Effective Degradation of Cellulose by Microwave Irradiation in Alkaline Solution

Lama Jabareen

Bar-Ilan University Department of Chemistry

Moorthy Maruthapandi

Bar-Ilan University Department of Chemistry

Arumugam Saravanan

Bar-Ilan University Department of Chemistry

Aharon Gedanken (✉ gedanken@mail.biu.ac.il)

Bar-Ilan University

Research Article

Keywords: lignocellulosic biomass, sustainable society, acetic acid.

Posted Date: July 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-613178/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Cellulose on November 1st, 2021. See the published version at <https://doi.org/10.1007/s10570-021-04274-y>.

Abstract

The utilization of lignocellulosic biomass is effective to produce chemicals and fuels, which are of importance for the establishment of a sustainable society. The conversion of cellulose, which is the main component of the lignocellulosic biomass, into significant chemicals that can be further converted to different chemicals or fuels in the subsequent step, under gentle conditions is a promising route. Organic acids such as acetic acid, glycolic acid and formic acid are significant chemicals are examples of such products. A novel method to producing important platform chemicals from Micro-crystalline cellulose was developed. Micro-crystalline cellulose was degraded as a result of an oxidation with potassium chlorate by microwave radiation, in a one-pot procedure, efficient reaction conditions such as short reaction time and full conversion of the cellulose were identified. The reaction products have been analyzed by ^1H , ^{13}C NMR, XPS, TGA and XRD.

Introduction

Cellulose is the most abundant renewable resource of polysaccharides on earth, it is found in almost all plant sources, such as cotton (90%), corn cobs (45%), wood (40–45%), bagasse (40%), and on stalks (35%) (Sundarraj and Ranganathan 2018). Cellulose has broad applications in chemical industries due to its high availability, biocompatibility, biodegradability, and good mechanical properties. Cellulose is a linear polysaccharide, which is composed of d-glucopyranosyl units bonded by β (1 $\rightarrow$ 4)- glycosidic linkage. Each d-glucose molecule has hydroxyl (OH) groups connected with C2, C3, and C6, which can create intramolecular hydrogen bonds within and between the cellulose macromolecules. Therefore, it is apparent that these OH groups and their intramolecular hydrogen bonds construct the crystalline structure and the rigid structure of cellulose, making it insoluble in common organic solvents and water hindering the applications of cellulose (Liu et al. 2021). The passage from nonrenewable carbon resources (petroleum) to renewable bioresources is inescapable to meet the growing societal needs. The chemical industry presently crosses a paradigm shift from the utilization of fossil fuels to plants (cellulose) for the extraction of fine and bulk chemicals (Lin and Tanaka 2006). The conversion of renewable carbohydrates into an important platform chemical like levulinic acid, gluconic acid, lactic acid, and formic acid has attracted much importance in recent years (Deng et al. 2014). Various significant organic acids are derived from cellulose, for instance, gluconic acid, formic acid, lactic acid, isosorbide, xylitol, erythritol, glycerol, methanol, ethylene glycol, glycolaldehyde, glycolic acid, hydroxymethylfurfural, and levulinic acid by catalysis, hydrolysis, and oxidative cleavage (Li et al. 2018; Delbecq and Len 2018; Wang et al. 2018b). These organic acids are used in many commercial industries as food preservative, antibacterial agent in livestock feed, textiles, fuel cell, leather, cosmetics, curing agent, and flavoring agent. Particularly, formic acid (FA) is a value-added chemical that is applied for the production of medicaments, solvents, fragrances, and fibers, as well as for the conservation of food products, forage and is also used in pulp and leather industries (Aguilo and Horlenko 1980). FA is a very promising substrate for the synthesis of molecular hydrogen over metal catalysts (Zacharska et al. 2015; Wang et al. 2013; Zhang et al. 2013). The yield of formic acid from cellulose is as important as

converting CO₂ to formic acid owing to the renewable nature of cellulose (Herrick and Lipták 2003). As already mentioned microcrystalline cellulose (MCC) is mostly insoluble in water as well as in the most common organic solvents at gentle temperatures. This is an obstacle in the activation of MCC under mild conditions. Also, there are different types of bonds (C-C and C-O) in MCC macromolecules that create difficulty in the breakdown of cellulose (MCC). Hence, the cleavage or oxidation of C-C and C-O bonds in MCC allows selective production of a compound (Deng et al. 2014).

