



Microwave directly accelerated cleavage of C-C and C-O bonds of lignin by copper oxide–peroxide reaction

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Abstract: Model erythro, phenolic and non-phenolic lignin β -O-4 dimer compounds were reacted with copper oxide and H2O2 at the electronic field maximum position of a single-mode 2.45-GHz microwave system equipped with a cavity resonator. The reaction products obtained via microwave heating and an oil bath heating in the same reaction vessel and same temperature profile were quantitatively compared. Dimer degradation proceeded through consecutive elementary reactions. The phenolic dimer was dehydroxylated and followed by the spontaneous cleavage of C_{α} -C_B and C-O-C bonds to produce guaiacol, vanillin, and vanillic acid. The reaction of the non-phenolic dimer produced veratric acid, veratraldehyde, and guaiacol. Microwave irradiation accelerated cleavage of the side chain and the oxidation of vanillin to vanillic acid. However, no acceleration of veratraldehyde oxidation to veratric acid or aromatic ring cleavage to produce dicarboxylic acids was observed. The selective acceleration of elementary reactions during the degradation of model lignin compounds indicated that microwaves interacted with reaction intermediates that were sensitive to electromagnetic wave.

Introduction

Concerns about the environmental impact of fossil fuels and the limited long-term supply of petroleum have stimulated the search for new energy resources. Woody biomass is a natural resource with the potential to meet this challenge.^[1] Lignin is one of the main components of woody biomass. It is considered as a source energy and fine chemicals through various processes.^[2] It is important to develop a new, efficient, and cost-effective depolymerization method for the utilization of woody biomass.

Woody biomass degradation usually requires elevated temperatures. Microwave (MW) energy generates heat by inducing the rotation of molecules in an electromagnetic field. It is known that MW irradiation also expedites some organic reactions compared to conventional conductive heating.^[3,4] It has

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been reported that the microwave-assisted depolymerization of lignin requires significantly less reaction time and/or increases the depolymerization yield over that of traditional methods.^[5-7] Zhu et al. reported that MW heating contributed to the selective cleavage of C_{α} - C_{β} bonds for the degradation of several β-O-4 model compounds, such as 2-(2'-methoxyphenoxy)-4'-hydroxyl-1-phenylethanol, in the presence of Pd/C or ferric sulfate as a catalyst.^[8,9] The degradation products obtained with microwave heating (MWH) and conventional heating (CH) were then compared. The authors reported that the heating method affected the reaction products. Pan et al. reported that with the assistance of MWH, degradation yields of the α -O-4 and β -O-4 lignin model dimers and some monomeric compounds were higher than those obtained from CH-assisted reactions. They screened various ionic liquids and alkali metal salts in their study of lignin model compound degradation and proposed degradation mechanisms. [10,11] Liu et al. reported efficient cleavage of lignin-carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent.^[12]

Our group developed a method for the direct production of vanillin and vanillic acid from wood particles using copper oxide (CuO) and peroxide (H₂O₂) under alkaline conditions. ^[13] Obvious microwave acceleration effects were observed in a precise comparison of the woody biomass depolymerization reactions performed with MWH and CH using the same reaction conditions and reaction vessel.

effects of electromagnetic waves on lignin The degradation have not been well studied closely at the molecular level. MW photons correspond to a frequency of 2.45 GHz is 0.0016-eV. This is not a sufficient amount of energy to break any chemical bonds. ^[14,15] However, we found that MW irradiation accelerated the reactions that produced vanillin and vanillic acid from wood particles when CuO and H₂O₂ were used under alkaline conditions. ^[13] There were two plausible explanations for the observed yield enhancement. (1) MW irradiation heated water molecules in the wood cell walls and promoted wood swelling. This, in turn, assisted the impregnation of the oxidative catalysts and solvents into the cell walls, leading to the enhanced cleavage of ether and C_{α} - C_{β} bonds in lignin. (2) MW irradiation directly accelerated the scission of covalent bonds in lignin. In this study, we focused on the second possibility and investigated whether MW irradiation directly accelerated the cleavage of the covalent C-C and C-O bonds in lignin using β -O-4 lignin dimer model compounds (Figure 1). To date, this is the first study to provide direct evidence of the acceleration of bond cleavage in lignin by MW irradiation using precisely controlled MW equipment. The findings of this investigation will facilitate the optimization of MW- assisted lignin volarization strategies for future industrial applications.

