Front. Chem. Sci. Eng. 2019, 13(4): 718–726
https://doi.org/10.1007/s11705-019-1804-5

RESEARCH ARTICLE

Microwave-assisted catalyst-free hydrolysis of fibrous cellulose for deriving sugars and biochemicals

Songshan Jiang[1,2,3], Helen Daly[1], Huan Xiang[1], Ying Yan[3], Huiping Zhang[3], Christopher Hardacre (✉)[1], Xiaolei Fan (✉)[1]

1 School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester M13 9PL, UK
2 School of Chemistry and Chemical Engineering, Chongqing University of Science and Technology, Chongqing 401331, China
3 School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

Abstract Microwave (MW) assisted catalyst-free hydrolysis of fibrous cellulose (FC, cellulolysis) at 200°C promoted a cellulose conversion of ca. 37.2% and quantitative production of valuable C5/C6 sugars (e.g., glucose) and the according platform biochemicals (e.g., 5-hydroxymethylfurfural), corresponding to an overall selectivity of 96.5%. Conversely, conventional hydrothermal cellulolysis under similar conditions was not effective, even after 24 h, carbonising the FC. Based on the systematic study of MW-assisted cellulolysis, the specific interaction between water molecules and macroscopic FC under the MW irradiation was proposed, accounting for the interpretation of the experimental observation. The kinetic energy of water molecules under the MW irradiation facilitated the C–C (in the non-hindered surface $–CH_2OH$ groups) and C–O–C bond breaking (inside the cellulose cavities) in FC, producing primary cellulolysis products of xylose, glucose and cellobiose.

Keywords microwave, fibrous cellulose, hydrolysis, sugars, mechanism

1 Introduction

The future depletion of fossil carbon reserves/resources and global warming has meant that biomass valorisation is required as a sustainable and green route for producing C5/C6 sugars, platform chemicals and fuels. Cellulose can be easily obtained from biomass such as grasses, wood and other agriculture residuals and can be converted to sugar monomers/oligomers via various routes such as hydrolysis (cellulolysis), pyrolysis (thermolysis) and enzymatic hydrolysis [1,2]. Among these, cellulolysis is a preferable method to obtain sugars being a mild and clean process. In cellulolysis, acid catalysts (e.g., mineral or solid acids) are commonly used to promote proton transfer to break β-1,4 glycosidic bonds [3–7]. However, the corrosive nature of acids, as well as the associated separation issues (e.g., the liquid-phase separation of mineral acids from the soluble products and the solid-phase separation of solid catalysts from the cellulose residuals), hinder their operations at scales [8,9]. Although enzymatic hydrolysis is highly selective to glucose in reducing sugar (above 83%) [10], the long reaction time (e.g., 72 h), highly diluted system and separation issues make it impractical for biomass valorisation [2,11,12]. Microwave (MW) treatment has shown to be able to intensify various processes including hydrolysis [13–16]. To intensify cellulolysis, especially under catalyst-free conditions, microwave irradiation was found favourable to promote the transformation of cellulose to C6 molecules with high selectivities [13].

Various theories were proposed to explain the observed phenomena in experimental studies of cellulolysis in the MW. In general, the bulk temperature phenomenon by the MW heating (regarding the heat-generating capacity of the MW system) contributed to the hydrolysis since the MW systems generally outperformed the conventional hydrothermal systems [17], especially with ionic liquids under the MW via the ionic conduction mechanism [18–20]. Specific MW effects were also reported recently, indicating that a molecular level interaction between the MW and cellulose (via the primary alcohol groups, i.e., $–CH_2OH$ groups) is responsible for transferring the MW energy to their surrounding molecular structure to initiate the cleavage of polysaccharide chains [13]. The cellulose samples used in the hydrolysis research are largely

Received July 2, 2018; accepted December 9, 2018

E-mails: c.hardacre@manchester.ac.uk (Hardacre C); xiaolei.fan@manchester.ac.uk (Fan X)

crystalline [18,21] with amorphous cellulose found to be unstable in aqueous systems forming partially crystalline cellulose II [22]. Therefore, cellulose is very likely to be MW-transparent as the polysaccharide chains are constrained in the crystal lattice and not able to respond to the MW irradiation microscopically. The reported fast MW depolymerisation of the cellulose in the literature [13] might be accounting for the amorphous part which takes 13% of the microcrystalline cellulose (MCC). In MW chemistry, the MW-solvent interaction is responsible for MW heating (via the dielectric heating) [23], in which the high rotational velocity of the polar solvent molecules (caused by the oscillating electric field of the MW) results in molecular friction and heat generation [24,25]. Hence, under MW irradiation, the interaction between the macroscopic cellulose and the highly excited vibrating water molecules should be responsible for the effective performance observed in the cellulolysis experiments. Herein, we performed a systematic investigation of the MW-assisted catalyst-free hydrolysis of fibrous cellulose (FC) at 200°C aimed at revealing the pathway of the MW promoted cellulolysis of FC.

2 Materials and methods

2.1 Materials

Cellulose (fibres, medium), D-(+)-glucose (ACS Reagent), D-(−)-fructose (BioReagent), D-(+)-cellobiose (BioReagent), 1,6-anhydro-β-D-glucopyranose (levoglucosan, 99%), D-(+)-xylose ($\geqslant$99%), furfural (ACS reagent, 99%) and 5-hydroxymethylfurfural (5-HMF, 99%) were all purchased from Sigma Aldrich and used as received. Sulfuric acid (95%) was obtained from Fisher Scientific. Ethanol (99.7%–100%, absolute) was purchased from VWR International. Ultrapure water (Direct-Q® Water Purification System, 18.2 MΩ·cm@25°C) was used in this work.