Considering the novelty of the paper it must be pointed out that some of the oxidizing materials used in the current experiments were already attempted towards the degradation of cellulose. For example, potassium persulfate were used by Davaritouchaee et al. (Davaritouchaee et al. 2019). In the oxidation of wheat straw and revealed an increase in cellulose degradation temperature and decrease in activation energy from 259 to 223 KJ/mol compared to the raw material. In another works, potassium permanganate was used to oxidize the cellulose, the oxidation leads to introduce the carboxyl groups into the oxidized polymer (Milanovic et al. 2021; Zhou et al. 2018). Cotton yarns were oxidized with potassium periodate solution with TEMPO systems. Sodium chlorite was also employed for the same purpose and yielded (Toshikj et al. 2019). However, Microwave radiation was never used in the oxidation of cellulose.

The current work reports on the successful oxidative degradation of MCC into important organic acids such as formic acid (FA), acetic acid (AA), and glycolic acid (GA) by an inorganic oxidizing reagent potassium chlorate (KClO₃) under short and facile one-step microwave-assisted method without employing any additives. The different time of microwave operation was optimized in this study. This technique not only reduces the energy consumption and the processing time but enables the service of novel chemistry tool.

Materials And Method

Materials

The chemicals used in this study, namely, microcrystalline cellulose (MCC), KClO₃, and NaOH were purchased from Sigma Aldrich, Israel. Potassium permanganate (KMnO₄), ammonium perchlorate (NH₄ClO₄), potassium persulfate (K₂S₂O₈), potassium chromate (K₂CrO₄), potassium dichromate (K₂Cr₂O₇), potassium periodate (KIO₄), potassium perchlorate (KClO₄), and sodium periodate (NaIO₄) were obtained from Sigma Aldrich, Israel and used as oxidizing reagents. The chemicals were used as received without another purification. Deionized water was used in all the experiments.

Sample Preparation

Dissolution of microcrystalline cellulose (MCC) in aqueous NaOH

A 0.5 g of cellulose was suspended in 26.9 mL of water and 2.5 g of NaOH was then added to the suspension. The mixture was shaken to dissolve the NaOH at room temperature. The suspension was cooled and held in the refrigerator until it became a solid frozen mass. The frozen solid was then allowed to thaw at room temperature and was transformed into a gel-like mass. 20.6 mL of water was added to the gel-like compound, after a gentle shaking, a clear cellulose solution was obtained (Isogai and Atalla 1998).

Oxidation And Degradation Of The Mcc

The oxidation of the MCC was attempted using different oxidizing reagents conducting the reaction with both methods i. e. microwave and hydrothermally. The various oxidation agents used in this study are presented in Table 1. In addition, it is worth noting that all the experiments were carried out under basic conditions (pH = 12) and the Microwave oven was operated for 1, 3, or 5 minutes in all the experiments. You didn't mention the nature of the MW oven was it a domestic oven or a commercial oven

0.1g of the potassium chlorate was added to a 250 mL round bottom flask (RB) that contained 50 ml of the clear cellulose solution and then the RB was subject to microwave irradiation for 5 min. The resulting product was centrifuged at 8000 rpm for 30 min. The formation of the gel-like product was allowed for all the characterizations.

Table 1
Summary of literature reports on the degradation of cellulose by oxidation using various oxidizing reagents.

Reagent	Solvent	PH	Time (min)	Final product
Potassium permanganate	Alkaline solution	Basic	1,3, and 5	-
Ammonium perchlorate	Alkaline solution	Basic	1,3, and 5	-
Potassium persulfate	Alkaline solution	Basic	1,3, and 5	-
Potassium chromate	Alkaline solution	Basic	1,3, and 5	-
Potassium dichromate	Alkaline solution	Basic	1,3, and 5	-
Potassium periodate	Alkaline solution	Basic	1,3, and 5	-
Sodium periodate	Alkaline solution	Basic	1,3, and 5	-
Potassium perchlorate	Alkaline solution	Basic	1,3, and 5	-
Potassium chlorate	Alkaline solution	Basic	1,3, and 5	FA, AA, and GA

Table 1 reveals that only KClO₃ was successfully oxidizing the cellulose.

