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Conversion of Pretreated Biomass into Levulinic Acid via Continuous Extraction at Atmosphere Pressure

Ming-hui Fan, Li-feng Yan*

Department of Chemical Physics and Anhui Province Key Laboratory of Biomass Clean Energy, University of Science and Technology of China, Hefei 230026, China

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Conversion of biomass to chemicals or fuels under mild condition is still a challenge. As a platform molecule for chemicals and fuels, levulinic acid (LA) has been prepared by liquefaction of biomass at high pressure. In order to carry out the conversion from wheat straw to LA at atmosphere pressure, continuous extraction of the reactive system by an organic solvent with a higher density than that of water was utilized for degradation of pretreated biomass. Yields of LA were measured by means of gas chromatography-mass spectrometry and nuclear magnetic resonance. The results revealed that a maximum yield of 30.66% of LA can be obtained from wheat straw. In addition, the effects of biomass pretreated conditions on the LA conversion have been studied. The study provides a new route to convert biomass to valuable chemicals at atmosphere pressure.

Key words: Biomass, Pretreatment, Continuous extraction, Levulinic acid, Atmosphere pressure

I. INTRODUCTION

The crisis of fossil resource makes a huge requirement for conversion of biomass into energy and value-added chemicals [1]. Ethanol, *n*-butanol, sorbitol, dimethylfuran, methyl-furfural (MF), 5-hydroxy-methylfurfural (HMF), levulinic acid (LA) are the most reported chemicals from the conversion of biomass [2]. Recently, Horvath *et al.* suggested that γ -valerolactone (GVL) may be used as a next generation fuel instead of gasoline, and LA is the feedstock for GVL synthesis [3]. So many attentions have been paid to the conversion of biomass to LA [4, 5].

Chang *et al.* reported a method to degrade wheat straw for levulinic acid at 209.3 °C in a pressurized reactor with the maximum yield of 19.86% [6]. Yan *et al.* developed a method of LA production from bagasse and paddy straw by liquefaction in the presence of hydrochloride acid in a cylindrical pressurized reactor, and the maximum yield of LA can arrive at 23.7% [7]. However, it is still a difficult task to convert biomass to LA under atmosphere pressure.

The mechanism of the conversion of biomass to LA is the hydrolysis of cellulose, one of the major composite of biomass (Scheme 1). The studies on hydrolysis of cellulose or glucose to LA have been carried out for many years. Both liquid and solid acid can work as

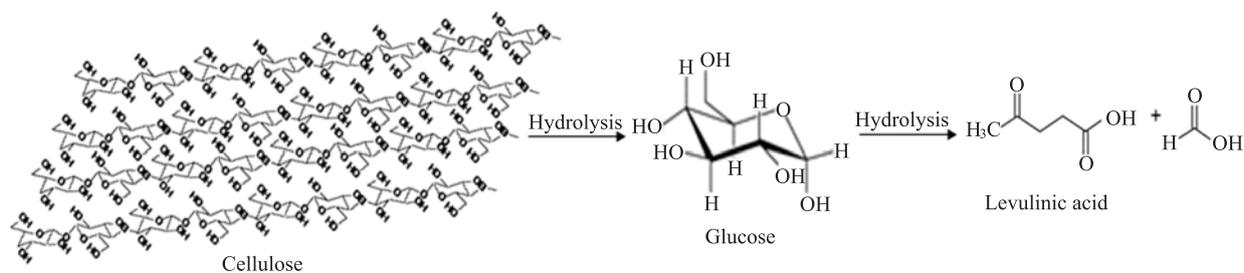
catalysts for hydrolysis of cellulose [8, 9].

Recently, a standard apparatus for continuous extraction of aqueous solution with a solvent of greater density than water has been employed for direct and high-yield conversion of cellulose into 5-(chloromethyl)furfural [10]. In addition, small quantities of LA, HMF, and 2-(2-hydroxyacetyl)furan are also formed during the process. The conversion was carried out under atmosphere press, which makes it possible to operate for continuously processing. However, there is still no report on conversion of biomass by this kind of method.