2.2 MW-assisted and hydrothermal (HT) hydrolysis of fibrous cellulose and raw biomass

Hydrolysis of fibrous cellulose was carried out using a CEM Discover SP-D MW reactor in 35 mL Pyrex vials sealed by pressure caps (with TFM septa). The maximum pressure of the system was set as 250 PSI, and experiments were run in the Ramp-to-Temperature mode under stirring at ca. 570 r/min. A standard procedure of the cellulolysis experiment is described as: (i) FC suspended in water was prepared by stirring FC (300 mg) with the deionised water (10 mL) in the Pyrex vial (2 min); (ii) the vial containing the suspension was transferred to the MW reactor for treatment (temperature programme: room temperature to 200°C over 5 min with a maximum power input of 150 W, then at 200°C for various holding time of 2.5 min to 4 h at 50 W, the system pressure was monitored as ca. 200 PSI); (iii) the hydrolysed products was centrifuged at 4400 r/min to separate the solid residual from the liquid fraction.

The centrifuged FC were dried in the oven at 60°C for 48 h and then weighted to calculate the cellulose conversion ($X_{\text{cellulose}}$) according to Eq. (1). For the selectivity (S_{n}), which is the relative selectivity based on the ratio of the absolute concentration of a product (C_{n}) divided by the overall concentration of all identified products in the liquid phase (C_{total}) by high performance liquid chromatography (HPLC), as defined in Eq. (2).

$$X_{\text{cellulose}} = \frac{m_0 - m_{\text{t}}}{m_0} \times 100\%, \tag{1}$$

$$S_{\text{n}} = \frac{C_{\text{n}}}{C_{\text{total}}} \times 100\%, \tag{2}$$

where m_0 and m_{t} are the mass of cellulose at the initial time and sampling time, respectively. m_{t} was corrected according to the solid mass loss due to the work-up which was measured as (7.2±2)% using blank experiments.

The obtained liquid fractions were filtered (Millex filter, 0.45 μm, sterile) prior to the HPLC analysis which was performed on a Thermo U3000 HPLC equipped with a Bio-rad Aminex HPX-87H Column, a refractive index (RI) detector (for sugar) and a UV detector (for 5-HMF and furfural, wavelength adjusted at 210 nm). Relevant HPLC conditions are: sample injection volume = 10 μL, oven temperature = 50°C, RI detector temperature = 50°C; UV detector wavelength = 210 nm; and mobile phase = 0.005 mol/L sulfuric acid aqueous solution, flow rate = 0.6 mL/min. External standard methods were used for calibrations in the HPLC analysis (Fig. S1, cf. Electronic Supplementary Material (ESM)).

For comparison, conventional HT hydrolysis of FC (300 mg in 10 mL water) was also carried out using an autoclave reactor (with a 50 mL Teflon liner) at 200°C for 1 h and 24 h (in a Memmert oven). Catalyst-free MW treatment of cellulose, xylose and cellobiose (2000 mg/L) was performed at 200°C using the same MW programme as in the cellulolysis. MW-assisted treatment of the raw biomass (i.e., maple leaves and fresh grass) were performed at 200°C without the catalyst for 1 h. Prior to the hydrolysis under the MW irradiation, maple leaves were collected and dried at 100°C and fresh grass was firstly treated in methanol to remove chlorophyll and then dried at 100°C.

2.3 Characterisation of materials

Scanning electron microscopy (SEM) images of materials were obtained by using a FEI Quanta 200 ESEM in high voltage mode of 20 kV. Platinum coating of samples was performed using an Emitech K550X sputter coater under

vacuum conditions of 1×10^{-4} mbar. X-ray diffraction (XRD) and SEM characterisation of materials was performed. XRD patterns of the FC (fresh and spent ones) and microcrystalline were obtained on PANalytical X'PERT powder diffractometer using CuKα_1 (λ = 1.5406 Å) radiation (at 30 kV and 30 mA) with a scanning rate of 2°/min in a range of from 5° to 90°.

3 Results and discussion

3.1 Comparative study of catalyst-free hydrolysis of fibrous cellulose by microwave and conventional hydrothermal heating

Based on the MW input (50 W) and reaction volume (i.e., 10 mL), the MW density (ρ_{MW}) of the current system is estimated as 5 kW/L. Under this specific condition, the softening temperature of FC in pure water was determined as 200°C, evidenced by the sudden conversion of FC to glucose (cf. ESM). As shown in Table S1 (cf. ESM), a significant increase of glucose yield in the liquid fraction (by ca. 2502%) was measured by raising the system temperature from 180°C to 200°C. A relatively high MW power of 150 W was used in the temperature ramp from the room temperature to 200°C (5 min). Therefore, in order to decouple the effect of 150 W power input on the cellulolysis system, an experiment with a short reaction time of 2.5 min was performed, showing no quantitative conversion of cellulose fibres (0.7%), as well as no production of C5/C6 sugars and biochemicals (Figs. 1(a) and 1(b)). Extending the MW treatment time to 1 and 4 h was beneficial to the conversion of FC into glucose, 5-HMF and furfural, as shown in Fig. 1 (relevant selectivities are 43.7%, 30.1% and 14.5%, respectively, after 4 h MW treatment). Under acid-free conditions, conventional HT treatment was found to be ineffective in the hydrolysis of FC, as observed from the comparative results of 1 h and 24 h reaction in Figs. 1(b–d) (the relevant HT conditions are as in ESM). Although a 60.7% conversion of cellulose was achieved by the HT treatment (Fig. 1(a)) at 200°C, the FC was carbonised and converted into a dark, sticky residue after 24 h (Fig. S2(a)) with no relevant products detected in the liquid fraction. These experiments demonstrated that the MW irradiation (ρ_{MW} = 5 kW/L) was needed to achieve the selective conversion of FC into C5/C6 sugars and biochemicals.