Results and Discussion

1. MWH- and CH-assisted degradation of lignin dimer model compounds

Lignin is a heterogeneous aromatic polymer composed of phenylpropane units connected by C–O–C and C–C bonds. Lignin dimer model compounds with β -O-4 structures with the most abundant linkage type in lignin were selected for the study. A phenolic β -O-4 dimer model (*erythro form*) compound (**1a**) was selected to represent lignin substructures with free phenolic hydroxyl groups at their terminal ends. A non-phenolic β -O-4 dimer compound (*erythro form*) (**1b**) was used to model lignin substructures with guaiacyl nuclei joined to adjacent phenyl propane units via ether linkages (Figure 1).

The lignin model compounds were reacted with CuO and H_2O_2 and heated by either MWH or CH in an alkaline medium. The same reaction time, temperature profile, stirring speed, and reaction vessel were used for both heating types (Figure S1). The reactions allowed us to precisely evaluate the effects of each heat source.

A MW cavity heating system was used for the MW heating study. Microwaves are electromagnetic waves. With this reactor, the maximum electronic field (E_{max}) and the maximum magnetic field (H_{max}) positions could be separated. This allowed us to compare the lignin depolymerization reactions in the maximum MW electronic field (E_{max}) to those of a conventionally heated process using an oil bath. In this study, the MW reactions were located in the E_{max} position (Figure 2). The input MW power and reflected MW power were recorded, and the reverse power was not allowed to exceed ~10% of the forward power (Figure S1).



Figure 1. Chemical structures of lignin β -O-4 model compounds used in this study.

2. Comparison of elementary reactions during the degradation of lignin dimer model compounds with MWH and CH assistance

The gas chromatography-mass spectrometry (GC-MS) spectra of the phenolic lignin dimer (1a) degraded at 150 °C for 20 min with MWH and CH are shown in Figure 3. The GC-MS spectra of the non-phenolic lignin dimer (1b) degraded at 170 °C for 20 min with MWH and CH are shown in Figure 4. Distinct differences were observed in the reactivities of the phenolic and non-phenolic lignin β -O-4 model compounds in the presence of CuO and H₂O₂ under alkaline conditions. The main degradation products of the phenolic lignin dimers were vanillin, vanillic acid, and guaiacol. The main degradation products of the nonphenolic lignin dimer were veratraldehyde, veratric acid, vanillin, vanillic acid, and guaiacol. Acetoveratrone and several dicarboxylic acids, including malonic acid, succinic acid, maleic acid, malic acid, and fumaric acid, were also detected. The identities of the products were confirmed by comparing their spectra to those of authentic samples. High-molecular-weight products were also detected by GC-MS.

The reaction fragments produced from the phenolic and nonphenolic dimer model compounds were the same between MWH and CH, indicating that the mechanisms of MWH and CH were essentially the same. Kim et al. and Zhu et al. reported that the reaction products obtained from the degradation of sulfonate lignin in the presence of potassium hydroxide or methanol using MWH were entirely different from those obtained when CH was used. They speculated that the differences between the reaction products arose from different reaction mechanisms. However, the CH and MWH reaction conditions were not identical in their experiments, because the MW reactor stopped the reaction at the maximum holding pressure.^[8,16]



Figure 2. (a) Cavity resonator. The sample was placed at the E_{max} position (H = 0) in the single-mode MW heating apparatus. (b) Schematic illustration of the 2.45-GHz MW heating system.

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Figure 3. (a) Total ion chromatogram (TIC) of phenolic dimer lignin model compound degradation products obtained with MWH (blue) and CH (red) at 150 °C for 20 min. (b) TIC of the dicarboxylic acid fraction of the phenolic dimer degradation products obtained with MWH at 150 °C for 20 min.

