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Overcoming biomass recalcitrance for enhancing sugar production from fast pyrolysis of biomass by Microwave pretreatment in Glycerol

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ABSTRACT

Levoglucosan, mainly derived from cellulose fast pyrolysis, is a versatile precursor to fuels, pharmaceuticals, and other value-added chemicals. However, Biomass fast pyrolysis produces very low amount of levoglucosan when compared to the theoretical yield based on cellulose fraction. Microwave pretreatment of biomass in glycerol is a potential pretreatment method prior to fast pyrolysis for enhancing levoglucosan yield since it can achieve the rapid heating and specific molecular activations for promoting the delignification and demineralization of biomass. In order to examine the validity of the pretreatment method, pretreatment of corncob in

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glycerol was conducted in a microwave reactor under ambient pressure. The pretreated corncobs were subsequently fast pyrolyzed in a semi-batch pyroprobe reactor. The experimental results show that microwave pretreatment in glycerol can serve as an effective pretreatment method for improving the sugar yield. The levoglucosan yield from fast pyrolysis of corncob pretreated at 150 W for 18 min was about 189 times higher than that of raw corncob. It was mainly ascribed to the effective removal of alkali and alkaline earth metals during microwave pretreatment of corncob in glycerol. In addition, the selective removal of lignin and hemicellulose fractions of corncob during pretreatment also plays positive roles in enhancing the levoglucosan yield.

Keywords: Biomass recalcitrance ; Microwave pretreatment ; Fast pyrolysis; Sugar production

Introduction

Growing concerns regarding the rapid consumption of limited fossil resources and the resulting environmental issues, have driven many efforts towards the development of alternative feedstock for the production of liquid fuels and chemicals[1-5] . Biomass is the only current renewable source of organic carbon which can be used as an alternative to fossil fuel for producing liquid fuels and chemicals[6-7] . Currently, there are several main technologies that can be used to convert biomass into liquid products, including fermentation, fast pyrolysis, aqueous phase reforming, gasification followed by Fischer-Tropsch synthesis and so on[8-10]. Among them, Biomass fast pyrolysis has gained great interesting from both academia and industry since it can provide for the highest yield of liquid products (as high as 70–80 wt.%) and lowest cost[11-12]. However, the widespread use of fast pyrolysis liquids is hindered by several critical issues: (1) the pyrolysis liquids contain many oxygen-containing functionalities and unsaturated bonds, resulting in its poor stability, (2) the complex composition of pyrolysis liquids make it hard to extract desired molecules or to utilize the existing petroleum refining infrastructure for upgrading[13-14]. Hence, fast pyrolysis of biomass in a controlled manner to obtain high concentrations of desirable molecules with stable structure (e.g. levoglucosan) could be an effective solution to address these challenges.

Previous studies showed that fast pyrolysis of pure cellulose can produce high yield of levoglucosan (20-60 wt.%)[15-16]. However, Biomass fast pyrolysis yields very low amount of levoglucosan when compared to the theoretical yield based on cellulose fraction[17]. Biomass consists of three main structural units: cellulose, hemicellulose, and lignin. Additionally, minor amounts of extractives and ash (containing alkali and alkali earth metals, AAEM) are present. Robert C. Brown and co-workers reported that AAEM can strongly catalyze the fragmentation of holocellulose to light oxygenates and permanent gases compared to the thermally-induced cleavage of glycosidic bonds that yield anhydrosugars[15, 17-18]. They also found that the interactions between cellulose and lignin during fast pyrolysis can inhibit the formation of levoglucosan due to the inherent covalent linkages between cellulose and lignin[19]. A.V. Bridgwater suggested that thin layers of biomass can achieve rapid heating rate for reducing secondary reactions because of the poor thermal conductivity of biomass (ca. 0.05 W mK^{-1} across the grain, 0.1 W mK^{-1} along the grain)[20]. Paul J. Dauenhauer and co-workers demonstrated that cellulose pyrolysis proceed through a short-lived intermediate liquid. Cellulose thin-films can prevent the secondary pyrolysis reactions owing to the shorter residence time in thin-film experiments which enable levoglucosan to escape the intermediate liquid before reacting[21-25]. However, in biomass, cellulose is trapped in a complex matrix composed of hemicelluloses and lignin chemically bound together, which forms a strong and complex sheath around cellulose and presents challenges to overcoming the recalcitrance for effective releasing of levoglucosan without secondary reactions during biomass fast pyrolysis.