Characterization

The chemical structure of the oxidized MCC was characterized by ^1H and ^{13}C nuclear magnetic resonance (NMR). It was carried out on a Bruker 300 spectrometer using NaOH/D₂O as the solvent. The elemental composition and chemical bonding were analyzed using X-ray photoelectron spectroscopy (XPS, Nexsa spectrometer (England)). The detection and identification of the degradation of the microcrystalline cellulose were also measured by thermogravimetric analysis (TGA), which was performed on a Perkin Elmer Clarus 680/Clarus SQ 8C. The flow rate of nitrogen was 20 ml/min, and the temperature rate was increased at 10°C/min. The samples (MCC and the oxidized MCC) were heated from 30°C to 950°C. The difference in the morphology of the surface and the size of the pure MCC's particles and the DMCC (degraded MCC) was characterized by environmental scanning electron microscopy (E-SEM) using (*Quanta* FEG 250 of FEI) device at 5 KV. The crystalline nature of the MCC and oxidized MCC composites were assessed using an X-ray diffraction technique measured by a Bruker (Germany) AXS D8 Advance diffractometer.

Results And Discussion

NMR spectrum of the attained product

The ^1H NMR and ^{13}C NMR spectra of the oxidized MCC were given in Figs. 1a and 1b. The evidence for the successful oxidation of the MCC is obtained from the ^1H NMR (Fig. 1a) and ^{13}C NMR (Fig. 1b) aqueous solution of the product. Significant differences are observed between the initial MCC and the final MCC after the oxidation in an aqueous solution. The ^{13}C NMR spectra of initial material are obtained from previous literature (Heinze and Koschella 2005). The results showed the comparison between the original NMR spectrum of the starting compound and the product obtained after the oxidation of the MCC. Likewise, Fig. 2 displays the ^{13}C Solid-State NMR (SSNMR) spectrum of the cellulose. The SSNMR in Fig. 2 matches very well other spectra that have been published previously (Hussin et al. 2018; Okushita et al 2012; Newman 1996; Wang et al 2013). The main peaks of the cellulose appear at 65.28, 71.85, 72.55, 75.15, 89.08, and 105.36 ppm and are assigned to C6, C2, C3, C5, and C1, respectively (Scheme 2). It is clear from Figs. 1a, b that these peaks have disappeared in the product indicating the successful oxidation and elimination of the cellulose. Because of Figs. 1a and b, the successful oxidation of cellulose is corroborated by the peak changes in the final product.

Figure 1 illustrates results for the aqueous ^1H NMR of the NaOH treated product. Figure 1b presents the corresponding ^{13}C NMR of the solution in D₂O of the NaOH solution of the product. The disappearance of the cellulose peaks is the most remarkable feature, indicating the successful oxidation of the cellulose.

Figure 1b shows the peaks of the ^{13}C NMR spectrum located at 24 and 172 ppm which represent the carbons of acetic acid. The two peaks at 62 and 182 ppm represent the carbons of glycolic acid, and the peak at 169 ppm is attributed to formic acid. Moreover, the peaks of the proton NMR spectrum also matching the hydrogens of the formic acid, acetic acid, and glycolic acid, which are found in H (t) at

1.811, 1.837 and 1.847 ppm assigned for acetic acid, for formic acid it had presented at 8.111 ppm and for glycolic acid it had located at 3.586ppm.

Table 2
¹H and ¹³C chemical shift (δ, ppm) values of the decomposition products of cellulose.

