Bioethanol Production from Unpretreated Cellulose under Neutral Selfsustainable Hydrolysis/Hydrogenolysis Conditions Promoted by the Heterogeneous Pd/Fe$_3$O$_4$ Catalyst

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S Supporting Information

ABSTRACT: The direct conversion of untreated microcrystalline cellulose into C$_2$−C$_3$ alcohols, through a one-pot process promoted by the heterogeneous bimetallic Pd/Fe$_3$O$_4$ catalyst, is presented. The process is selfsustainable without the addition of external molecular hydrogen or acid/basic promoters and is mainly selective toward ethanol. At 240 °C, a complete cellulose conversion was reached after 12 h with an ethanol molar selectivity of 51% among liquid products. The synergistic effect played by water (which aids in the chemical pretreatment means of cellulose through the hydrolysis process) and the Pd/Fe$_3$O$_4$ catalyst (which catalyzes the hydrogenolysis reaction driving the pattern of obtained products) is elucidated.
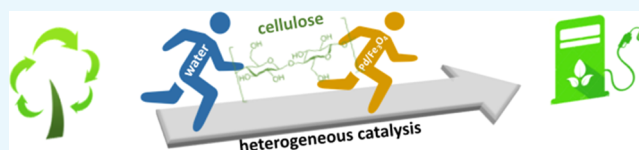
1. INTRODUCTION

Nonedible lignocellulosic biomasses, including recovered wastes from agriculture and food industries, represent a powerful feedstock for the sustainable production of fuels and chemicals.[1−5] At present, the most adopted technologies for the catalytic upgrading of waste lignocellulosic feedstocks generally require the separation of lignocellulose in its key constituents (cellulose, hemicellulose, and lignin). An important class of these pretreatments are organosolv processes in which the (very low) conversion of the cellulosic part and the catalyst recycling have been recognized as key tasks to be tackled.[6,7] In this context, the valorization of cellulose, the main constituent of lignocellulosics, plays a crucial role for its catalytic upgrade.[8,9] Several strategies to transform cellulose into valuable products have been investigated. However, the heterogeneously catalyzed hydrolysis of cellulose is still a challenging process because a solid–solid reaction needs to be activated, the polymer being insoluble in water or other common reaction media;[10−12] for this reason, acid or basic additives are quite often used.[10−15] Furthermore, deoxygenative processes (hydrogenolysis), through the breaking of C−O, C−C, C−H, and O−H bonds, allow the reduction of the oxygen content in lignocellulosic biomasses with the simultaneous addition of H$_2$.[16] Therefore, it can be possible to promote, in a unique step, the conversion of cellulose into short polyols and alcohols, through the tandem hydrolysis/hydrogenolysis reaction, which is considered as a key tool to obtain high-value added products starting from biomass-based feedstocks.[17−19] In this regard, since one of the main drawbacks of the cellulose hydrogenolysis process is closely related to the use of high-pressure molecular hydrogen (some examples of

metal catalysts applied to the conversion of cellulose in the presence of molecular H$_2$ are reported in Table S1), which limits the application of such a process because of economical and safety reasons, the use of an indirect H-source has been generally proposed. At present, probably one of the best approaches, suggested by Fukuoka and co-workers, involves the use of 2-propanol as an indirect H-source for the production of hexitols from cellulose.[19,20] Moreover, to favor the conversion of the microcrystalline cellulose (MCC) into useful chemicals, a physicochemical pretreatment to break down its robust structure is generally required to make cellulose more suitable for its catalytic conversion.[21−23] However, these pretreatments present important limitations in terms of time and sustainability of the valorization process. Therefore, the ideal approach is to use unpretreated cellulose as the starting material, avoiding, at the same time, the use of acid or basic additives having more efficient and less costly catalytic processes.