Considering that most of the structural ash in biomass locates in the cross-linking structure of lignin[26], Fractionating biomass by shell peeling through the selective organosolvolysis of lignin and, to a tunable degree, hemicellulose to obtain cellulose-rich material is the key to obtain high yield of pyrolytic sugar[23, 27]. Walter Leitner and co-works reported that oxalic acid or formic acid can catalyze selective solvolysis of the lignin and hemicellulose fractions of biomass to obtain pulp in a biphasic system[28]. Roberto Rinaldi demonstrated that Raney Ni can catalyze the fractionation of biomass in 2-propanol/water system under autogeneous pressure in an autoclave to obtain non-pyrolytic lignin bio-oil and pulp through hydrogen transfer reaction[29]. Organsolvolysis typically requires high pressure, a longer residence time and high energy consumption. Microwave pretreatment of biomass in glycerol could be an alternative energy-saving way that can selectively remove the lignin fraction of biomass under ambient pressure due to the high boiling point and dielectric loss factor of glycerol[30]. However, very few pieces of information have been reported so far and little is known about the influence of microwave pretreatment in glycerol on levoglucosan yield from fast pyrolysis of pretreated biomass. Here, The pretreatment of corncobs using microwave in glycerol was performed in a homemade microwave reactor with varying power (150W, 300W or 400W) and residence times (1 min, 5 min, 10 min and 18 min). Then the fast pyrolysis of pretreated corncobs was conducted in a semi-batch pyroprobe reactor. Corncob was selected as feedstock because it has high xylan and AAEM content, and thus it might be more sensitive to pretreatment when compared to other forms of lignocellulosic biomass. The effects of pretreatment severity on levoglucosan yield from fast pyrolysis of pretreated corncobs are investigated.

Experimental

Feedstocks and Reagents

Corncob was obtained from Baodi feed mill, Tianjin. Before experiments, it was ground and sieved to a particle size of 0.25-0.425 mm, and then dried at 105 °C for 8 h. Glycerol (99%) was purchased from Tianjin fuyu fine chemical Co., Ltd.

Microwave Pretreatment of Corncob in Glycerol

The microwave pretreatment of corncob in glycerol was conducted in a homemade microwave reactor. The schematic diagram of microwave reactor was shown in Fig.1. The microwave reactor was operated at a frequency of 2.45 GHz with a maximum power of 750 W. A 40 ml open quartz vessel was used as the reactor zone. About 2 g corncob mixed with 16g glycerol was loaded in the quartz vessel. The reaction temperature was measured by a thermocouple. Nitrogen (99.9%) with a flow rate of 400 ml/min was used as purge gas. The microwave power and residence time were varied from 150 to 450 W and 1 min to 18 min, respectively. The corresponding temperature profiles were also shown in Fig.1. After microwave pretreatment, the pretreated corncobs were filtered off, washed thoroughly with deionized water and dried at 80 °C for 12 h under vacuum.

Characterization of raw and pretreated Corncobs

The elemental analysis of raw and pretreated corncobs was performed on a Vario EL (Elementar Analysensysteme, Hanau, Germany). The Fourier transform infrared Spectroscopy (FTIR) analysis was carried out on a Bruker TENSOR27 in order to characterize the main functional groups of raw and pretreated corncobs. KBr discs were prepared by mixing about 2 mg of sample with 200 mg of KBr. The resulting spectra were normalized to the highest peak in the fingerprint region between 2000 and 600 cm^{-1}. BET surface area, total pore volume and average pore diameter of raw and pretreated corncobs were measured by N^2 physisorption at 77 K using a Micromeritics ASAP 2010 instruments. The samples were degassed under vacuum at 378 K for 11 h before measurement. Thermogravimetric analyzer (STA409PC, Netzsch, Germany) coupled with FTIR (TENSOR27, Bruker, Germany) was used to investigate the weight loss (thermogravimetry, TG) and weight loss rate (differential thermogravimetry, DTG) of pretreated corncobs and formation of typical products at the same time. In the thermogravimetric experiment, the sample was heated from 40 to 800 °C at a constant heating rate of 15 K/min, then held at 800°C for 20 min, and a nitrogen gas flow of 40 mL/min was used as the purge gas. The DTG profiles of corncobs were deconvolved into five peaks corresponding to moisture, extractives, hemicellulose, cellulose and lignin using Gaussian fitting according to the procedure in literature[31-33]. The R^2 was 99.4%~99.8% in this study.