It is well-known that biomass is a compact composite of cellulose, hemi-cellulose, and lignin. Pretreatment is usually required for conversion of biomass to chemicals for it could loose the complex structure. Organosolvent delignification is an efficient method for the pretreatment [11]. Among many organosolvents, formic acid has an interesting feature of effective delignification and gets good pulp yield in the presence of catalyst, and the three dominant components in wheat straw can be effectively separated by formic acid [12]. During the process, nearly all of the lignin and most hemi-celluloses are separated from cellulose fibers, leaving the surface of fibers more open and porous. The pulping process can be carried out at atmospheric pressure and mild conditions, and the acid can be easily recovered by distillation.

Here, we try to develop a method to convert biomass to LA via a continuous extraction at atmosphere pressure. To improve the efficiency of conversion, biomass was pretreated by organic acid at first to separate hemi-cellulose and lignin from biomass. After the organic acid treatment, bleaching was carried out using 1.8%

* Author to whom correspondence should be addressed. E-mail: lfyang@ustc.edu.cn



Scheme 1 The reactive route of levulinic acid formation from cellulose by hydrolysis.

TABLE I Effect of pretreated conditions on yield of isolated cellulose, water-soluble sugars and acid insoluble lignin of wheat straw. Y_1 : yield of acid insoluble lignin, Y_2 : yield of residue, Y_3 : yield of water-soluble sugars, Y_4 : yield of cellulose, X : residual lignin in the cellulose.

Sample	$T/^\circ\text{C}$	Time/h	$Y_1/\%$	$Y_2/\%$	Sample	$T/^\circ\text{C}$	Time/h	$Y_3/\%$	$Y_4/\%$	$X/\%$
A1	65	1.5	14.33	43.95	B1	85	4	6.62	36.06	3.79
A2	65	1.5	14.17	44.87	B2	85	4	7.54	36.91	3.99
A3	65	1.5	9.63	64.74	B3	85	4	6.69	51.87	5.87
A4	65	1.5	9.70	63.67	B4	85	4	4.14	59.44	9.62
A5	65	1.5	7.64	81.25	B5	85	4	5.95	70.95	10.82
A6	65	0.5	12.58	49.11	B6	85	4	6.67	40.92	5.88
A7	65	1.0	13.39	46.34	B7	85	4	6.51	37.83	4.62
A8	65	2.0	15.40	39.56	B8	85	4	6.70	32.10	2.00
A9	60	1.5	12.58	49.70	B9	85	4	6.27	42.86	4.31
A10	70	1.5	14.02	43.16	B10	85	4	6.55	35.62	3.75
A11	65	0.5	9.27	68.74	B11	85	4	3.62	64.31	11.06
A12	140, 65	3, 1.5	6.91	42.05	B12	85	4	4.04	31.44	2.49
A13	65	1.0	11.20	50.05	B13	85	4	5.25	41.85	7.71

H_2O_2 at 85°C at $\text{pH}=10.0$ for 4 h to dissolve the remaining hemi-celluloses and lignin. At the same time, the isolated lignin and derivatives of hemi-cellulose were also collected as products to the full application of biomass feedstock.

II. EXPERIMENTS

A. Materials

Wheat straw was collected from a farm field in the east of China. The chemical compositions (mass ratio) of the straw are shown as: cellulose 38.9%, hemi-celluloses 38.2%, lignin 17.2%, ash 2.1%, and wax 2% on a dry weight basis. It was cut into small pieces and crushed to pass a 0.3 mm size screen. All the chemicals with AR purity except especially indicated were purchased from Sigma Chemical Co., and used as received. Milli-Q water ($18.2\text{ M}\Omega$) was prepared using a Milli-Q synthesis system (Millipore, USA).