3. Lignin model compound reaction mechanisms

Degradation of the lignin model compounds involved several consecutive reactions: (1) the cleavage of C_{α} and C_{β} aryl ether linkages; (2) the cleavage of the C–O bond in the side chain; (3) the cleavage of the C–O bond in the methoxy group at the C4 position; (4) oxidation reaction of the aldehydes, (5) aromatic ring opening, and (6) repolymerization reactions (Table S1).

In the alkaline medium, the phenolic β -O-4 lignin model compound was oxidized to a quinone methide intermediate after deprotonation of the phenolic hydroxyl group. According to the mechanism proposed by Gierer, the quinone methide is transformed into a peroxy anion, which is then converted into a dioxetane in the presence of an oxidant. This leads to the cleavage of the C_{\alpha}-C_{\beta} bond to yield a phenolic aldehyde (Figure 5A).^[17-21] On the other hand, the mechanism proposed by Tarabenko for the anaerobic alkaline oxidation of the phenolic β -O-4 lignin model compound involves the consecutive formation



Figure 4. TIC of non-phenolic dimer lignin model compound degradation products obtained with MWH (blue) and CH (red) at 170 $^\circ C$ for 20 min.

of a phenoxy radical and a cinnamaldehyde-like intermediate, followed by C_{α} – C_{β} bond cleavage via a retro-aldol reaction that does not involve oxygen (Figure 5A). ^[22,23] Degradation of the phenolic β -O-4 lignin dimer in the presence of CuO and H₂O₂ could proceed in both pathways after formation of the quinone methide intermediate to produce vanillin (**2a**), vanillic acid (**3a**), and guaiacol (**4**). We found that MWH provided higher yields of these monomers than CH (Figure 6A–C).

Under aerobic alkaline conditions, *o*- and *p*-quinone intermediates were generated from the phenolic β -O-4 lignin dimer and decomposed into dicarboxylic acids via aromatic ring opening and the formation of muconic acid derivatives (Figure 5B). Oxidation by hydrogen peroxide and aromatic ring opening to produce dicarboxylic acids have been observed under mildly acidic conditions. ^[24,25] We found that dicarboxylic acids, including malonic acid, maleic acid, succinic acid, fumaric acid, and malic acid, were produced in the CuO/H₂O₂ system under alkaline conditions with either MWH or CH. Unlike the production of guaiacol, vanillin, and vanillic acid, yields of the dicarboxylic acids were not higher with MWH. Repolymerization was observed over the course of the reactions.

It has been proposed that degradation of the non-phenolic β -O-4 dimer under alkaline conditions proceeds via the formation of an epoxide intermediate through the cleavage of the C_a-C_β bond and the generation of phenolic units. ^[26–30] The reaction with CuO and H₂O₂ produced veratraldehyde (**2b**) and veratric acid (**3b**) as major degradation products. This suggested that this reaction proceeded via epoxide formation, as shown in Figure 5 (Route I Major). Remarkable accelerating effects of MWH were observed in these reactions (Figure 7C and D). Veratric acid formed through the oxidation of veratraldehyde, but MWH did not accelerate this reaction. The methoxy group at the C4 position was removed during the CuO/H₂O₂ reactions. This was

verified experimentally using veratraldehyde as the starting material. Vanillin was produced from veratraldehyde, but no MW-accelerated effects were observed in the demethylation step. MWH had a slight accelerating effect on the oxidation of vanillin to vanillic acid. In addition to the major route through the epoxide, a separate reaction pathway following the removal of the methoxy group was possible (Route II Minor). This was a minor pathway, because only a small amount of vanillin, vanillic acid, and trace amounts of the dicarboxylic acids were produced (Figure 7A, B, and F). Because no α -ketone derivatives were detected throughout the reactions, degradation pathway starting from formation of α -ketone is not included in Figure 5.