Fast Pyrolysis Experiments

Fast pyrolysis of raw corncob and pretreated corncobs was carried out in a semi-batch pyroprobe reactor (Pyroprobe 5200, CDS Analytical, U.S.A.) coupled to a gas chromatograph (7890A, Agilent Technologies, U.S.A.) with a mass spectrometer (5975C, Agilent Technologies, U.S.A.). In each typical run, a sample size of approximately 0.2-0.4 mg was weighed using a microbalance with an accuracy of 0.001 mg (XP6152, METTLERTOLEDO, Germany). The pyrolysis temperature, residence time and heating rate were fixed to 500 °C, 20 s and 10 K/ms, respectively. Helium (99.999%) was used as the carrier gas. HP-INNOwax capillary column (Agilent 19091N-133, 30 m × 0.25 mm, 0.25 μm film thickness) with a carrier gas flow velocity of 36.4 cm/s was used for the chromatographic separation of pyrolysis products. The compounds were identified by comparison with NIST mass spectral data library, and their response factors for GC quantification were determined using external standard method. All experimental runs were conducted three times and averaged to compensate experimental reproducibility.

Results and discussion

The mass yields and elemental analysis of pretreated corncobs

Table 1 shows the mass yields of pretreated corncobs. The yields of pretreated corncobs were strongly depended upon power and residence time of microwave pretreatment in glycerol. At the microwave power of 150 W, as the residence time increased from 1 min to 18 min, the yields of pretreated corncobs decreased gradually from 93.60 to 53.24%. At the residence time of 1 min, as the microwave power increased from 150 W to 450 W, the yields of pretreated corncobs dropped from 93.60 to 69.23%. Table 1 also shows the elemental analysis of raw corncob and pretreated corncobs. The carbon, hydrogen, oxygen and nitrogen content of raw corncob was 46.63, 6.62, 52.13 and 0.39%, respectively. As the residence time increased from 1 to 18 min, the carbon content of pretreated corncobs decreased from 45.74 to 42.73%, which was close to the carbon content of pure cellulose, whereas the oxygen content raised from 50.25 to 52.25%. It indicates that microwave pretreatment can selectively remove lignin fraction since lignin has the highest carbon content and lowest oxygen content[34]. The O/C and H/C ratios of pretreated corncobs were raised slightly while the residence time increased from 1 min to 18 min. The same variation trends were observed with increasing microwave power. It is worthy of note that the nitrogen species in biomass can also be selectively removed by microwave pretreatment. After corncob pretreated at 150 W for 18 min, the nitrogen remove rate can achieve 90.4%.

Table 2 shows the AAEM contents of raw corncob and pretreated corncobs. The Na, K, Ca and Mg contents of raw corncob were 218, 10390, 790 and 1601 mg/kg, respectively. The AAEM contents of corncobs dropped remarkably when applying microwave pretreatment. Moreover, a longer residence time or higher microwave power led to more removal of AAEM from corncob. In particular, Compared to alkali earth metals, alkali metals can be more effectively removed by microwave pretreatment. The lowest content of AAEM can be achieved after corncob pretreated at 150W for 18 min. The extractable ash (the soil remaining in biomass) can be removed by washing or extracting with glycerol. Most of the structural ash in biomass locates in the cross-linking structure of lignin[26]. Hence, the delignification of corncob during pretreatment can be accompanied by the removal of structural ash. After filtration, the AAEM removed from the solid corncob was redistributed into the liquid glycerol and lignin dissolved in glycerol.

The FTIR analysis of raw and pretreated corncobs

The structural changes of corncobs pretreated by microwave in glycerol with varying severity can be characterized by Fourier transform infrared spectroscopy (FTIR). Fig. 2 shows the FTIR spectra of raw corncob and pretreated corncobs. Some of the signals with noticeable differences in peak height and peak area are tagged and assigned to specific functional group as follows: (1) 1738-1734 cm^{-1} for unconjugated C=O stretch vibration in xylan (hemicellulose), (2) 1593-1609 and 15010-1530 cm^{-1} for aromatic skeletal vibration in lignin, (3) 1244-1268 cm^{-1} for C=C breathing of the aromatic ring and C–O stretching in lignin and xylan, (4) 896-910 cm^{-1} for C-H deformation in cellulose[35]. With increasing microwave power or residence time, the intensities of the signals (1), (2), (3) and (4) related to the functional groups in hemicellulsoe and lignin evidently decreased until they vanished. Simultaneously, the signal at 896-910 cm^{-1} assigned to C-H deformation in cellulose were heightened in peak height and peak area . These changes can be attributed to the selective removal of lignin and hemicellulose during microwave pretreatment to form cellulose-rich materials.