B. Pretreatment of biomass by organic acids

Prior to organosolvent delignification, the dried powder was extracted with ethanol-toluene (1:2, volume ratio) in a Soxhlet extractor at 90°C for 4 h, and then the residue was dried in an oven at 55°C for over 16 h to obtain powder of dewax straw. The delignification process using organic acids were carried out under different reaction conditions, and thirteen samples were prepared. Table I lists the pretreated conditions for the 13 samples with yields of isolated cellulose, lignin, and degraded sugars from hemi-cellulose. The pretreated conditions for straw powder include 98% formic acid (A1), 88% formic acid (A2), formic acid (98%)-acetic acid (2:1, volume ratio) in the presence of 0.1% HCl as catalyst at 65°C for 1.5 h (A3), 88% formic acid in the presence of 0.1% HCl as catalyst at 65°C for 1.5 h (A4), formic acid (88%)-acetic acid (2:1,v/v) in the absence of HCl at 65°C for 1.5 h (A5), formic acid (88%) in the presence of 0.1% HCl as catalyst at 65°C for 0.5 h (A6), 1 h (A7), and 2 h (A8), formic acid (88%) in the presence of 0.1% HCl as catalyst for 1.5 h at 60°C (A9) and 70°C (A10), formic acid (88%) in the absence of

HCl as catalyst at 65 °C for 0.5 h (A11), and with glycerol at 140 °C for 3 h following treated with formic acid (88%) in the presence of 0.1% HCl as catalyst at 65 °C for 1.5 h (A12). Raw straw powder without dewax was used as a control (A13). In addition, the residues after delignification were washed with acetic acid and ethanol subsequently and dried in oven at 55 °C overnight. The hydrogen peroxide bleaching of the dried residues was carried out in the presence of 1.8% H₂O₂ at pH=10.0 at 85 °C for 4 h, and the samples were labeled as B1–B13.

C. Isolation of acid-insoluble lignin

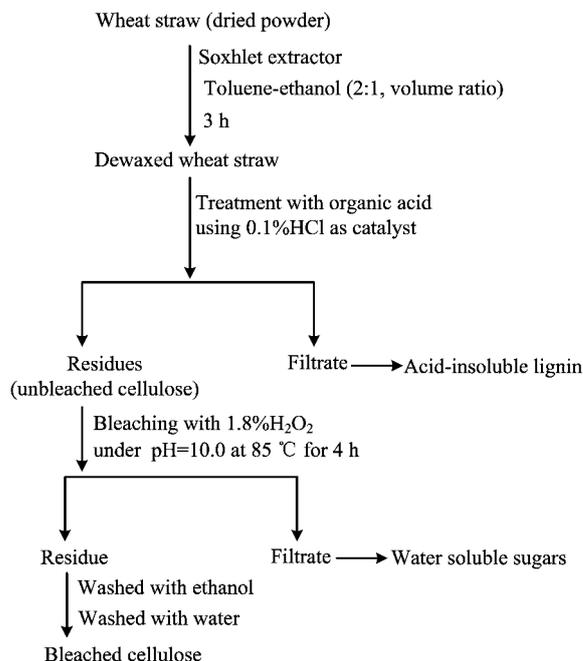
The organic pulping liquor was separated from the residue by filtration, and organic acid was distilled under reduced pressure for recovery. Then deionized water was added to precipitate the acid-insoluble lignin, and the precipitations were washed carefully with water and dried in oven at 60 °C overnight to obtain tawny powder.

D. Isolation of water-soluble sugars

The filtrate separated from the bleaching procedure was concentrated at normal pressure at 80 °C, and then the condensed golden yellow liquor was subsequently lyophilized. The obtained residue was light yellow and water-soluble sugars, which are mainly from the degradation of hemi-celluloses. The whole separation process can be seen in Scheme 2.

E. Conversion of cellulose to Levulinic acid

The degradation of the isolated cellulose to LA was carried out in an apparatus for continuous extraction using 1,2-dichloroethane as a solvent of higher density than that of water to extract LA from the aqueous reaction system. In brief, isolated cellulose (2.05 g) was dispersed in an aqueous solution of lithium chloride in concentrated hydrochloric acid. The mixture was added into a continuous extraction chamber. A boiling flask containing 1,2-dichloroethane (350 mL) was attached to the extraction chamber and the solvent was heated to reflux. Next the mixture was subjected to continuous extraction for 18 h at 65 °C under continuous stirring. Then, further lithium chloride in concentrated hydrochloric acid and fresh 1,2-dichloroethane (150 mL) was introduced to the extraction chamber to react for another 12 h. The combined extracts were first distilled at reduced pressure to recovery the solvent, and then they were filtered. The filtered liquor was heated at 60 °C at atmospheric pressure for 4 h in order to remove the remaining organic solvent and lithium chloride. The ultimate obtained product is a kind of light yellow liquor and labeled as the relative experimental



Scheme 2 Pretreatment of wheat straw for full utilization of cellulose, hemi-cellulose, and lignin.

group. We used five different isolated cellulose samples (B2, A6, B6, B11, and B13) as feedstock for degradation, and microcrystalline cellulose was used as a control for comparison.