Unassigned peaks at retention time 19.4, 20.6 and 20.7 min in Figure 4 are estimated as γ -carboxylic compounds by mass fragment patterns. One possible route for this reaction is oxidation of γ -position to aldehyde, subsequent β -ether cleavage and further oxidation of the aldehyde to carboxylic acid. ^[31]



Figure 5. Proposed reaction mechanisms in the MW system. (a) Cleavage of the phenolic β -O-4 model compound; (b) formation of various dicarboxylic acids; and (c) cleavage of the non-phenolic dimer compound under alkaline conditions in the presence of CuO and H₂O₂.^[22-31]

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4. Time course of lignin model compound degradation and temperature-related effects of MWH and CH

The phenolic lignin dimer model was degraded at 130, 140, and 150 °C for 20 min with MWH and CH. The yields of vanillin and vanillic acid with MWH were 1.6- and 1.4-fold higher, respectively, than they were with CH at 150 °C (Figure 6). Yields of the major reaction products vanillin, vanillic acid, and guaiacol increased with increasing reaction temperature when MWH was used. However, the yields of these products did not increase noticeably with increasing temperature when CH was used. The time course of degradation differed in the two reaction systems. The MWH-assisted reactions generated higher yields during the first 10 minutes, but the yields of the MWH- and CH-assisted reactions were nearly equal at 15 minutes. The yields of the MWH-assisted reactions then increased until completion of the experiment, while those of the CH-assisted reactions showed slightly dropping. (Figure 8).

The non-phenolic β -O-4 lignin dimer compound was reacted at 130, 150, and 170 °C for 20 min with MWH and CH (Figure 7 and Figure S6). The non-phenolic dimer completely decomposed in the MWH-assisted reaction at 170 °C and generated decomposition products in higher yields than the CHassisted reaction. With CH at 170 °C, approximately 3.4% of the non-phenolic dimer remained at the end of the experiment. The yield of veratric acid obtained with MWH at 170 °C was 2.28 times higher than that obtained with CH. The yields of vanillin and vanillic acid with MWH at 170 °C were 25% and 9.6% higher, respectively, than those obtained with CH (Figure 7). The dependence of the veratraldehyde and guaiacol yields on temperature with MWH differed from that observed with CH. The time course of non-phenolic lignin dimer degradation is shown in Figure 9. The yields of guaiacol and veratric acid obtained with MWH and CH differed markedly, particularly after 10 min.

To further clarify the degradation process, veratraldehyde was used as a starting compound. During the 10-min reaction with CuO and H_2O_2 at 150 °C, the decomposition of veratraldehyde yielded veratric acid, vanillin, and vanillic acid with both MWH and CH (Figure 10). This indicated that veratraldehyde served as a reaction intermediate.

The production of vanillin and vanillic acid from veratraldehyde indicated the removal of the methoxy group at the C4 position. The cleavage of the methoxy C-O bond produced a phenolic nucleus, and the subsequent reaction pathway proceeded from the phenolic lignin units. There was a significant difference between the yields of veratraldehyde conversion to vanillin obtained with MWH (5.5%) and CH (6.2%). Vanillin and guaiacol were also subjected to degradation with MHW and CH at 150 °C for 10 min. Vanillic acid was generated via the oxidation of vanillin, with slight acceleration by MWH. Dicarboxylic acids were produced from the vanillin and guaiacol degradation. Veratric acid was stable at 150 °C for 10 min with either MWH or CH. No dicarboxylic acids or other degradation products were detected in the reaction products of veratric acid. In a control experiment, the lignin dimer model compounds were reacted in the absence of CuO and H_2O_2 , with the CuO catalyst alone, or with H_2O_2 in the absence of CuO (Figure S5 and Table S2). The results demonstrated that the combination of the catalyst and H_2O_2 was necessary to promote degradation.

The rate constant of non-phenolic dimer degradation reaction by MWH and CH at 170 °C were $4.1 \cdot 10^{-3} \cdot s^{-1}$ and $3.3 \cdot 10^{-3} \cdot s^{-1}$ respectively. The rate constant for labile phenolic dimer by MWH and CH was determined at 150 °C to give $3.0 \cdot 10^{-3} \cdot s^{-1}$ and $2.6 \cdot 10^{-3} \cdot s^{-1}$ respectively. Furthermore, the dielectric loss factors of substances in the reaction system affect the energy consumption efficiency. Dielectric loss factor of the alkaline solution used in this reaction system is higher than water, indicating that the MWH system is advantageous than CH in terms of energy efficiency in addition to the acceleration of bond cleavage in lignin.