The variation in Compositions of raw and pretreated corncobs characterized by

TG/DTG analysis

Fig.3 shows the TG/DTG curves and their corresponding deconvolution signals of raw and pretreated corncobs. The overlapping temperature range for the devolatilization of extractives, hemicellulose, cellulose and lignin made it hard to obtain quantitative results from DTG curves. In order to separate the contributions of different components, each DTG profile was deconvolved into five peaks corresponding to the minimum number to obtain a good superposition of experimental and fitting profile using Gaussian fitting[32-33]. As shown in Fig.3, The signals centered at 88~92 °C, 268~303 °C, 305-325°C, 335-363 °C and 361-397 °C were assigned to the mass loss rates of moisture, extractives, hemicellulose, cellulose and lignin, respectively. The normalized integration values of these signals, indicating the weight loss fractions (the weight loss of specific component divided by the total weight loss) , were tabulated in Table 3 to provide an insight into the variation of the constituents affected by microwave pretreatment. The peak temperature of weight loss rates of different components and pyrolysis residue of corncobs was also given in Table 3.

As shown in Table 3, the weight loss fractions of corncobs were apparently influenced by applying microwave pretreatment. The weight loss fractions for moisture, extractives, hemicellulose, cellulose and lignin during pyrolysis of raw corncob were 1.04, 8.54, 40.86, 27.11% and 22.44%, respectively. The weight loss fraction of lignin declined monotonously with increasing residence time. The weight loss fraction of hemicellulose increased to the highest value first and then decreased when the residence time was greater than 5 min. With increasing microwave power, the variation trends were similar to that with increasing residence time. Considering the corresponding temperature profiles of microwave pretreatment, these results could be explained by that the removal of lignin was mainly ascribed to the non-thermal microwave assisted organosolvolysis and the release of hemicellulose was predominately attributed to the thermal effects, suggesting that the selective removal of lignin and, to a tunable degree, hemicellulose can be achieved by controlling microwave temperature. The weight loss fraction of cellulose was raised rapidly with increasing residence time and reached the highest value of 88.56% at the residence time of 18 min, implying that the lignin and hemicellulose can be almost entirely removed by controlling proper residence time. These results were in line with the FTIR analysis. The pyrolysis residue of corncobs decreased sharply when microwave pretreatment was performed. The decrease in pyrolysis residue could be mainly due to the reduced amount of ash and its catalytic activity. In addition, the removal of lignin also played some roles because the lignin generally produced more char than cellulose and hemicellulose during pyrolysis[36].

The particle size distributions and textural properties of raw and pretreated corncobs

Table 4 demonstrates the particle size distributions and textural properties of raw and pretreated corncobs. The mean particle size of corncob decreased obviously when applying microwave pretreatment. Due to the poor thermal conductivity of biomass, biomass with a small particle size is beneficial to increase the heating rates, suppress the secondary reaction and reduce the char yield in biomass fast pyrolysis[37]. The textural properties of raw and pretreated corncobs such as BET surface area, total pore volume and average pore diameter are also listed in Table 4. The BET surface area increased significantly when the microwave pretreatment was performed, and it further improved as increasing residence time. The average pore diameter exhibited an opposite variation trend. The total pore volume of corncob pretreated at 150 W for 10 min was larger than that of raw corncob. As residence time increased from 10 min to 18 min, the total pore volume decreased. These results indicate that the large pores in corncob were probably destroyed during pretreatment and small pores were formed. The increase in surface area also facilitates the heat transfer during biomass fast pyrolysis.

Yields of identified compounds from fast pyrolysis of raw and pretreated corncobs

The main identified compounds from fast pyrolysis of corncob were classified into six groups, including anhydrosugars, pyrans, furans, phenols, light oxygenates and others. The list of main identified compounds and their yields (based on pretreated corncob) are tabulated in Table 5. Compared to raw corncob, the yields of all identified compounds increased when microwave pretreatment was performed at 150W for 1 min. It can likely be attributed to the effective removal of extractable ash (AAEM), since the high concentrations of AAEM, especially potassium, can strongly catalyze the fragmentation of biomass to permanent gases. The yield of levoglucosan from fast pyrolysis of raw corncob was 0.2 %. The yield of levoglucosan increased significantly when applying microwave pretreatment. The yield of levoglucosan was raised drastically with further increase in residence time or microwave power. The highest yield of levoglucosan (38.0%) was achieved by fast pyrolysis of corncob pretreated at 150 W for 18min. It was about 189 times higher than the yield of levoglucosan from fast pyrolysis of raw corncob. The absolute yields of levoglucosan (based on raw corncob) as a function of the normalized total AAEM valencies were demonstrated in Fig.4. It should be noted that the absolute yield of levoglucocan increased remarkably from 9.6 to 20.2% as the residence time was raised from 5 min to 18min, although the normalized total AAEM valencies of them were very close. These results suggest that, in addition to the catalytic functions of AAEM, the interactions between cellulose and lignin and the heat/mass transfer limitation also play key roles in the formation of levoglucocan during biomass fast pyrolysis.