F. Characteristic of samples

The lignin content in the cellulose samples was determined using a UV-Vis Spectrophotometry (UV-2550, Shimadzu) according to an US Patent [13]. Fourier transforms infrared (FT-IR) spectra of the cellulose samples were recorded on a Bruker vector-2 spectrophotometer using KBr disc as carrier. A Shimadzu SEM (Superscan SSX-550, Japan) was used for the space resolved analysis, and the apparatus is equipped with an energy dispersive X-ray spectrometer (EDX) to detect the major elements in the sample. ¹H NMR spectra were recorded on a Bruker AV 400 spectrometer. Elementary analysis was carried out on a VAR10 ELIII. The samples were analyzed by GC/MS (Trace2000-MS, Finnigan, USA). Helium was used as the carrier gas, and the gas flow was held constant at 1 mL/min. The injector temperature was 280 °C. The temperature program was 3 min at 40 °C, then at 4 °C/min to 280 °C, and 10 min at 280 °C.

III. RESULTS AND DISCUSSION

Scheme 2 shows the pretreatment process of biomass for the separation of hemi-cellulose and lignin from biomass. In brief, wheat straw was extracted by

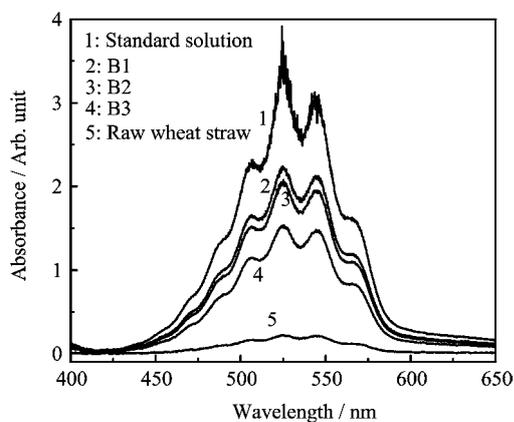


FIG. 1 UV-Vis absorption spectra of acidic KMnO_4 aqueous solution before and after reaction with cellulose samples B1, B2, B3, and untreated wheat straw.

toluene-ethanol (2:1, volume ratio) for dewax. Then a delignification step was carried out by using organic acid, and the residue was continuously bleached by hydrogen peroxide in the presence of alkali, and the isolated cellulose was obtained. The acid filtrate was evaporated to recycle acid liquor, and then water was added to precipitate the acid insoluble lignin. Water soluble sugars degraded from hemi-cellulose can be collected by freeze-drying of the alkali liquor after the bleaching procedure. Both acid insoluble lignin and water soluble sugars are by-products. Table I summarizes the effect of pretreated conditions on the yield of isolated cellulose, lignin and sugars from wheat straw. The content of residual lignin was calculated by the Kappa values obtained by UV-Vis measurements. It can be found that factors such as temperature, catalyst, the kinds of organic acid, dewax procedure significantly affect the ultimate yield of cellulose, acid-insoluble lignin and water-soluble sugars. Harsh conditions will not only give pure cellulose but also will significantly decrease the rate of cellulose recovery. The obtained acid-insoluble lignin (Klason lignin) was tawny powder, and its yield depends on the usage of catalyst. But the effect should not be so significant if acid treatment time is short (A6, A11). Generally, long formic acid treatment time in the presence of HCl as catalyst will bring higher Klason lignin recovery. The water-soluble sugars are the degradation products mainly from hemi-celluloses which need further research.