In this work, we present a simple heterogeneous catalytic process for the conversion of cellulose into ethanol, avoiding energy-intensive pretreatment, high initial hydrogen pressure, special solvents, or harsh hydrolysis conditions. The reactivity of unpretreated microcrystalline cellulose under an inert atmosphere (self-hydrolysis/hydrogenolysis conditions) in the presence of the coprecipitated Pd/Fe$_3$O$_4$ catalyst for the sustainable production of ethanol is highlighted. Water was used as a green reaction solvent, and under the adopted reaction conditions, it was able to promote, through its

Table 1. Conversion of Microcrystalline Cellulose (MCC) under Neutral Selfsustainable Hydrolysis/Hydrogenolysis Conditions[a,b]

entry	catalyst	temp. (°C)	conv. (%)	C_{Liq} (%)	molar selectivity (%)										
					Sorb	Xyl	Eryth	1,2-BDO	2,3-BDO	Gly	1,2-PDO	1-PO	EG	EtOH	OP
1	Pd/Fe$_3$O$_4$	150	10	10	6	4	0	10	5	15	45	0	0	10	5
2	Pd/Fe$_3$O$_4$	180	21	21	2	5	0	13	5	4	37	2	0	27	5
3	Pd/Fe$_3$O$_4$	210	86	60	0	2	0	10	5	1	24	18	0	33	7
4	Pd/Fe$_3$O$_4$	240	100	42	0	1	0	4	4	0	10	12	0	58	11
5	Pd/C	240	79	39	0	7	8	3	1	2	12	8	3	7	49
6	Fe$_3$O$_4$	240	67	28	2	11	13	0	4	0	3	0	3	0	64

[a]Operating conditions: 40 mL of water, 4% wt of MCC; 0.25 g of catalyst, initial pressure of N$_2$: 5 bar, 24 h. [b]Sorb: sorbitol; Xyl: xylitol; Eryth: erythritol; 1,2-BDO: 1,2-butanediol; 2,3-BDO: 2,3-butanediol; Gly: glycerol; 1,2-PDO: 1,2-propanediol; 1-PO: 1-propanol; EG: ethylene glycol; EtOH: ethanol; OP: other products.

autoprotolysis reaction, the in situ hydrolytic pretreatment of cellulose favoring its further reductive conversion.

The heterogeneous Pd/Fe$_3$O$_4$ catalyst used in this study was efficiently employed by different research groups in several processes for the reductive upgrading of cellulose-, hemi-cellulose-, and lignin-derived molecules.[24−45] The most significant physicochemical peculiarities of the catalyst, prepared by the coprecipitation technique, have been already reported and can be summarized as follows: (i) partially positively charged palladium nanoparticles, having an average particle size ranging from 1 to 2 nm, well dispersed into the Fe$_3$O$_4$ support[27−43][27−43] and (ii) the existence of Pd−Fe bimetallic clusters on the catalyst surface (characterized by a shorter scattering Pd−Fe path of 2.51 Å with respect to the Pd−Pd distance of about 2.70 Å[34−37]).

2. RESULTS AND DISCUSSION

At the beginning of our investigation, the commercially available microcrystalline cellulose (MCC) was mechanically pretreated, with the aim to reduce the crystallinity index (CrI %). A ball-milling process of 3 h at 400 rpm was sufficient to reduce the index of crystallinity at a value of 12%, starting from that of 92% for the MCC used (Figure S1).

The hydrogenolysis of the ball-milled cellulose (BMC) was studied in the temperature range of 180−240 °C, using a very low initial pressure of 5 bar of H$_2$, within 24 h of reaction, in presence of the prereduced bimetallic Pd/Fe$_3$O$_4$ catalyst (Table S2, entries 1−3). The hydrogenolysis of BMC reached a significant value even at the lowest temperature investigated (60% at 180 °C), and became complete at 210 °C. As the temperature increases, the product distribution is directed toward ethanol formation, which becomes the main reaction product in the liquid phase at 240 °C, reaching a molar selectivity of 65%. Other minor products, including other alcohols (n-butanol, methanol) and acids (acetic acid, lactic acid, butanoic acid) were also detected.

As expected, on using the unpretreated microcrystalline cellulose (MCC) as the starting material, minor conversions were registered at lower temperatures (180 and 210 °C), whereas at 240 °C, a full conversion was obtained (Table S2, entries 4−6). Upon increasing the initial H$_2$ pressure up to 20 bar, the reaction proceeded to a complete MCC conversion, whereas a slight change in the product selectivity was registered (Table S2, entry 7).