3.2 Production distribution in the liquid phase from MW-assisted catalyst-free hydrolysis of FC

Figure 2(a) shows the relationship between the conversion of cellulose and the MW irradiation time under catalyst-free conditions which is closing to linear. After 4 h MW treatment (5 kW/L), 37.2% conversion of FC was obtained. Glucose, 5-HMF and furfural were detected by HPLC (as evidenced in Figs. 2(b,c)) as the main chemicals in the liquid fractions from the MW-assisted cellulolysis, resulting in the colour change of the hydrolysis solution from light brown to dark brown by increasing MW treatment time (Fig. S2(b), cf. ESM). Figure 2(b) shows that the concentration profile of glucose and 5-HMF increased steadily as a function of the hydrolysis time. Xylose and cellobiose appeared to be intermediates in the reaction as their concentrations showed maxima over the course of MW-assisted cellulolysis. Dehydration of xylose to furfural using acid catalysts (HCl) under the MW has been reported as highly effective, resulting in the full conversion within 20 min (35 mmol/L xylose in 4 mL water, at 200°C, estimated ρ_{MW} = 1.25 kW/L) [26]. In this study, MW irradiation over reaction times of 60 to 240 min, resulted in xylose conversion under catalyst-free hydrolysis of 7.28 mg (Table S2, cf. ESM), which is consistent with the furfural production over the same period during the MW treatment (Fig. 2(c)). This indicates that the MW was effective in converting xylose to furfural without acid catalysts, using relatively high MW densities.

According to previous studies, the hydrolytic depolymerisation of cellulose was enabled by the cleavage of β-1,4 glycosidic and hydrogen bonds to produce glucose and cellobiose [4,18], which are then transformed into fructose and 5-HMF. In the MW system reported, herein, xylose was detected at the beginning of the cellulolysis reaction for reaction times of < 30 min with a relatively high concentration of ca. 1007.6 mg/L (at 30 min). This was much higher than the glucose production (ca. 297.6 mg/L at 30 min). Therefore, it is likely that, in the catalyst-free MW-assisted hydrolysis of FC (at 200°C), the unhindered primary alcohol groups (–CH_2OH terminal groups) may react initially and result in cleavage of the C–C bonds (Fig. 3) with then cleavage of the 1,4-β-glycosidic bond depolymerising the polysaccharide chains in cellulose yielding soluble C5 (xylose) or C6 (glucose) sugars, as well as a C12 chemical of cellobiose. By extending the time of MW treatment, cleavage of the C–O–C bonds predominated, as seen by the increase in glucose yield, as shown in Fig. 2(b). Levoglucosan was formed steadily in the liquid phase as shown in Fig. 2(d) (selectivity at 4 h = 3.1%), which might be attributed to the dehydration of glucose in the polar solvent [27].

3.3 Mechanism of MW-assisted catalyst-free hydrolysis of FC

Based on the experimental findings of this work, it is proposed that the dominant pathway accounting for the depolymerisation of FC in MW-assisted cellulolysis lies in the molecular interaction between the FC and solvent molecules. In deionised water, dipolar polarisation is the main mechanism for the MW-induced heating of the cellulolysis system, in which the polar water molecules rotate with high velocities to align themselves with the