Compound	¹ H Chemical shift (δ, ppm)	¹³ C Chemical shift (δ, ppm)
Formic acid	¹ H (singlet) at 8.111	169
Acetic acid	¹ H (triplet) at 1.811, 1.837 and 1.847	24, 172
Glycolic acid	¹ H (singlet) at 3.586	62 and 182

Moreover, in previous studies, the oxidizing materials that were used for cellulose degradation, such as vanadium (V(V))-contained catalyst, a high-cost material, usually undergo at least two reactions (Lu et al. 2018). Another oxidizing catalyst, Mo-V-P heteropoly acids (HPA), have a long catalytic synthesis (Gromov et al. 2016) carbon electrodes modified by gold nanoparticles (Sugano et al. 2016) are also expensive, TEMPO-mediated oxidation system requires preparation steps (Isogai et al. 2018) The oxidation of cellulose with the catalytic aqueous mixture of, H₅PV₂Mo₁₀O₄₀ + H₂SO₄ with molecular oxygen (Lu et al. 2016), is a very slow process compared to our method.

Thermochemical conversion of cellulosic materials can also be achieved by microwave heating (Motasemi and Afzal 2013; Al Shra’Ah and Helleur 2014; Wang et al. 2008). In conventional thermal heating, the energy is transferred from source to the center of material via radiation, convection, and conduction, while in the microwave or dielectric heating the electromagnetic energy is converted to thermal energy from inside the sample.

The microwave-assisted reactions can be completed more efficiently in comparison with other thermal methods due to efficient heat transfer profiles. For this reason, microwave heating appears as one of the promising techniques for carrying out the biomass pyrolysis process, accelerating chemical reactions and reducing the processing costs. The combination of microwave radiation and KClO₃ is novel and has never been reported before.

3.2. Thermogravimetric Analysis (Tga)

Thermal degradation behavior of oxidized MCC

The TGA analysis (Fig. 3) shows the curves of the thermal decomposition of the MCC and the DMCC obtained after the potassium chlorate treatment under microwave conditions. The thermal decomposition

(T_d) point of the DMCC (degraded MCC) was approximately 38°C, which was lower than the original decomposition temperature of pristine cellulose (300°C). From 30 °C to 300°C, the mass of cellulose was almost unchanged, In contrast, the onset decomposition temperature for the degraded cellulose was 38 °C and the weight loss continues till 90 °C. The difference between the two curves is clear indicating the absence of cellulose from the DMCC. The difference between MCC and DMCC is also reflected in their stability. The highest boiling point of the degradation products (AA, FA and GA) is 118 °C which is belongs to acetic acid. The curves of the DMCC showing that there is a continuously weight loss in temperature less than 200 °C. At 450°C, MCC and DMCC show residual weights of 0 and 23%. The DMCC was collected from the reaction mixture after the completion of the oxidation process (Rosli et al. 2015). The 18% of the DMCC left after heating to 800 C⁰ is perhaps carbon char that was left from the decomposition of the degradation products.

3.3.SEM

SEM helps to reveal the morphological and topographical features of the precursors and the resulting carbon composites. The E-SEM images of cellulose before and after the oxidation are presented in Fig. 4a (before) and 4b (after). Before the oxidation and the degradation, the cellulose particles resembled blocks and logs of wood. After degradation, the original crystallinity of the cellulose particles is lost. The results show that the morphology structure of cellulose crystals has changed after the oxidation which indicates substantiate the TGA results on the successful degradation of the cellulose.

3.4. X-ray diffraction (XRD)

To further determine the change in crystallinity, the XRD patterns of microcrystalline cellulose and degraded cellulose are shown in Fig. 5. For the MCC there are crystallographic diffraction peaks at about $2\theta = 34.45^\circ$, $2\theta = 22$ and $2\theta = 15$ (Pang et al. 2014), indicating the characteristic cellulose I crystal structure. After the oxidation and degradation, the crystalline peaks near 22° and 35° disappeared. Also the peak around $2\theta = 15$ gets more wide and less sharp. These results demonstrate that the crystallinity of cellulose was noticeably decreased. The peak at 30° belongs to the holder, as it can be seen by the curves of the empty holder, that it contains peaks around $2\theta = 30^\circ$ and $2\theta = 41^\circ$. This result is in accordance with the SEM results, confirming that the oxidation reaction decomposes the whole cellulose polymer and diminishes its crystallinity.