Afterward, to overcome the limitation related to the use of molecular hydrogen, the unpretreated microcrystalline cellulose (MCC) was directly processed in the presence of the Pd/Fe$_3$O$_4$ catalyst under an inert atmosphere (Table 1, entries 1−

4). Surprisingly, a complete MCC conversion was registered at 240 °C, obtaining ethanol as the main product in the liquid phase (58% molar selectivity). The pattern of products appears unchanged with respect to that obtained in the presence of molecular hydrogen, although at lower conversion values of MCC (10, 21, and 86% at 150, 180, and 210 °C, respectively). Together with diols and alcohols, in the presence of the Pd/Fe$_3$O$_4$ catalyst, a small amount of acids (mainly acetic acid), probably derived from the degradation of cellulose sugars,[46] is always registered.

In general, the distribution of products in the liquid phase closely resembles the performance observed in the hydrogenolysis of sorbitol and other cellulose-derived C$_5$−C$_3$ polyols promoted by the Pd/Fe$_3$O$_4$ catalyst, where it was demonstrated that the reaction pattern involves a preliminary dehydrogenation, followed by decarbonylation and retro-aldol reactions, subsequently followed by a series of hydrogenolitic cascade reactions, which lead to the high selectivity of ethanol.[39,44]

In agreement with studies conducted by Palkovits and co-workers on the hydrogenolysis of cellulose over a Cu-based catalyst,[47] we propose a reaction mechanism in which the terminal glucose (preliminary data related to glucose conversion at 240 °C in the presence and the absence of molecular H$_2$ are reported in Table S3) is converted into sorbitol via a hydrolysis/hydrogenation reaction. Sorbitol is then rapidly (100% conversion in 3 h at 240 °C) converted into ethanol. Other reaction mechanisms, generally proposed in the hydrogenolysis of cellulose (e.g., the glucose or fructose retro-aldol condensation route), should be discarded in the light of the observed reaction products. However, further investigations are currently in progress to fully elucidate all reactions involved in the hydrolysis/hydrogenolysis of cellulose both in the presence and in the absence of the Pd/Fe$_3$O$_4$ catalyst.

Results obtained both in the presence and in the absence of added hydrogen highlight that under the adopted operating conditions, it is not necessary to pretreat the microcrystalline cellulose.

Indeed, under the reaction conditions adopted, water is in a quasi-subcritical state, and thus, having a higher concentration of protonic species, it is able to catalyze the initial hydrolytic step of cellulose.[48,49] This effect is more evident at a higher temperature, such as 240 °C, with cellulose becoming more available for the following steps of hydrogenolysis, promoted by the Pd/Fe$_3$O$_4$ catalyst.

To corroborate this hypothesis, in a reference experiment, MCC was allowed to react in the absence of any catalyst (240

°C, 24 h, 5 bar of initial N_2 pressure). Cellulose-derived sugars were obtained as the main reaction products with an overall MCC conversion of 66% (Figure 1). Moreover, the presence
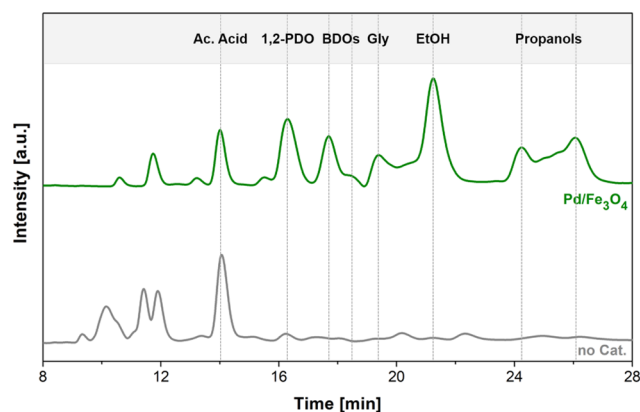

Figure 1. Comparison of high performance liquid chromatography (HPLC) chromatograms of MCC conversion in the presence of the Pd/Fe_3O_4 catalyst (green profile) or in the absence of a catalyst (gray profile) at 240 °C (reaction conditions: catalyst (when used) 0.25 g; 60 mL solution of MCC (4 wt %); solvent, water; initial N_2 pressure, 5 bar; stirring, 500 rpm).

of acetic acid as a reaction product, which progressively increases on increasing the reaction temperature (Figure S2), confirms its derivation from thermal degradation processes or oxidative sugar decomposition catalyzed by water at high temperatures.