Figure 6. Yields of phenolic lignin dimer degradation products obtained with MWH (blue) and CH (red) at 130 °C, 140 °C, and 150 °C for 20 min. (a) Vanillin; (b) vanillic acid; (c) guaiacol; (d) dicarboxylic acids: malonic acid, maleic acid, succinic acid, fumaric acid, and malic acid



Figure 7. Yields of non-phenolic lignin dimer degradation products obtained with MWH (blue) and CH (red) at 130 °C, 150 °C, and 170 °C for 20 min. (a) vanillin, (b) vanillic acid, (c) veratric acid, (d) veratraldehyde, (e) guaiacol, and (f) succinic acid.

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Figure 8. Time course for the production of (a) vanillin, (b) vanillic acid, and (c) guaiacol from the phenolic dimer compound with MWH (blue) and CH (red) at 150 $^\circ$ C for 10-20 min.



Figure 9. Time course for the production of (a) vanillin, (b) vanillic acid, (c) guaiacol, (d) veratric acid, and (e) veratraldehyde from the non-phenolic dimer model compound with MWH (blue) and CH (red) at 170 °C for 10-20 min.



Figure 10. TIC of degradation products. (a) veratraldehyde, (b) vanillin, (c) guaiacol, and (d) veratric acid obtained at 150 °C after 10 min with MWH.

5. Mechanistic insight for the selective acceleration of elementary reactions by MW irradiation

In this study, we found that the cleavage of C-C and C-O-C bonds in lignin side chains and the oxidation of vanillin were selectively accelerated. However, no acceleration of aromatic ring C-C cleavage was observed. The selective acceleration of elementary reactions indicated that microwaves interacted with reaction intermediates that were sensitive to electromagnetic wave. The mechanism of promotion could be explained by selective heating, a thermal effect, and/or MW specific effect (non-thermal effect). In both cases, acceleration could be attributed to either an increased dielectric loss factor in the transition state that generated thermal effects or to non-thermal effects, such as perturbation of the dipole moments of the reaction intermediates by microwaves. If electromagnetic waves affected their dipole moments, it would induce rotation of the molecules. It has been suggested that MW specific effects arise from the perturbation of the bonding angles in reactive species, although such effects await confirmation in future studies.^[15] A number of MW-specific effects have been reported in organic syntheses, including enantioselectivity.^[32] This phenomenon has been ascribed to an increase in frequency factor (A) by MW irradiation. In our reaction system, MWH generated larger A values than CH during the degradation of both the phenolic and nonphenolic dimers (Table S3). This result was consistent with non-thermal effects on elementary reactions. However, this conclusion awaits confirmation, because microscale increases in temperature would affect the Arrhenius factors.

Conclusions

Phenolic and non-phenolic β -O-4 lignin dimer model compounds were reacted with copper oxide and H₂O₂ using CH and microwave (MW) heating in the maximum electronic field position. CH and MWH generated the same reaction products, but the reaction rates in the two reaction systems differed. MW irradiation accelerated side chain cleavage and the oxidation of vanillin to vanillic acid. However, no acceleration was observed in the oxidation of veratraldehyde to veratric acid or aromatic ring cleavage for the production of dicarboxylic acids. The selective acceleration with MWH could not be explained by the activation of the CuO catalyst. The selective acceleration of elementary reactions during the degradation of lignin model compounds indicated that microwaves interacted with elementary reaction intermediates that were sensitive to electromagnetic waves. These results provide new insights into the MW effect on the intermediates involved in consecutive reactions pathways. This study is also important for lignin volarization due to the high reactivity of interunit linkages and aromatic rings in lignin.