3.5. X-ray photoelectron spectroscopy (XPS)

XPS analysis provides an information about the surface elemental composition and functional groups. The images in Fig. 6, obtained from XPS patterns of the MCC and the DMCC which present the difference in the functional groups that appear in the product. Both of them consist mainly of carbon and oxygen. The cellulose polymer had two types of functional group, the multiple hydroxyl groups, per unit of the polymer had one primary alcohol, two secondary alcohol, and one ether group. Figure 6a shows the C1s

spectra of MCC which is deconvoluted into two peaks located at 285 and 286.3 eV, representing C–C/C–H and C–O–C /C–OH groups. However, in the C1s spectra of the DMCC, reveal additional peaks were found at 288.04 eV and 289.3 eV, corresponding to C = O and COO[−] as well as a shoulder at 286.e eV assigned to C-OH functional group. These peaks belong to the organic acids after the degradation (FA, AA and GA). Also in Fig. 6c,d appears the comparison of the two oxygen (O1s) spectra of the MCC and DMCC, these results reveal the new bonds in the product (DMCC) that didn't appear in the original pattern of the MCC. The peaks here in the O1s spectra of the DMCC disclosed three main classes of oxygen bonds:

Bond	Peak value (eV)
O-(C = O [*])-C bonds peaks	532.2 which exist in GA and AA
O [*] -(C = O)-C bonds peaks	533.7 which exist in GA and AA
Carbonyl, Organic C = O bonds	532.6

All the characterization experiments lead to the same conclusion the DMCC is a product different from the cellulose. In this work, we found that only potassium chlorate was able to oxidize the MCC. None of the other nine well-known oxidizing agents was successful in the same oxidation process neither by Microwave nor hydrothermally. Even for the Chlorate ions, negative results were obtained when the reaction was carried out hydrothermally. We are therefore left with two major questions 1) why only ClO₃^{−1} can oxidize the MCC under MW radiation and secondly why these products are obtained only by Microwave irradiation?

At first, we tried to correlate the oxidizing power to the standard oxidation potential of these ten oxidizing agents which are presented in Table 4. The table indicates evidently that the chlorate is not the strongest oxidizing agent. However, to this table, we must add the basic conditions under which the reaction is performed, namely, pH ~ 11. Under these basic conditions, the chlorate is the strongest oxidizing agent, while for example, K₂S₂O₈, decomposes fast under these conditions to HSO₄[−]. Potassium permanganate is also a stronger oxidizing agent than ClO₃^{−1} but this is only true for acidic medium, it is a weak oxidant in neutral and alkaline medium (Peroxide et al. 2019). Potassium dichromate acts as an oxidizing agent only in an acidic medium. It doesn't act as an oxidizing agent in basic medium because as it involves in non-redox reaction. It forms chromate ion in basic medium. In a basic medium. Cr has (+ 6) oxidation state in dichromate as well as the as in the chromate form. It reacts according to the following reaction.

Table 4
Standard Oxidation potential
values of the reagents

Reagent	Oxidation potential
$K_2S_2O_8$	2.1
$KMnO_4$	1.49
$KClO_4$	1.39
NH_4ClO_4	1.39
$K_2Cr_2O_7$	1.36
$KClO_3$	1.15
$NaIO_4$	-0.7
KIO_4	-1.650
K_2CrO_4	-6.5

The main products in the one-step oxidation of cellulose by the chlorate ions were formic acid, glycolic acid and acetic acid.

To comprehend the mechanism of the cellulose's degradation, we have examined whether the degradation mechanism involves first the decomposition of the cellulose to glucose. This was done by a control experiment in which identical conditions were used to oxidize the glucose as for the cellulose. The NMR results (fig.S1) display different spectrum comparing with the peaks in Fig. 1b. The NMR peaks indicate that different products such as glucuronic acid and glucose are obtained in the oxidation of glucose. Moreover, unlike with cellulose the glucose was not completely degraded. These results show that the degradation of cellulose does not proceed via the glucose. Returning to the second question of why MW radiation. Microwave is a well-known mean for accelerating chemical reactions especially for reactants or catalysts with a dipole moment. The ability to accelerate chemical reaction is either attributed to heating effect in which the "real" temperature is higher than the measured temperature. This is frequently termed superheating (Tao et al. 2021) or the existence of hot spots (Liu et al. 2020). The other explanation is due to a drastically reduced activation energy offering the reaction to progress along a new mechanistic route. This is a special useful when the transition state has a dipole moment which will strongly interact with the MW radiation.