Pyrans and furans are generally considered as the products of acid-catalyzed carbohydrate dehydration. Their yields increased when applying microwave pretreatment. The pheonols, mainly derived from pyrolysis of lignin, decreased with increasing residence time or microwave power. These results were in accordance with the more removal of lignin with a longer residence time and higher microwave power from TG/DTG analysis. The yields of light oxygenates and cyclopentanes also declined with increasing residence or microwave power. It could be due to the removal of AAEM and its catalytic activity, thus resulting in the thermally-induced cleavage of glycosidic bonds of cellulose that yield levoglucocan. Acetic acid resulting from the decarbonylation of hemicellulose decreased drastically from 3.0 to 0.2% as the residence time increased from 1 min to 18 min. These results were in line with the variation trends in the hemicellulose content of corncob pretreated with varying residence time.

4. Conclusion

The possible factors affecting the yield of levoglucosan from biomass fast pyrolysis include: (1) the catalytic effects of AAEM (2) the interactions between cellulose and lignin, (3) the heat and mass transfer limitation caused by the poor thermal conductivity of biomass and its complex structure in which cellulose is surrounded by hemicellulose and lignin. Microwave pretreatment of corncob in glycerol can effectively remove the AAEM, lignin and hemicellulose fractions to form cellulose-rich materials, resulting in high yield of levoglucosan from fast pyrolysis of pretreated corncob. The levoglucosan yield from fast pyrolysis of corncob pretreated at 150 W for 18 min was about 189 times higher than that of raw corncob. These finding provides a green, efficient and cost effective way for overcoming biomass recalcitrance through delignification and demineralization to obtain high yield of levoglucosan. The recovery and utilization of lignin fragments and hemicellulose sugars dissolved in glycerol did not consider in this manuscript. We will try to convert them into chemicals or liquid fuel by metal catalyst in the next study.

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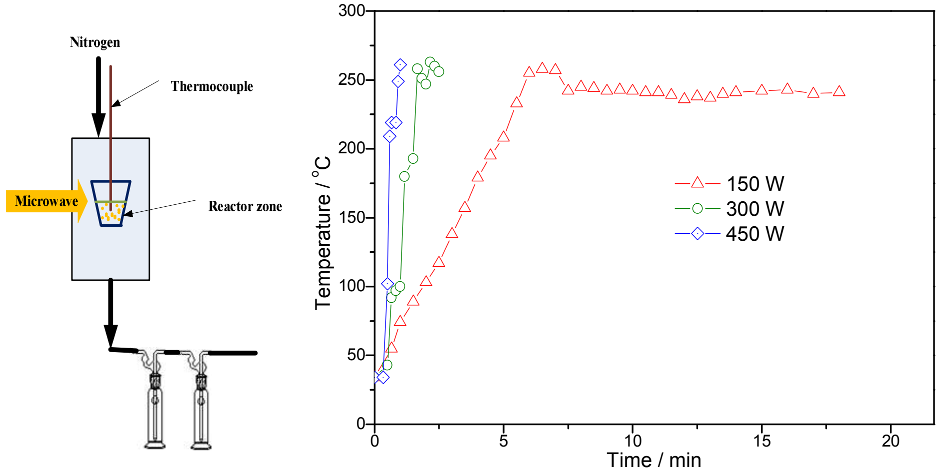

Fig.1. The schematic diagram of microwave reactor and the temperature profiles of microwave pretreatment of corncob in glycerol