Experimental Section

Chemicals

1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1a**, phenolic dimer), 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1b**, non-phenolic dimer), hydrogen peroxide (30 wt.%), copper (II) oxide (99.9%), 4-hydroxy-3-methoxybenzaldehyde (**2a**, vanillin), 4-hydroxy-3-methoxybenzoic acid (**3a**, vanillic acid), ferulic acid, malonic acid, succinic acid, maleic acid, malic acid, and fumaric acid were obtained from Wako Pure Chemical Co. (Osaka, Japan) and used as received. 1,3,5-Triisopropyl benzene (TIB), *N*,O-bis(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (BSTFA-TMCS), 2methoxyphenol (**4**, guaiacol), 3,4-dimethoxybenzaldehyde (**2b**, veratraldehyde), and 3,4-dimethoxybenzoic acid (**3b**, veratric acid) were purchased from TCI (Tokyo, Japan) and used as received.

MWH and CH experimental conditions

The cavity resonator (single-mode MW) heating system (Figure 2) consisted a waveguide, a semiconductor amplifier, a three-stub tuner, a plunger, and an isolator. The iris, which had a 50-mm slit parallel to the electric field, was used for concentrating the microwaves in the TE₁₀₃-mode cavity. The system enabled spatial separation of the electronic and magnetic fields that comprised the microwaves. The sample was placed in the maximum electric field position, and heated using 2.45-GHz microwave radiation. The internal temperature of the reaction vessel was monitored with a fiber optic thermometer (Neoptix, Québec City, Canada). The internal temperature and MW power data were recorded on a data logger. The structures of the lignin dimer model compounds (1a and 1b) were confirmed by nuclear magnetic resonance (MMR) spectroscopy prior to use in the depolymerization experiments (Supporting information).

Alkaline degradation of each lignin model compound (20 mg) was performed in a 2 N NaOH solution (5 mL) with CuO (20 mg) and 30% H₂O₂ (250 µL) in the cavity system. The reagents were placed in a 12-mL glass container with a silicon cover (Milestone General, Kawasaki, Japan). The MWH reaction was performed in the E maximum (E_{max}) field (N = 3) with constant magnetic stirring at 600 rpm. The reaction temperature was increased from room temperature to 130–170 °C within 5 min and maintained at that temperature for a total of 20 min. The reaction mixtures were then cooled to 50 °C (Figure S1).

Figure S2 contains a flow chart of the lignin compound degradation process and subsequent workup. A saturated Na₂SO₃ solution was added to the intermediate and final reaction mixtures to quench unreacted H₂O₂. The mixtures were filtered through cotton to remove CuO and acidified to pH ~2.0 using concentrated hydroxide chloride (35%). The acidified products were then extracted into ethyl acetate. The extracts were dried over MgSO₄ and filtered, and the solvent was evaporated under reduced pressure. CH experiments were conducted under conditions that were otherwise identical to those used for MWH experiments. The reactions were performed at the same agitation rate and internal temperatures in the same reaction vessel using an oil bath (TBX 203HA, Advantec Toyo Kaisha Ltd., Tokyo, Japan) (Figure S3).

Gas chromatography-mass spectrometry (GC-MS) analysis

The products were derivatized using BSTFA-TMCS and quantified from the total ion chromatograms (TIC) of GC–MS using 1,3,5-triisopropyl benzene as an internal standard. GC–MS analysis was performed on a QP2010SE GC–MS system (Shimadzu, Kyoto, Japan) using a 30 m x 0.25 mm (i.d.) DB-5 MS ultra-inert column with a 0.25-µm film thickness (Agilent Technologies). Helium was used as the carrier gas at a flow rate of 1.6 mL/min. Injection was performed in split mode using a 1:10 split ratio and an injection volume of 1.0 µL. The mass spectrometer was operated in electron impact ionization (EI) mode with an ionizing energy of 70 eV. The mass scan range was m/z 30–700. The column

temperature program began at an initial temperature of 50 °C for 3 min. The temperature was increased to 300 °C at a rate of 3 °C/min, then held at 300 °C for 7.5 min. Calibration curves were constructed using authentic standards. The identities of the reaction products were confirmed by comparing the mass peaks with those of the authentic standards and quantified using the calibration curves.