In the current reaction these two factors play an important role in accelerating the reaction. The presence of many ions ClO_3^{-1} and OH^{-1} plus their counter ions help to absorb the MW radiation and lead to hot spots. In addition, the transition state of the reaction is also having a dipole moment and speeding up

this chemical reaction. The first step; the reaction endures the base hydrolysis forms the glucose. The next step is the glucose oxidizes by KClO_3 and forms a different product with MW condition which is provided in the scheme 2. The formation of the acids was confirmed by NMR techniques (Wang et al. 2018a).

Conclusion

In conclusion, we presented a fast and facile method to convert the highly micro-crystalline commercial cellulose into precious and significant product like formic acid, acetic acid, and glycolic acid. The novelty of this strategy for decomposing cellulose comprises two concepts: (i) to use an inorganic oxidizing reagent to oxidized the cellulose and (ii) expose the degradation of cellulose by microwave irradiation for a maximum of 5 min. Therefore, the practicability of using cellulose as a feedstock for important chemicals extraction is demonstrated.

Declarations

Conflict of interest

The authors have no conflicts of interest to declare that they are relevant to the content of this article.

Human and animal rights

This article does not contain any studies with human participants or animals performed by any of the authors.

References

1. Aguilo A, Horlenko T (1980) Formic Acid. *Hydrocarb Process* 59:120–130.
<https://doi.org/10.4324/9780429447341-40>
2. Al Shra'Ah A, Helleur R (2014) Microwave pyrolysis of cellulose at low temperature. *J Anal Appl Pyrolysis* 105:91–99. <https://doi.org/10.1016/j.jaap.2013.10.007>
3. Davaritouchaee M, Hiscox WC, Martinez-Fernandez J, et al (2019) Effect of reactive oxygen species on biomass structure in different oxidative processes. *Ind Crops Prod* 137:484–494.
<https://doi.org/10.1016/j.indcrop.2019.05.063>
4. Delbecq F, Len C (2018) Recent advances in the microwave-assisted production of hydroxymethylfurfural by hydrolysis of cellulose derivatives — A review. *Molecules* 23:.
<https://doi.org/10.3390/molecules23081973>
5. Deng W, Zhang Q, Wang Y (2014) Catalytic transformations of cellulose and cellulose-derived carbohydrates into organic acids. *Catal Today* 234:31–41.
<https://doi.org/10.1016/j.cattod.2013.12.041>