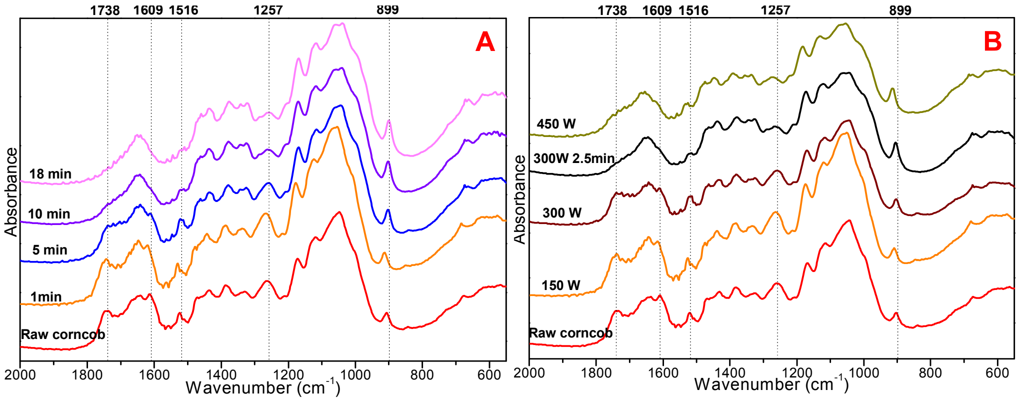

Fig. 2. FTIR spectra of raw and pretreated corncobs. A: Corncob pretreated at 150 W for varying residence time. B: Corncob pretreated for 1 min at varying microwave power

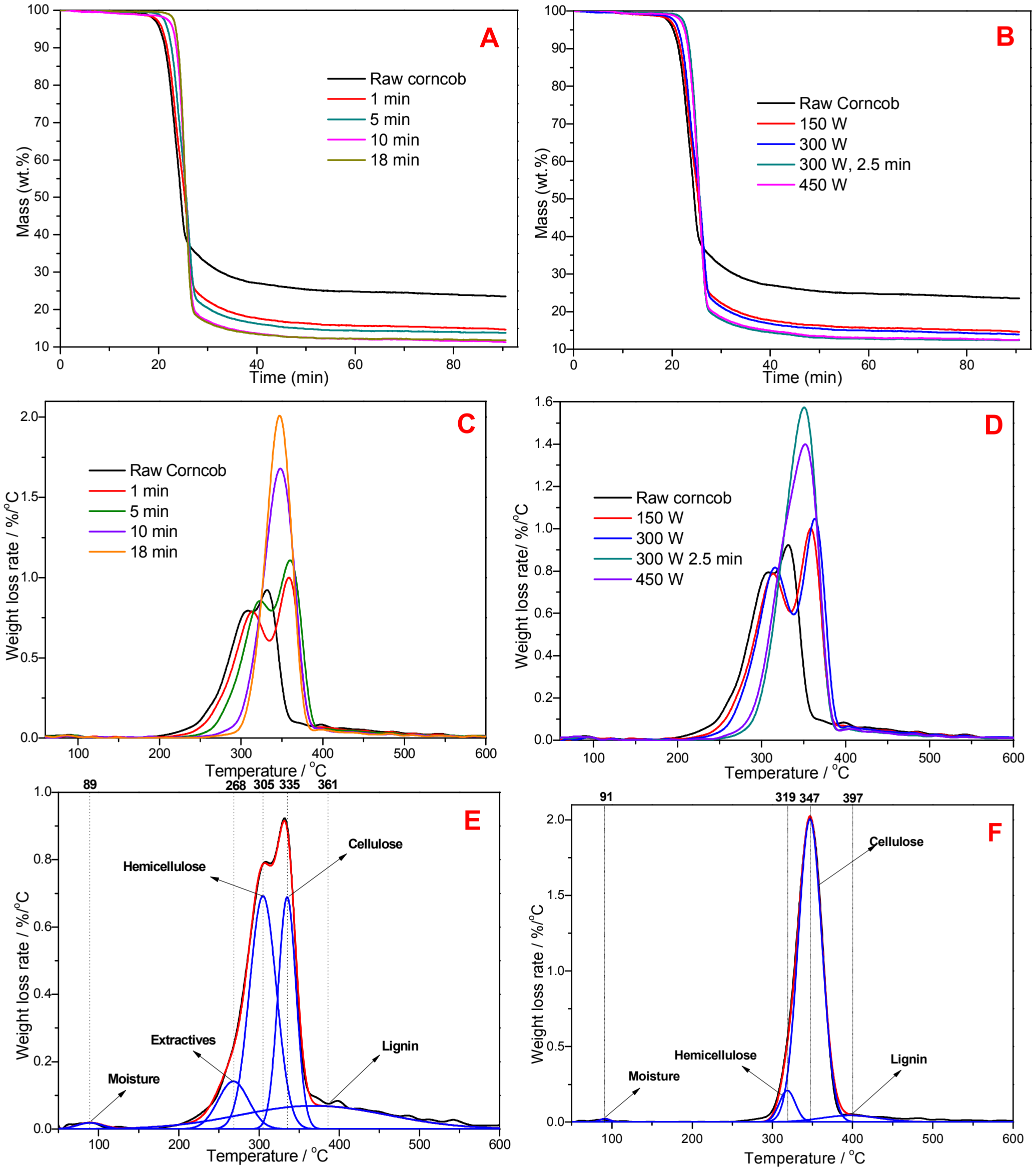

Fig. 3. TG/DTG curves and its corresponding deconvolution signals of raw corncob and pretreated corncobs. A,B: TG curves; C,D: DTG curves; E: Deconvolution signals from DTG curve of raw corncob; F: Deconvolution signals from DTG curve of corncob pretreated at 150 W for 18 min.