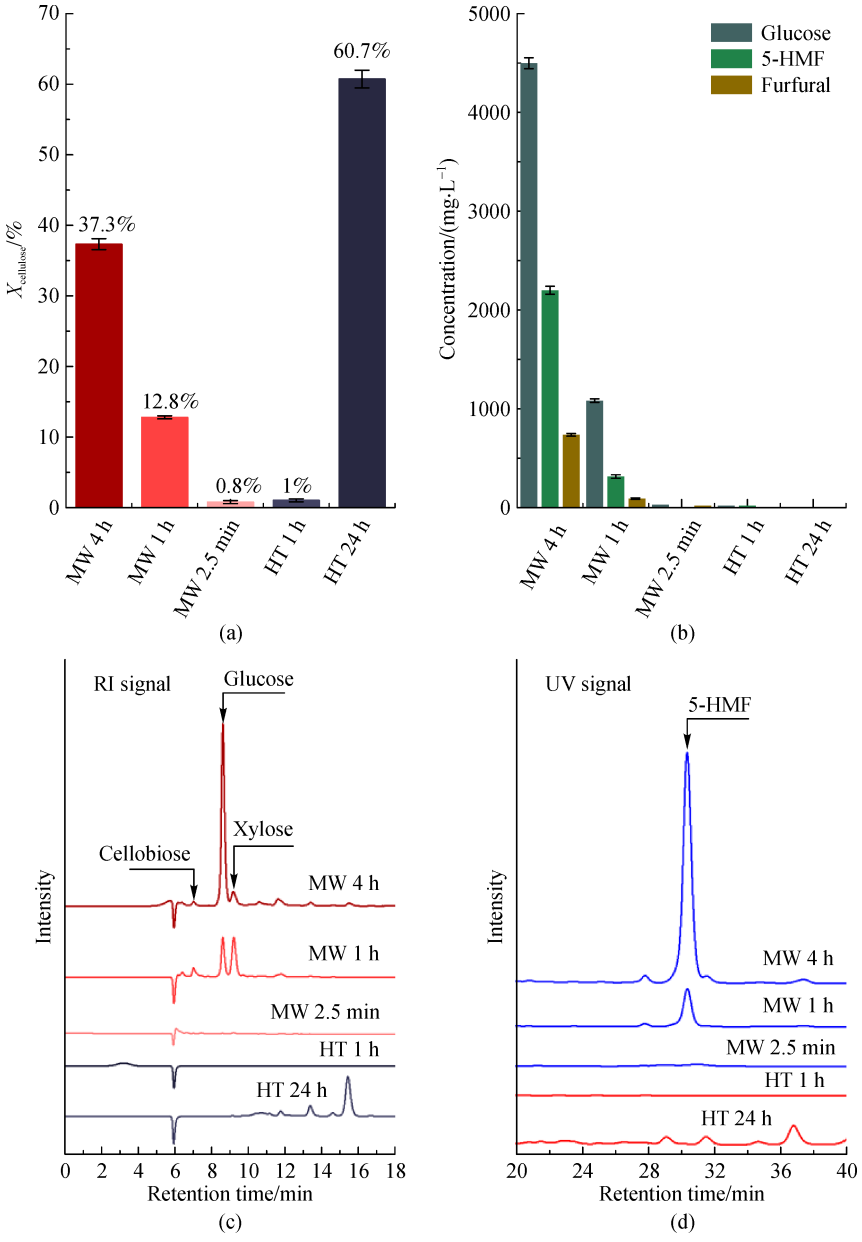

Fig. 1 Comparative studies of the hydrolysis of FC under MW and HT treatment: (a) conversion of cellulose, (b) distribution of hydrolysis products, (c) HPLC analysis (RI signals) and (d) (UV signals) of the cellulolysis liquid fractions

alternating electric field (an MW frequency of microwaves of 2.45 GHz is optimal to enable water molecules frictional losing energy to heat up the system [25]. Under the MW conditions, rotating water molecules primarily attack the surface primary alcohol groups of the FC (by frictional forces and transferring kinetic energy to activate the C–C bonds). Upon reaching the softening temperature, the water molecules penetrate into the intersheet space of the cellulose fibres, facilitating cleavage of the C–O–C bonds and giving rise to not only xylose but also glucose and cellobiose. With the sustained MW irradiation, the intersheet bond breaking reactions dominate, whereas the hindered $-CH_2OH$ groups are likely preserved by the inter-/intra-chain hydrogen bonds as is seen in the increasing selectivity to glucose over xylose/furfural with increasing MW irradiation time.

In order to elucidate the comprehensive mechanism in the liquid phase, MW-assisted catalyst-free treatments of the primary products xylose, glucose and cellobiose (2000 mg/L) were performed under the same MW conditions at 200°C (ρ_{MW} = 5 kW/L). For the reaction of glucose, MW irradiation resulted in 55.9% conversion of glucose after 0.5 h yielding mainly 5-HMF (yield = 34.5%) from dehydration of glucose, as well as small amounts of fructose (9.1%) and furfural (1.6%), as shown in Figs. 4(a) and 4(b). Hydrolysis of cellobiose under MW irradiation at

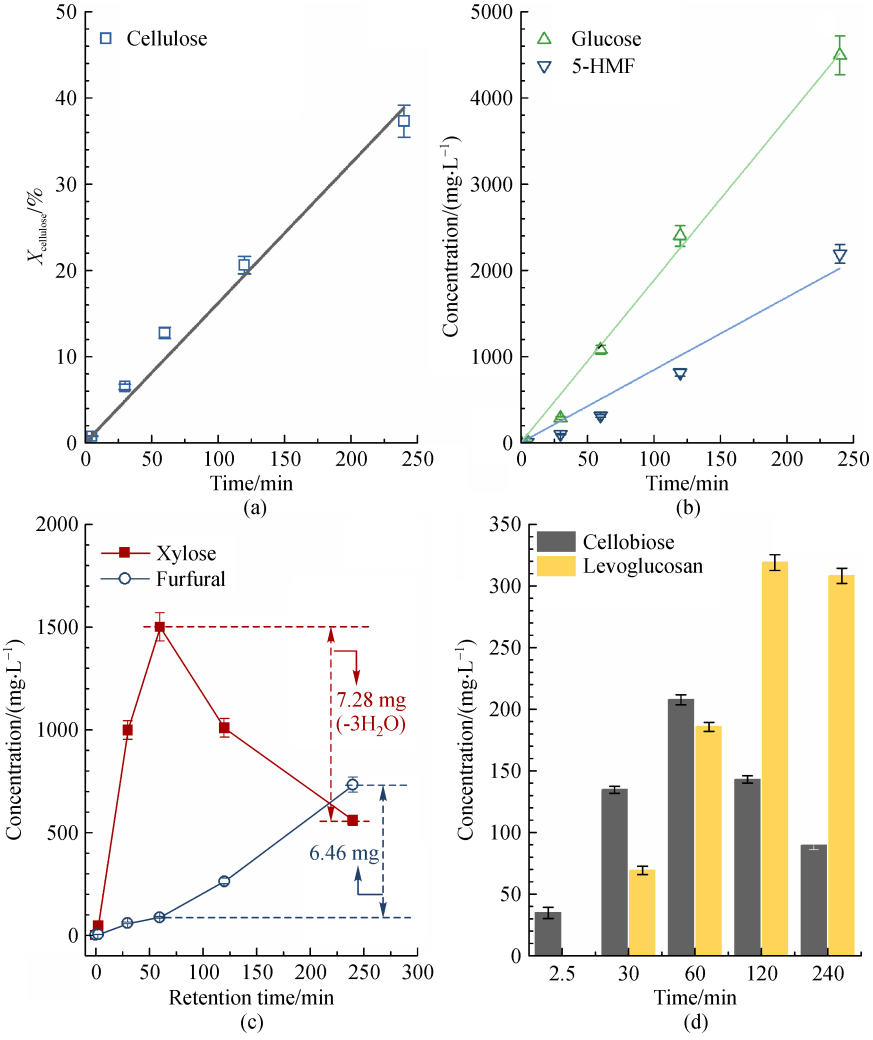

Fig. 2 (a) Cellulose conversion as a function of time in MW-assisted cellulolysis; (b) concentration profiles of glucose and 5-HMF; (c) concentration profiles of xylose and furfural; (d) concentration distribution of cellobiose and levoglucosan in the liquid fractions