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- [1] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, Science, 2014, **344**,1246843
- [2] P. C. Rodrigues Pinto, E. A. Borges da Silva, A. E. Rodrigues, Biomass conversion, Springer. London Edn, 2012.Ch 12, pp. 381-420.
- [3] R.Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, *Tetrahedron Lett.*, **1986**, *27*, 279-282.
- [4] C. O.Kappe, Chem.Soc.Rev. 2008, 37, 1127-1139.
- [5] H. Li, Y. Qu, J. Xu, Production of biofuels and chemicals with microwave, Springer. Dordrecht, 2015. Ch microwave-assisted conversion of lignin pp. 66-80.
- [6] X. Ouyang, Y. Tan, X. Qiu, Fuel Process. Technol., 2016, 144, 181-185.
- [7] X. Ouyang, Y. Tan, X. Qiu, J. Fuel Chem. Technol., 2014, 42, 677-682.
- [8] G. Zhu, D. Jin, L. Zhao, X. Ouyang, C. Chen, X. Qiu, *Fuel Process. Technol.*, **2017**, *161*, 155-161.

- [9] G. Zhu, X. Ouyang, Y. Yang, T. Ruan, X. Qiu, RSC. Adv., 2016, 6, 17880-17887.
- [10] J. Pan, J. Fu, S. Deng, X. Lu, Energy Fuels, 2014, 28, 1380-1386.
- [11] J. Pan, J. Fu, X. Lu, Energy Fuels, 2015, 29, 4503-4509.
- [12] Y. Liu, W. Chen, Q. Xia, B. Guo, Q. Wang, S. Liu, Y. Liu, Jian Li, H. Yu, *ChemSusChem*, **2017**, *10*, 1692-1700.
- [13] C. Qu, M. Kaneko, K. Kashimura, K. Tanaka, S. Ozawa, and T. Watanabe, ACS Sustainable Chem. Eng., 2017, 5, 11551-11557.
- [14] C. O. Kappe, Angew. Chem. Int. Ed. Engl. 2004, 43, 6250-6284.
- [15] T. Sawada, T. Yamada, J. Jpn. Pet. Inst. 2018, 61, 121-128.
- [16] H. G. Kim, Y. Park, Ind. Eng. Chem. Res. 2013, 52, 10059-10062.
- [17] J. Gierer, F. Imsgard, I. Noren, Acta. Chem. Scand. B., 1977, 31, 561-572.
- [18] J. Gierer, Wood Sci. Technol., 1980, 14, 241-266.
- [19] J. Gierer, Hozforschung, 1982, 36, 43-51.
- [20] J. Gierer, Wood Sci. Technol., 1985, 19, 289-312.
- [21] J. Gierer, Wood Sci. Technol., 1986, 20, 1-33.
- [22] V. E. Tarabanko, Y. V. Hendogina, D. V. Petuhov, E. P. Pervishina, *React. Kinet. Catal. Lett.*, **2000**, *69*, 361-368.
- [23] V. E. Tarabanko, D. V. Petukhov, Chemisty for sustainable development, 2003, 11, 655-667.
- [24] R. Ma, Y. Xu, X. Zhang, ChemSusChem, 2015, 8, 24-51.
- [25] R. Ma, M. Guo, X. Zhang, ChemSusChem 2014, 7, 412-415.
- [26] S. Shimizu, T, Yokoyama, Y. Matsumoto, J. Wood Sci., 2015, 61, 529-536.
- [27] S. Shimizu, T. Yokoyama, T. Akiyama, Y. Matsumoto, J. Agric. Food Chem., 2012, 60, 6471-6476.
- [28] Y-Z. Lai, Wood and cellulosic chemistry. Marcel Dekker, Inc., New York, Edn, 2001. Ch 10, pp. 443-512.
- [29] W. Schutyster, T. Renders, S. Van den Bosch, S.-F. Koelewijn, G.T. Beckham, B.F. Sels, *Chem. Soc. Rev.* 2018, 47, 852-908.
- [30] C. Li, X. Zhao, A. Wang, G. W. Huber, T. Zhao, Chem. Rev. 2015, 115, 11559-11624.
- [31] A. Rahimi, A. Azarpira, H.Kim, J. Ralph, S.S. Stahl, J. Am. Chem. Soc. 2013, 135,6415-6418.
- [32] Microwaves in organic synthesis. Wiley-VCH Verlag& Co. Weinheim, Germany, Edn, 2012.

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