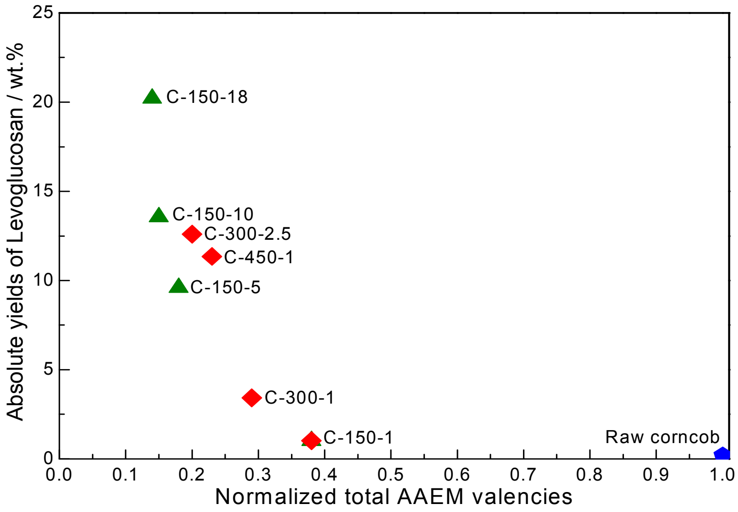

Fig. 4 The absolute yields of levoglucosan (based on raw corncob) from fast pyrolysis of raw and pretreated corncobs as a function of the normalized total AAEM valencies.

Table 1 The mass yield and elemental analysis of pretreated corncobs

Items		Microwave pretreatment conditions								
		Raw	Power: 150W				Residence time: 1 min			
		corncob	1min	5min	10min	18min	150W	300W	300W[a]	450W
Mass yield (%)		--	93.60	80.65	62.19	53.24	93.60	87.79	62.66	69.23
Elemental analysis /wt.%, daf[b]	C	46.63	45.74	44.04	43.09	42.73	45.74	44.99	43.40	43.51
	H	6.62	6.53	6.57	6.70	6.66	6.53	6.64	6.75	6.62
	O[c]	52.13	50.25	51.36	52.02	52.25	50.25	51.79	52.41	52.10
	N	0.39	0.29	0.18	0.08	0.07	0.29	0.26	0.08	0.10
	S	ND	ND	ND	ND	ND	ND	ND	ND	ND
N removal rate (%)		--	30.4	62.8	87.2	90.4	30.4	41.5	87.1	82.2
O/C		1.12	1.10	1.17	1.21	1.22	1.10	1.15	1.21	1.20
H/C		0.14	0.14	0.15	0.16	0.16	0.14	0.15	0.16	0.15

[a] Residence time: 2.5 min

[b] daf: Dry ash free basis

[c] The oxygen content was calculated by difference

Table 2 The alkali and alkali earth metals contents of raw and pretreated corncobs

Items	Microwave pretreatment conditions								
	Raw	Power: 150W				Residence time: 1 min			
	corncob	1 min	5 min	10min	18 min	150W	300W	300W[a]	450W
Na (mg/kg)	218	209	30	11	7	209	114	14	17
K (mg/kg)	10390	1364	123	128	112	1364	605	142	168
Mg (mg/kg)	790	671	351	253	285	671	500	449	496
Ca (mg/kg)	1601	1500	972	868	725	1500	1341	1025	1173
Normalized total AAEM valencies[b]	1.00	0.38	0.18	0.15	0.14	0.38	0.29	0.20	0.23

[a] Residence time: 2.5 min

[b] The normalized total AAEM valencies= (Na+K+2Ca+2Mg) of pretreated corncob/(Na+K+2Ca+2Mg) of raw corncob

Table 3 The weight loss fractions of raw and pretreated corncobs during pyrolysis