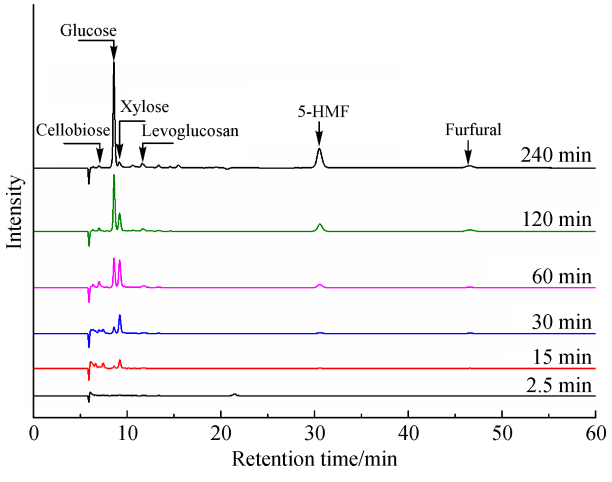

Fig. 3 Product distribution by HPLC in the liquid fractions of the MW-assisted treatment of FC (ρ_{MW} = 5 kW/L)

200°C formed glucose, 5-HMF, fructose, levoglucosan and furfural with yields of 51.1%, 14.1%, 6.4%, 3.3% and 0.9%, respectively (total carbon balance = 75.8%). The remaining carbon is likely to be composed organic acids and aldehydes which cannot be quantified by the HPLC method. The MW treatment of xylose revealed that the formation of furfural in the liquid phase was mainly from the dehydration of xylose. After 0.5 h MW irradiation at 200°C, xylose was quantitatively converted (conversion of xylose = 85.4%) to furfural (yield = 49.2%). Only trace amounts of xylose and furfural were detected in the solutions of glucose and cellobiose systems after MW treatment (Table S2, cf. ESM), indicating that the cleavage of –CH_2OH groups from individual glucose molecules was difficult, in agreement with the literature [13].

Based on the findings above, under the MW condition (5 kW/L and 200°C), a pathway of catalyst-free hydrolysis of FC is proposed as shown in Fig. 5. Under the MW

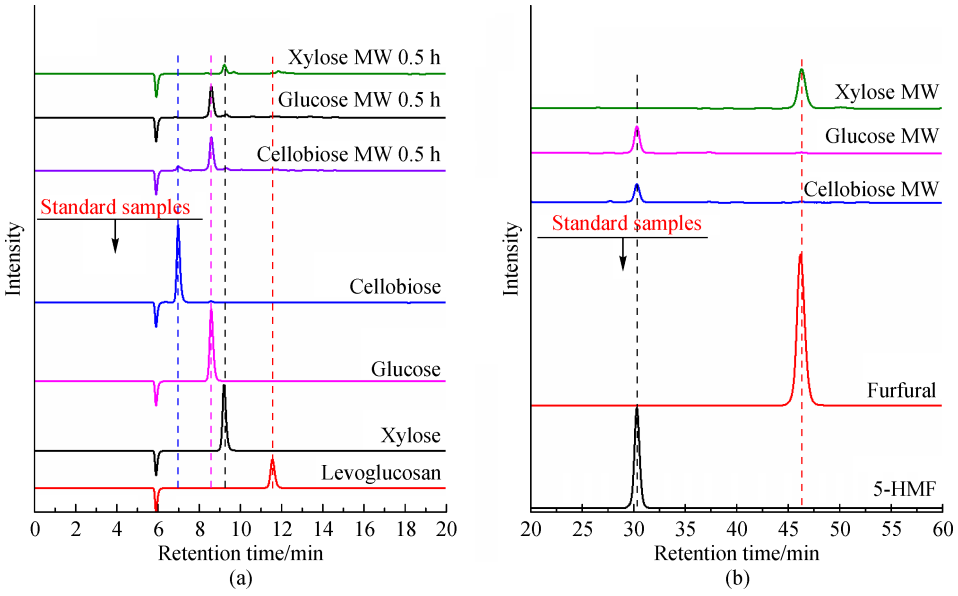

Fig. 4 HPLC analysis of the liquid fractions of (a) MW-assisted catalysts-free treatment of xylose, glucose and cellobiose (RI signals after 0.5 h) and (b) MW-assisted catalysts-free treatment of xylose, glucose and cellobiose (UV signals after 0.5 h)