It should be noted that in experiments carried out in the presence of the Pd/Fe_3O_4 catalyst, solutions were colorless. Furthermore, to confirm the absence of coke formation from the cellulose thermal decomposition, the used catalyst was filtered, washed with deionized water, dried overnight at 120 °C, and characterized by thermogravimetric analysis (TGA)− differential scanning calorimetry (DSC) analysis (Figure S3), where the typical combustion peak of coke above 500 °C was not observed. On the other hand, when the reaction was carried out in the absence of a catalyst, a light orange/brown solution was obtained, suggesting that some degradation or condensation products may be formed. However, these products were not identified and/or quantified.

At the same time, the formation of liquid-phase products typical of reductive processes in experiments carried out in the absence of added hydrogen poses the question of the origin of the necessary hydrogen for hydrogenation/hydrogenolysis reactions.

It is worth to underline that the hydrogen necessary for hydrogenolysis processes arises from the in situ aqueous phase reforming (APR) of cellulose-derived sugars and polyols[26,50,51]

$$C_xO_xH_{2(x+1)} + xH_2O \rightarrow xCO_2 + (2x + 1)H_2$$
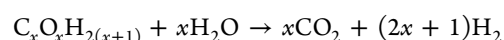
In this regard, the analysis of the gas phase relative to the reaction carried out at 240 °C under self-hydrolysis/hydrogenolysis conditions reveals a composition that includes mainly H_2 (another important feedstock for biorefineries) and CO_2 and only scarce traces of $C_3–C_1$ alkanes. The absence of CO, in gas-phase products, confirms the well-known high efficiency of Pd/Fe_3O_4 toward the water gas shift reaction.[39,43]

The time effect on the conversion of MCC, under an inert atmosphere at 240 °C, is reported in Figure 2 and Table S4. An impressive MCC conversion is observed even after 3 h of
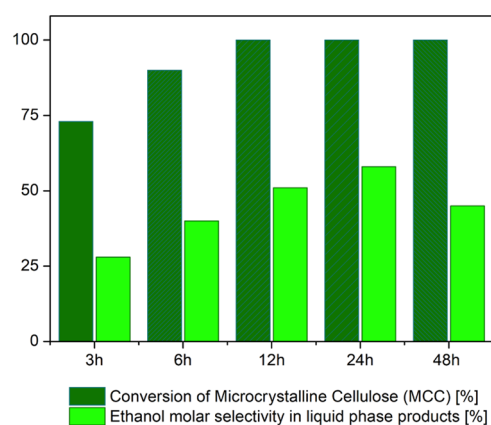

Figure 2. Time effect on the product distribution obtained in MCC conversion (%) and ethanol molar selectivity in liquid-phase products (%), when the reaction is carried out in the presence of N_2 at 240 °C (3−48 h).

reaction (73%) and it is completed after 12 h. As the reaction proceeds, the quantity of C_3 and C_2 polyols progressively decreases as a result of further hydrogenolysis/APR processes. At all investigated reaction times, ethanol is always the main product in the liquid phase.

Finally, the unicity of the Pd/Fe_3O_4 system in promoting the conversion of unpretreated cellulose under selfsustainable hydrolysis/hydrogenolysis conditions into ethanol was proved by comparing its catalytic activity with those of Pd/C and Fe_3O_4 benchmark catalysts (Table 1 and Figure S4). A complete MCC conversion and a high selectivity of ethanol were obtained only in the presence of the bimetallic Pd/Fe_3O_4 catalyst. In analogy with our previous studies on the $C_6–C_2$ polyols, the peculiar reactivity of Pd/Fe_3O_4 catalyst is ascribable to the presence of bimetallic ensembles that act as the active phase and are responsible for the pattern of observed products.[43]

3. CONCLUSIONS

In summary, on the whole, the reactivity of the coprecipitated bimetallic Pd/Fe_3O_4 catalyst applied to the conversion of both pretreated (BMC) and unpretreated (MCC) cellulose into short polyols and $C_2–C_3$ alcohols has been investigated. The possibility of converting microcrystalline cellulose in a selfsustainable, one-pot hydrolysis/hydrogenolysis process with the liquid phase mainly constituted of ethanol has been demonstrated. The process is performed under neutral conditions, without any chemical−physical pretreatment, no added molecular hydrogen, and/or further addition of acid or basic substances. Moreover, a synergistic role played by water (which, under the operating conditions, favors its autoprotolysis, by itself serving as a pretreatment means allowing the hydrolytic step) and the Pd/Fe_3O_4 catalyst (which activates the hydrogenolysis driving the pattern of obtained products) has been highlighted. Future studies will be focused on increasing the ethanol yield by investigating the best reaction conditions or by designing more selective and efficient heterogeneous catalysts.