6. Gromov N V, Taran OP, Delidovich I V, et al (2016) Hydrolytic oxidation of cellulose to formic acid in the presence of Mo-V-P heteropoly acid catalysts. *Catal Today* 278:74–81.
<https://doi.org/10.1016/j.cattod.2016.03.030>
7. Heinze T, Koschella A (2005) Solvents applied in the field of cellulose chemistry: a mini review. *Polímeros* 15:84–90. <https://doi.org/10.1590/s0104-14282005000200005>
8. Herrick RA, Lipták BG (2003) Carbon dioxide. *Instrum Eng Handb Process Meas Anal Fourth Ed* 1242–1244. <https://doi.org/10.1016/b0-12-227090-8/00095-6>
9. Hussin MH, Husin NA, Bello I, et al (2018) Isolation of microcrystalline cellulose (MCC) from oil palm frond as potential natural filler for PVA-LiClO₄ polymer electrolyte. *Int J Electrochem Sci* 13:3356–3371. <https://doi.org/10.20964/2018.04.06>
10. Isogai A, Atalla RH (1998) Dissolution of cellulose in aqueous NaOH solutions. *Cellulose* 5:309–319. <https://doi.org/10.1023/A:1009272632367>
11. Isogai A, Hänninen T, Fujisawa S, Saito T (2018) Review: Catalytic oxidation of cellulose with nitroxyl radicals under aqueous conditions. *Prog Polym Sci* 86:122–148.
<https://doi.org/10.1016/j.progpolymsci.2018.07.007>
12. Li S, Deng W, Wang S, et al (2018) Catalytic transformation of cellulose and its derivatives into functionalized organic acids. *ChemSusChem* 11:1995–2028.
<https://doi.org/10.1002/cssc.201800440>
13. Lin Y, Tanaka S (2006) Ethanol fermentation from biomass resources: Current state and prospects. *Appl Microbiol Biotechnol* 69:627–642. <https://doi.org/10.1007/s00253-005-0229-x>
14. Liu CF, Sun RC, Zhang AP, et al (2007) Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium. *Carbohydr polym* 68:17-25. <https://doi.org/10.1016/j.carbpol.2006.07.002>
15. Liu K, Du H, Zheng T, et al (2021) Recent advances in cellulose and its derivatives for oilfield applications. *Carbohydr Polym* 259:117740. <https://doi.org/10.1016/j.carbpol.2021.117740>
16. Liu Z, Meng H, Li C, et al (2020) Degradation of Biologically Treated Coking Wastewater over CuOx/PAC, CuOx/GAC, and CuOx/ACF Catalysts under Microwave Irradiation in the Presence of H₂O₂. *J Environ Eng* 146:04020014. [https://doi.org/10.1061/\(asce\)ee.1943-7870.0001653](https://doi.org/10.1061/(asce)ee.1943-7870.0001653)
17. Lu T, Hou Y, Wu W, et al (2018) Catalytic oxidation of cellulose to formic acid in V(V)-Fe(III)-H₂SO₄ aqueous solution with O₂. *Fuel Process Technol* 173:197–204.
<https://doi.org/10.1016/j.fuproc.2018.02.001>
18. Lu T, Niu M, Hou Y, et al (2016) Catalytic oxidation of cellulose to formic acid in H₅PV₂Mo₁₀O₄₀ + H₂SO₄ aqueous solution with molecular oxygen. *Green Chem* 18:4725–4732.
<https://doi.org/10.1039/c6gc01271j>
19. Milanovic JZ , Milosevic M , Jankovic-Castvan I , et al (2021) Capillary rise and sorption ability of hemp fibers oxidized by non-selective oxidative agents: hydrogen peroxide and potassium permanganate. *J Nat Fibers* 16:1-6. <https://doi.org/10.1080/15440478.2020.1870609>