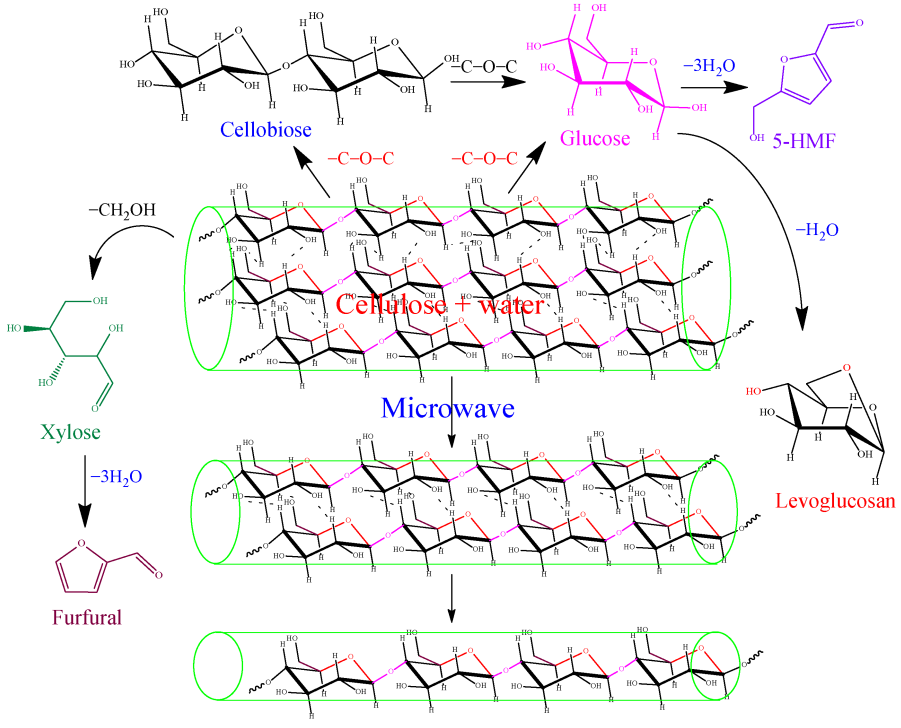

Fig. 5 Reaction pathway of MW-assisted catalyst-free hydrolysis of FC

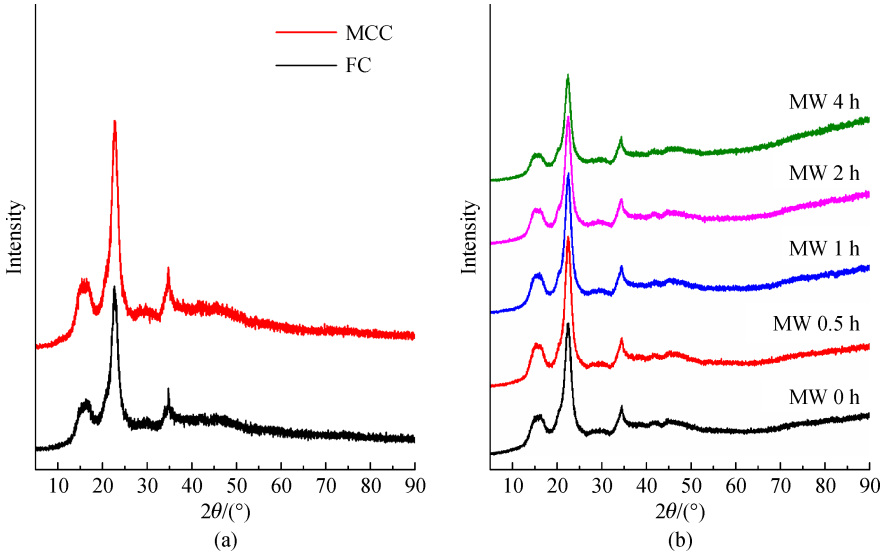

Fig. 6 XRD patterns of (a) MCC and FC and (b) FC residuals from the MW-assisted cellulolysis of FC after different MW irradiation times (ρ_{MW} = 5 kW/L)

treatment above the softening temperature, the MW-induced rotation of water molecules (kinetic energy) facilitated the breaking of C–C bonds on the outer surface of cellulose, removing the –CH_2OH groups exposed to the solvent and C–O–C bond breaking (inside the cellulose cavities) in the macroscopic structure of the FC, producing the first generation of cellulolysis products of xylose, glucose and cellobiose. The subsequent dehydration of these molecules in the liquid phase produced 5-HMF, furfural and levoglucosan.

A previous report performed at 220°C and a ρ_{MW} of 0.8 kW/L in a monomode MW reactor proposed that –CH_2OH groups function as the 'molecular radiators', transferring the MW energy to their nearby glucose rings to cleave the intrachain ether bonds (C–O–C) forming levoglucosan then glucose [13]. Concerning the 'molecular radiators' function of the –CH_2OH groups in the cellulose [13], it was not conclusive based on the findings of the current work. Such an effect was claimed based on a 'concentrated' system using MCC in deionised water (mass ratio = 1:10). The mass ratio of FC to deionised water was also varied herein to investigate its effect on the MW-assisted hydrolysis. As shown in Fig. S3 (cf. ESM), linear correlations between the hydrolysis products and the mass ratio were all established, indicating an identical mechanism under the conditions used.

Both amorphous and crystalline phases were found in FC (Fig. 6(a), similar to that of MCC), but preferential depolymerisation of the amorphous cellulose [13] was not found at 200°C, as evidenced by the PXRD analysis of the hydrolysis residues where XRD diffractograms showed insignificant changes following MW treatment for up to 4 h (Fig. 6(b)). The pristine and hydrolysed cellulose fibres were analysed by SEM (Fig. 7), showing a reduction in