4. EXPERIMENTAL SECTION

4.1. Pretreatment of Cellulose. The microcrystalline cellulose (Sigma-Aldrich, particle size 51 μm) was mechanically pretreated by planetary ball milling (Mono Mill II,

Fritsch) with a speed of 400 rpm for 3 h; about 10 g of microcrystalline cellulose (MCC) per run was treated.

Microcrystalline and ball-milled celluloses were characterized through X-ray diffraction measurements, performed at room temperature on a Philips X-Pert diffractometer by using the Ni β-filtered Cu Kα radiation ($\lambda = 0.15418$ nm) in the 2θ range of 20−80° at a scan speed of 0.5°/min. The crystallinity index (CrI%) was estimated through the Segal method using the ratio of the height of the 002 peak (I_{002}) and the height of the minimum (I_{AM}), between the 002 and the 101 peaks,[52−54] in agreement with the following equation

$$\text{CrI } (\%) = \frac{I_{002} - I_{AM}}{I_{002}} \times 100 \tag{1}$$

4.2. Catalyst Preparation. All chemicals were acquired from commercial suppliers and used without performing any further purification.

The bimetallic Pd/Fe$_3$O$_4$ catalyst (a nominal Pd loading of 5 wt %) was prepared by the coprecipitation synthetic method. The nitrate precursors of palladium (PdNO$_3$·H$_2$O) and iron (Fe(NO$_3$)$_3$·H$_2$O) were simultaneously added dropwise to an aqueous solution of sodium carbonate (Na$_2$CO$_3$).

The precipitated catalyst was filtered, washed, and dried under vacuum at 120 °C for 24 h. Finally, the catalyst was reduced at 200 °C under a hydrogen flow for 2 h to obtain it in the reduced form named Pd/Fe$_3$O$_4$.

The Pd/C catalyst was used after the identical reduction process adopted for Pd/Fe$_3$O$_4$.

4.3. Catalytic Tests. Catalytic reactions were performed in a 100 mL stainless steel autoclave (Parr Instruments) at a stirring speed of 500 rpm. The vessel was charged with 40 mL of an aqueous suspension containing 4% wt of cellulose and 0.25 g of reduced catalyst; then, the reactor was purged at least three times with N$_2$ (99.9%). Subsequently, the desired pressure (5 bars of H$_2$ or N$_2$) was reached and finally the reactor was heated at the reaction temperature (180−240 °C), continuously monitored through a thermocouple fixed into the autoclave and connected to the reactor controller, within the duration of the test (up to 24 h). Afterward, the system was cooled down and, when at room temperature, the pressure was released carefully, and the liquid phase was analyzed.

The conversion of cellulose was determined through the gravimetric method, considering the amount of solid cellulose put at the beginning and the final amount of the solid recovered at the end of the reaction on the basis of eq 2

$$\text{cellulose conversion } (\%) = \frac{g_{cellulose}^{IN} - g_{cellulose}^{OUT}}{g_{cellulose}^{IN}} \times 100 \tag{2}$$

The molar selectivity of each product detected in the liquid phase was calculated following eq 3

$$\text{molar selectivity } (\%)$$
$$= \frac{\text{moles of specific product}}{\text{sum of moles of all products}} \times 100 \tag{3}$$

The carbon balance at the end of each reaction was confirmed by using a liquid Total Organic Carbon analyzer (Shimadzu TOC-VCSH). Through the comparison of the carbon balance evaluated by HPLC analysis and by measurements of the total organic carbon content, the percentage of carbon loss in liquid phase has been estimated to be lower than 5%. The total organic carbon of the gas phase, when calculated, has been

estimated as the difference between the "total organic carbon" measurements before and after reactions. In all experiments, the analytical results of the gas chromatography (GC) analysis showed a carbon balance in the gas phase higher than 95%.

