioresour. Technol*., 2018, **268**, 531.

119 A. Sokolov, L. Lagerquist, P. Eklund and M. Louhi-Kultanen, *Chem. Eng. Process.: Process Intensif.*, 2018, **126**, 141.

120 W. Yunpu, D. Leilei, F. Liangliang, S. Shaoqi, L. Yuhuan and R. Roger, *J. Anal. Appl. Pyrolysis*, 2016, **119**, 104.

121 H. M. Morgan, Q. Bu, J. Liang, Y. Liu, H. Mao, A. Shi, H. Lei and R. Ruan, *Bioresour. Technol.*, 2017, **230**, 112.

122 R. Singh, B. B. Krishna, J. Kumar and T. Bhaskar, *Bioresour. Technol*., 2016, **199**, 398.

123 L. M. Kustov, A. L. Tarasov and A. L. Kustov, *Mendeleev Commun.*, 2020, **30**, 76.

124 L. M. Kustov, A. L. Tarasov, V. D. Nissenbaum and A. L. Kustov, *Mendeleev Commun*., 2021, **31**, 376.

125 A. T. Hoang, S. Nižetić, H. C. Ong, M. Mofijur, S. F. Ahmed, B. Ashok, V. T. V. Bui and M. Q. Chau, *Chemosphere*, 2021, **281**, 130878.

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