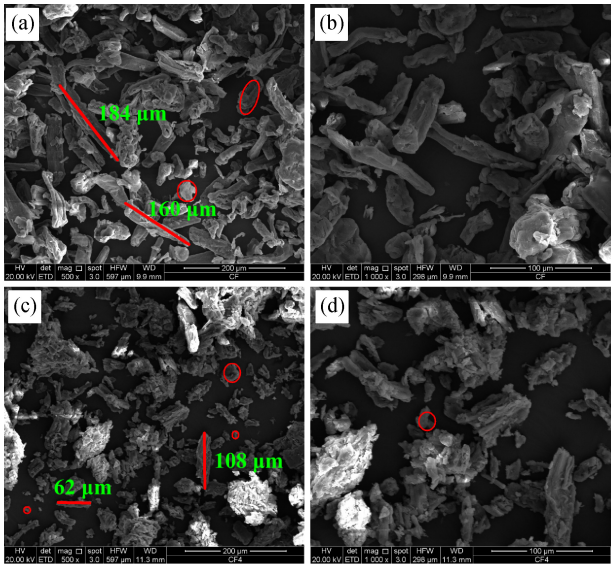

Fig. 7 SEM images of FC: (a) and (b) before the MW-assisted cellulolysis; (c) and (d) after the MW-assisted cellulolysis (4 h, ρ_{MW} = 5 kW/L)

fibre sizes after the MW treatment with comparable physical appearance. Interestingly, MW-hydrolysis of hydrolysed cellulose fibres under the same condition showed better efficiency than that of the pristine FC (Fig. 8) suggesting the simultaneous depolymerisation of amorphous and crystalline phases in FC under the condition used.

Finally, two types of raw biomass, namely maple leaves and fresh grass, were treated under the MW irradiation at 200°C without the catalyst for 1 h. Results presented in

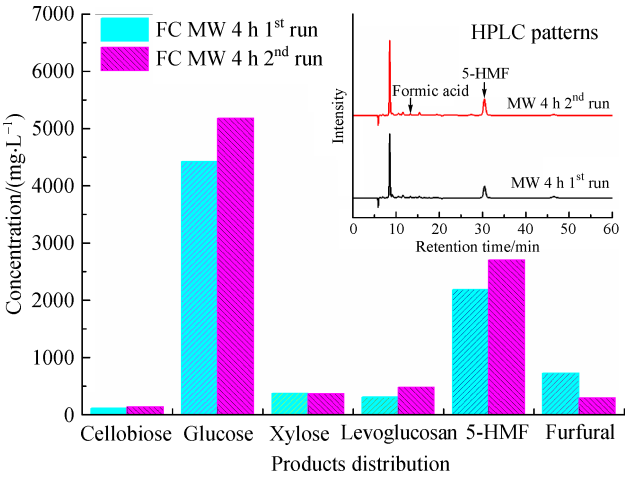

Fig. 8 Products distribution of MW-assisted cellulolysis: 4 h hydrolysis with the pristine cellulose (1st run) and 4 h hydrolysis with the hydrolysed cellulose (2nd run)

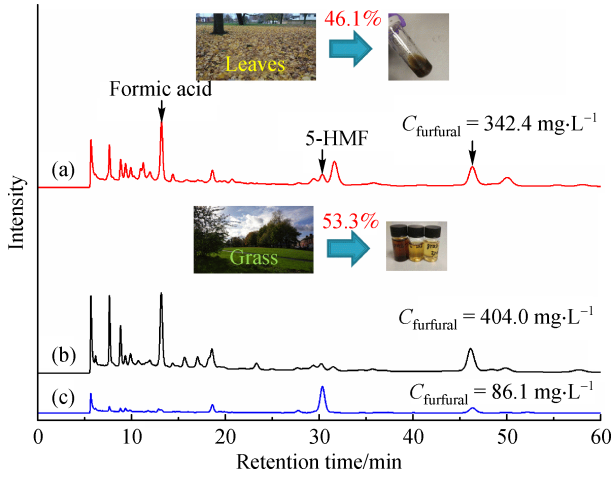

Fig. 9 HPLC spectra of MW-assisted catalyst-free hydrolysis of raw biomass: (a) maple leaves, (b) grass and (c) cellulose (as the reference)

Fig. 9 shows that high mass loss of grass and leaves are obtained, 46.1% and 53.3% respectively, with complex product distribution in the HPLC spectra which requires further separation and identification. These results indicate that the MW-assisted catalyst-free hydrolysis is a green and efficient technology in the biomass transformation for deriving C5/C6 sugars and other biochemicals, not limited to the processed cellulose.

4 Conclusions

The MW-induced catalyst-free hydrolysis of FC was studied at 200°C and 5 kW/L, suggesting the specific interaction between water molecules and FC under the MW. The kinetic energy of rotating water molecules under the MW activates the C–C and intrachain ether bonds of the FC to produce C5 (xylose) and C6 (glucose) sugars, which are subsequently converted into renewable platform biochemicals, such as 5-HMF and furfural, with a ca. 96.5% total selectivity to them. The present work demonstrated an MW intensified yet clean process to convert the FC and biomass to valuable C5/C6 and according biomolecules.

Acknowledgements The authors thank The UK-China Joint Research and Innovation Partnership Fund (known in the UK as the Newton Fund Ph.D. Placement Grant) by the China Scholarship Council (CSC, file No. 201603780091 for SJ) and the British Council for the financial support to this work. HX acknowledges The University of Manchester President's Doctoral Scholar Award and CSC (file No. 201606150068) for supporting her Ph.D. research.

Electronic Supplementary Material Supplementary material is available in the online version of this article at https://doi.org/10.1007/s11705-019-1804-5 and is accessible for authorized users.