4.4. HPLC and GC/Mass Spectrometry (MS) Analysis. A quantitative analysis of products in the liquid phase was performed using an off-line Shimadzu HPLC equipped with an Aminex HPX-87-H column. Gas-phase products were analyzed with a GC (Agilent 7890A) equipped with a molecular sieve column (Supelco, Porapak Q column 80/100 mesh) and a capillary column (HP-PLOT/Q, internal diameter: 0.53 mm; length: 30 m; film thickness: 40 μm) linked with the TCD detector and a capillary column (HP-Al, internal diameter: 0.53 mm; length: 50 m; film thickness: 15 μm) connected to an flame ionization detector.

Products in the liquid phase were also cross-checked by GC/MS analysis with head space (HS)-GC/MS and HS-solid phase microextraction (SPME)−GC/MS for the identification of volatile products in the head space, as well as with GC/MS using the derivatized liquid sample. The derivatization procedure was carried out by collecting 150 μL of a filtered liquid sample (Millipore filter 0.22 μm) that was transferred into a 1.5 mL vial and dried in a vacuum concentrator at room temperature. Successively, to the dried sample, 40 μL of methoxyaminehydrochloride (20 mg/mL in pyridine) was added. The solution was incubated in a thermomixer (950 rpm) for 2 h at 37 °C to allow metoximation. Successively, the metoximated sample was further silylated adding 70 μL of N-methyl-N-trimethylsilyltrifluoroacetamide and incubating the solution for 30 min at 37 °C. The derivatized sample (110 μL) was then transferred into a glass vial suitable for GC/MS analysis. The extract after derivatization was injected into a TG-5MS capillary column (30 m × 0.25 mm × 0.25 μm) using a Thermo Fisher gas chromatograph apparatus (Trace 1310) equipped with a single quadrupole mass spectrometer (ISQ LT); the gas carrier was helium with a flow of 1 mL/min.

For GC/MS analysis of the derivatized liquid samples, the injector and source were settled at temperatures of 250 and 260 °C, respectively. One microliter of the sample was injected in the splitless mode using the following programmed temperature: isothermal 5 min at 70 °C followed by a 5 °C/min ramp to 330 °C and a final 5 min heating at 330 °C. Mass spectra were recorded in the electronic impact (EI) mode at 70 eV, scanning in the 45−500 m/z range. The mass spectrometric solvent delay was settled as 9 min. Metabolite identification was carried out by comparing the mass spectra with reference spectra in mass spectral libraries (NIST, mainlib, wiley8, wiley fragrances, Pflegrer Maurer Weber, Ehrenstorfer).

For HS-GC/MS and HS-SPME−GC/MS, samples were chemically characterized using a Thermo Fisher gas chromatograph apparatus (Trace 1310) equipped with a single-quadrupole mass spectrometer (ISQ LT). In particular, we used the technique of the head space, collecting just the volatiles concentrated in the air space above the sample, and the HS-SPME using a gray fiber (StableFlex, divinylbenzene/carboxen on poly(dimethylsiloxane) coating; 50/30 μm coating; Supleco). For the HS method, samples were incubated for 10 min at 40° and 1 μL of the head space was injected in the split mode with a split ratio of 60. For the HS-SPME method, the sample was equilibrated for 10 min at 40° and then the fiber was exposed to volatile organic compounds for 20 min to allow the adsorption on the fiber of a suitable and

representative number of volatiles. The capillary column was a TG-5MS, 30 m × 0.25 mm × 0.25 μm, and the gas carrier was helium with a flow rate of 1 mL/min. The injector and source were settled at 200 and 260 °C, respectively. The following temperature was programmed: isothermal for 7 min at 45 °C, from 45 to 80 °C with a rate of 10 °C/min, from 80 to 200 °C with a rate of 20 °C/min, and then isocratic for 3 min at 200 °C. Mass spectra were recorded in the electronic impact (EI) mode at 70 eV, scanning in the 40−500 m/z range. For HS and HS-SPME, no solvent delay was settled. Compound identification was carried out by comparing the relative retention times and mass spectra of molecules with those of the libraries (NIST 2005, Wiley 7.0 etc.).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03088.

> Cellulose characterization based on diffraction patterns of MCC, comparisons of HPLC chromatograms, effects of different catalysts applied to the conversion of cellulose, TGA data, time effect on the conversion of MCC, and other reaction data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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