Microwave pretreatment conditions		Weight loss fractions (%)					Residue (wt.%)
		Moisture	Extractives	hemicellulose	cellulose	lignin	
Raw corncob		1.04(89)[b]	8.54(268)	40.86(305)	27.11(335)	22.44(361)	23.54
	1 min	0.74(89)	6.35(276)	41.58(314)	31.89(359)	19.44(373)	14.64
Power:	5 min	0.82(91)	6.12(288)	42.76(323)	37.33(361)	12.97(381)	13.74
150 W	10 min	0.51(91)	--	18.95(313)	70.75(349)	9.79(374)	11.32
	18 min	0.43(91)	--	6.26(319)	88.56(347)	4.74(397)	11.76
	150 W	0.74(89)	6.35(276)	41.58(314)	31.89(359)	19.44(373)	14.64
Residence time:	300 W	0.32(92)	3.46(273)	46.07(315)	36.65(363)	15.50(380)	13.93
1 min	300 W [a]	0.27(88)	3.72(303)	23.25(325)	64.16(352)	8.60(367)	12.35
	450 W	0.54(88)	3.38(290)	37.65(325)	48.95(355)	9.49(378)	12.57

[a] Residence time: 2.5 min

[b] The value in parentheses represents the peak temperature of its corresponding deconvolution signal.

Table 4 The particle size distributions and textural properties of raw and pretreated corncobs.

Item			Mean particle Size [a] (µm)	Particle size distribution (µm)			Textural properties		
				d(0.1) [b]	d(0.5)	d(0.9)	S_{BET} m^2/g	V_{Total} $10^{-3}cm^3/g$	$D_{pore\ size}$ nm
Raw corncob			541.35	254.90	549.03	834.87	0.87	6.33	29.30
Pretreatment conditions	150W	10min	442.09	74.94	444.60	786.12	2.48	9.74	15.71
		18min	361.64	48.24	343.04	732.76	3.37	6.53	7.75

[a] Volume-weighted mean particle diameter

[b] The d(0.1), d(0.5) and d(0.9) values indicate that 10%, 50% and 90% of the particles measured were less than or equal to the size stated

Table 5 Main compounds identified in fast pyrolysis of raw and pretreated corncobs and their yields (based on pretreated corncobs)

Compound	Raw corncob	Microwave pretreatment conditions							
		Power: 150W				Residence time: 1 min			
		1min	5min	10min	18min	150W	300W	300W[a]	450W
Anhydrosugars									
Levoglucosan	0.2	1.1	11.9	21.8	38.0	1.1	3.9	20.1	16.4
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	0.2	0.4	0.5	0.5	0.4	0.4	0.4	0.4	0.5
Pyrans									
2H-Pyran-2,6(3H)-dione	0.1	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.4
3,5-dihydroxy-2-methyl-4H-Pyran-4-one	0.1	0.2	0.4	0.4	0.4	0.2	0.1	0.3	0.4
Furans									
Furfural	0.2	0.3	0.5	0.5	0.5	0.3	0.3	0.5	0.5
2-Furanmethanol	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1
2(5H)-Furanone	0.1	0.2	0.1	0.0	0.1	0.2	0.1	0.0	0.1
5-Hydroxymethylfurfural	0.1	0.2	0.5	0.5	0.6	0.2	0.2	0.5	0.5
Phenols									
2-methoxy-Phenol	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.0
Phenol	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.0	0.0
2-Methoxy-4-vinylphenol	0.3	0.4	0.4	0.1	0.0	0.4	0.3	0.1	0.2
2,6-dimethoxy-Phenol	0.1	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Vanillin	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.0
2,3-dihydro-Benzofuran	0.4	0.5	0.4	0.1	0.0	0.5	0.3	0.1	0.2
Light Oxygenates									
2,3-Butanedione	0.2	0.3	0.2	0.1	0.0	0.3	0.1	0.1	0.1
1-hydroxy-2-Propanone	1.2	1.3	0.7	0.5	0.4	1.3	0.9	0.5	0.6
hydroxy-Acetaldehyde	1.2	2.4	2.3	2.0	1.8	2.4	1.7	1.9	2.1
1-Hydroxy-2-butanone	0.3	0.2	0.4	0.1	0.1	0.2	0.2	0.1	0.1
Acetic acid	2.6	3.0	2.0	0.3	0.2	3.0	1.7	0.3	0.7
Formic acid	0.5	0.7	0.5	0.3	0.2	0.7	0.5	0.3	0.3
Propanoic acid	0.2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1
Others									
2-Cyclopenten-1-one	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.1
1,2-Cyclopentanedione	0.2	0.3	0.1	0.1	0.1	0.3	0.2	0.1	0.1
2-Cyclohexen-1-ol	0.0	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1
2-hydroxy-3-methyl-2-Cyclopenten-1-one	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

[a] Residence time: 2.5 min

Table of contents entry

Microwave pretreatment can selectively remove AAEM, lignin and hemicellulose fractions for enhancing levoglucosan yield from fast pyrolysis of pretreated corncob