20. Motasemi F, Afzal MT (2013) A review on the microwave-assisted pyrolysis technique. *Renew Sustain Energy Rev* 28:317–330. <https://doi.org/10.1016/j.rser.2013.08.008>
21. Newman RH, Davies LM, Harris PJ (1996). Solid-state ¹³C nuclear magnetic resonance characterization of cellulose in the cell walls of *Arabidopsis thaliana* leaves. *Plant physiol* 111:475-85. <https://doi.org/10.1104/pp.111.2.475>
22. Okushita K, Komatsu T, Chikayama E, et al (2012) Statistical approach for solid-state NMR spectra of cellulose derived from a series of variable parameters. *Polym J* 44:895-900. <https://doi.org/10.1038/pj.2012.82>
23. Pang Q, Wang L, Yang H, et al (2014) Cellulose-derived carbon bearing–Cl and–SO₃H groups as a highly selective catalyst for the hydrolysis of cellulose to glucose. *RSC adv* 4:41212-8.
24. Peroxide H, Kelly MT, Blaise A, et al (2019) Permanganate FOOD AND NUTRITIONAL ANALYSIS | Wine Physical and Chemical Treatment Processes for Leachate Redox Transformations SPECTROPHOTOMETRY | Inorganic Compounds Fundamentals: Ligands , Complexes , Synthesis , Purification , and Structure SECONDAR
25. Rosli N, Ambak K, Daniel BD, et al (2015) *Jurnal Teknologi*. 1:1–6
26. Sugano Y, Kumar N, Peurla M, et al (2016) Specific Electrocatalytic Oxidation of Cellulose at Carbon Electrodes Modified by Gold Nanoparticles. *ChemCatChem* 8:2401–2405. <https://doi.org/10.1002/cctc.201600190>
27. Sundarraj AA, Ranganathan TV (2018) A review on cellulose and its utilization from agro-industrial waste. *Drug Invent Today* 10:89–94
28. Tao Y, Teng C, Musho TD, et al (2021) Direct Measurement of the Selective Microwave-Induced Heating of Agglomerates of Dipolar Molecules: The Origin of and Parameters Controlling a Microwave Specific Superheating Effect. *J Phys Chem B* 125:2146–2156. <https://doi.org/10.1021/acs.jpcc.0c10291>
29. Toshikj E, Tarbuk A, Grgić K, et al (2019) Influence of different oxidizing systems on cellulose oxidation level: introduced groups versus degradation model. *Cellulose* 26:777–794. <https://doi.org/10.1007/s10570-018-2133-4>
30. Wang G, Meng Y, Zhou J, Zhang L (2018a) Selective hydrothermal degradation of cellulose to formic acid in alkaline solutions. *Cellulose* 25:5659–5668. <https://doi.org/10.1007/s10570-018-1979-9>
31. Wang M, Ma J, Liu H, et al (2018b) Sustainable Productions of Organic Acids and Their Derivatives from Biomass via Selective Oxidative Cleavage of C-C Bond. *ACS Catal* 8:2129–2165. <https://doi.org/10.1021/acscatal.7b03790>
32. Wang T, Park YB, Caporini MA, et al (2013) Sensitivity-enhanced solid-state NMR detection of expansin's target in plant cell walls. *Proc Natl Acad Sci* 110:16444-9. <https://doi.org/10.1073/pnas.1316290110>
33. Wang X, Chen H, Luo K, et al (2008) The influence of microwave drying on biomass pyrolysis. *Energy and Fuels* 22:67–74. <https://doi.org/10.1021/ef700300m>

34. Wang Z-L, Yan J-M, Ping Y, et al (2013) An Efficient CoAuPd/C Catalyst for Hydrogen Generation from Formic Acid at Room Temperature. *Angew Chemie* 125:4502–4505.
<https://doi.org/10.1002/ange.201301009>
35. Zacharska M, Podyacheva OY, Kibis LS, et al (2015) Ruthenium Clusters on Carbon Nanofibers for Formic Acid Decomposition: Effect of Doping the Support with Nitrogen. *ChemCatChem* 7:2910–2917. <https://doi.org/10.1002/cctc.201500216>
36. Zhang S, Metin Ö, Su D, Sun S (2013) Monodisperse AgPd alloy nanoparticles and their superior catalysis for the dehydrogenation of formic acid. *Angew Chemie - Int Ed* 52:3681–3684.
<https://doi.org/10.1002/anie.201300276>
37. Zhou L, Li N, Shu J, et al (2018) One-Pot Preparation of Carboxylated Cellulose Nanocrystals and Their Liquid Crystalline Behaviors. *ACS Sustain Chem Eng* 6:12403–12410.
<https://doi.org/10.1021/acssuschemeng.8b02926>

Figures

a

b

Figure 1

a. ^1H NMR of the DMCC b. ^{13}C NMR spectrum for the DMCC

Figure 2

^{13}C Solid-State NMR (SSNMR) spectrum of the cellulose.

Figure 3

The TGA curves of the compounds MCC (microcrystalline cellulose) and DMCC (degraded MCC).

Figure 4

Scanning electron microscopy (SEM) images of (A) Commercial microcrystalline cellulose (MCC) (B) degraded Microcrystalline cellulose (DMCC).

Figure 5

XRD patterns of the microcrystalline cellulose before and after the oxidation and the degradation.

Figure 6

XPS patterns of the (a) C1s spectra of MCC, (b) C1s spectra of DMCC c) O1s spectra of MCC, (d) O1s spectra of DMCC.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [Scheme2.png](#)
- [supportinginformation72710.docx](#)