References

1. Jérôme F, Chatel G, Vigier K D O. Depolymerization of cellulose to processable glucans by non-thermal technologies. Green Chemistry, 2016, 18(14): 3903–3913
2. Hamelinck C N, Van Hooijdonk G, Faaij A P. Ethanol from lignocellulosic biomass: Techno-economic performance in short-, middle-and long-term. Biomass and Bioenergy, 2005, 28(4): 384–410
3. Chimentão R J, Lorente E, Gispert-Guirado F, Medina F, López F. Hydrolysis of dilute acid-pretreated cellulose under mild hydro-thermal conditions. Carbohydrate Polymers, 2014, 111: 116–124
4. Zhou L, Yang X, Xu J, Shi M, Wang F, Chen C, Xu J. Depolymerization of cellulose to glucose by oxidation-hydrolysis. Green Chemistry, 2015, 17(3): 1519–1524
5. Sun B, Duan L, Peng G, Li X, Xu A. Efficient production of glucose by microwave-assisted acid hydrolysis of cellulose hydrogel. Bioresource Technology, 2015, 192: 253–256
6. Mission E G, Quitain A T, Sasaki M, Kida T. Synergizing graphene oxide with microwave irradiation for efficient cellulose depolymerization into glucose. Green Chemistry, 2017, 19(16): 3831–3843
7. Sweygers N, Alewaters N, Dewil R, Appels L. Microwave effects in the dilute acid hydrolysis of cellulose to 5-hydroxymethylfurfural.

Scientific Reports, 2018, 8(1): 7719
8. Wu Y, Fu Z, Yin D, Xu Q, Liu F, Lu C, Mao L. Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids. Green Chemistry, 2010, 12(4): 696–700
9. Mok W S, Antal M J Jr, Varhegyi G. Productive and parasitic pathways in dilute acid-catalyzed hydrolysis of cellulose. Industrial & Engineering Chemistry Research, 1992, 31(1): 94–100
10. Chakraborty S, Singh P K, Paramashetti P. Microreactor-based mixing strategy suppresses product inhibition to enhance sugar yields in enzymatic hydrolysis for cellulosic biofuel production. Bioresource Technology, 2017, 237(suppl C): 99–107
11. Dutta S, Wu K C W. Enzymatic breakdown of biomass: Enzyme active sites, immobilization, and biofuel production. Green Chemistry, 2014, 16(11): 4615–4626
12. Wang J, Xi J, Wang Y. Recent advances in the catalytic production of glucose from lignocellulosic biomass. Green Chemistry, 2015, 17 (2): 737–751
13. Fan J, De Bruyn M, Budarin V L, Gronnow M J, Shuttleworth P S, Breeden S, Macquarrie D J, Clark J H. Direct microwave-assisted hydrothermal depolymerization of cellulose. Journal of the American Chemical Society, 2013, 135(32): 11728–11731
14. Li H, Li J, Fan X, Li X, Gao X. Insights into the synergetic effect for co-pyrolysis of oil sands and biomass using microwave irradiation. Fuel, 2019, 239: 219–229
15. Li H, Shi P, Fan X, Gao X. Understanding the influence of microwave on the relative volatility used in the pyrolysis of Indonesia oil sands. Chinese Journal of Chemical Engineering, 2018, 26(7): 1485–1492
16. Ou X, Xu S, Warnett J M, Holmes S M, Zaheer A, Garforth A A, Williams M A, Jiao J, Fan X. Creating hierarchies promptly: Microwave-accelerated synthesis of ZSM-5 zeolites on macrocellular silicon carbide (SiC) foams. Chemical Engineering Journal, 2017, 312: 1–9
17. Budarin V L, Clark J H, Lanigan B A, Shuttleworth P, Macquarrie D J. Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. Bioresource Technology, 2010, 101(10): 3776–3779
18. Benoit M, Rodrigues A, Zhang Q, Fourré E, De Oliveira Vigier K, Tatibouët J M, Jérôme F. Depolymerization of cellulose assisted by a nonthermal atmospheric plasma. Angewandte Chemie International Edition, 2011, 50(38): 8964–8967
19. Zhang Z, Zhao Z K. Solid acid and microwave-assisted hydrolysis of cellulose in ionic liquid. Carbohydrate Research, 2009, 344(15): 2069–2072
20. Ma H Y, Zhao Z P, Lu P. Cellulose hydrolysis by acidic Ionic liquids enhanced with microwave heating. Advanced Materials Research, 2018, 1145(8): 75–79
21. Nasution H. Yurnaliza, Veronicha, Irmadani, Sitompul S. Preparation and characterization of cellulose microcrystalline (MCC) from fiber of empty fruit bunch palm oil. In: IOP Conference Series: Materials Science and Engineering, 1st Annual Applied Science and Engineering Conference. Bandung: IOP Publishing, 2017, 180: 012007
22. Ciolacu D, Ciolacu F, Popa V I. Amorphous cellulose-structure and characterization. Cellulose Chemistry and Technology, 2011, 45(1–2): 13–21
23. Kappe C O. Unraveling the mysteries of microwave chemistry using silicon carbide reactor technology. Accounts of Chemical Research, 2013, 46(7): 1579–1587
24. Gabriel C, Gabriel S, Grant E H, Grant E H, Halstead B S J, Michael P, Mingos D. Dielectric parameters relevant to microwave dielectric heating. Chemical Society Reviews, 1998, 27(3): 213–224
25. Kappe C O, Stadler A, Dallinger D. Microwaves in Organic and Medicinal Chemistry. Weinheim: John Wiley & Sons, 2012
26. Xiouras C, Radacsi N, Sturm G, Stefanidis G D. Furfural synthesis from D-xylose in the presence of sodium chloride: Microwave versus conventional heating. ChemSusChem, 2016, 9(16): 2159–2166
27. Cao F, Schwartz T J, McClelland D J, Krishna S H, Dumesic J A, Huber G W. Dehydration of cellulose to levoglucosenone using polar aprotic solvents. Energy & Environmental Science, 2015, 8 (6): 1808–1815