Kappa value is an important parameter that is used to indicate the lignin content indirectly. Figure 1 shows the UV-Vis absorption spectra of acidic KMnO_4 aqueous solution of samples B1, B2, B3 and the untreated wheat straw. The residual lignin in the isolated cellulose was calculated according to the method in Ref.[13]. As shown in Table I, the purity of the ultimate cellulose depends on the conditions of pretreatment. The content of residual lignin changes from 4.31% to 3.75% when reaction temperature increased from 60 °C to 70 °C,

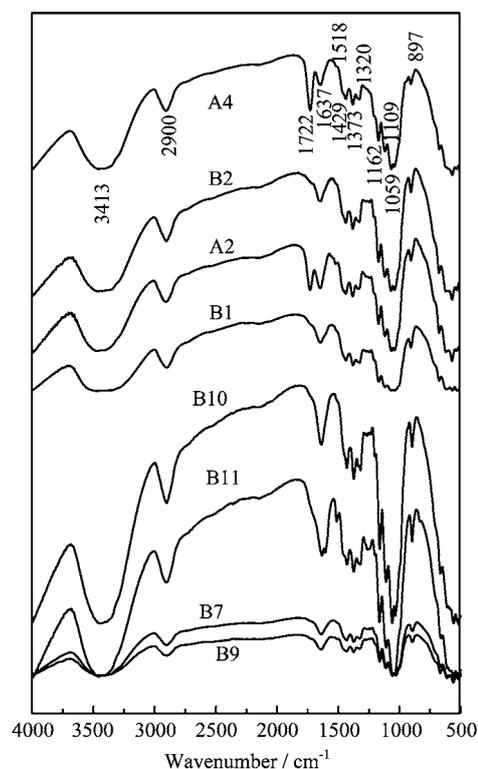


FIG. 2 FT-IR spectra of samples A4, B2, A2, B1, B10, B11, B7, and B9.

and it changes from 5.88% to 2.00% if the acid treatment time was extended from 0.5 h to 2 h. Catalyst always plays an important role in chemical reactions and with its help the residual lignin content decreased dramatically from 9.62% (B4) to 3.99% (B2). Sun *et al.* suggested that acetic acid-formic acid- H_2O (60/30/10, volume ratio) is an effectively system for delignification of wheat straw [14]. However, the results of B2 and B3 in Table I reveal a better delignification result when only formic acid was utilized. The main component of wax is rich of Si-O groups and it makes up a wall-like protect system of straw, and dewax will make lignin to be removed easily. The results of B7 and B13 show the effect of dewax on the delignification.

FT-IR spectroscopy has been widely used to obtain direct information on chemical changes of straw as a result of various chemical treatments [14]. Figure 2 shows the FT-IR spectra of the samples A2, A4, B1, B2, B7, B9, B10, and B11. The peak at 3413 cm^{-1} is contributed to the stretching of -OH groups while at 2900 cm^{-1} is assigned to the C-H stretching. The band at 1637 cm^{-1} corresponds to the bending mode of residue water. Each spectrum gives a peak at 1429 cm^{-1} , which is attributed to the CH_2 bending, and the one at 1373 cm^{-1} is due to the O-H bending. The absorbance at 1320 cm^{-1} arises from the C-C and C-O skeletal vibration. The absorption band at 1162 cm^{-1} is related to the C-O anti-symmetric

bridge stretching. The peak at 1059 cm^{-1} is originated from the C–O–C pyranose ring skeletal vibration. The sharp peak at 897 cm^{-1} represents the C1 group frequency or ring frequency and is the characteristic of β -glycosidic linkages between the sugar units. For B11, the peak at 1518 cm^{-1} is attributed to the presence of the lignin-associated absorbance, and the curves of A4 also show a minor shoulder at 1518 cm^{-1} , which proves that there will be considerable lignin remaining in the product in the absence of HCl as catalyst. As the reaction time for formic acid treatment increased from 0.5 h (A11) to 1.5 h (A4), the intensity of absorption peak of lignin decreased, indicating more reaction time could result in less lignin residual. The peaks at 1429, 1373, 1320, 1162, 1059, and 899 cm^{-1} are associated with the typical values of cellulose. Clearly, adding HCl as catalyst in the formic acid treatment procedure can remove near all the lignin, indicated by the disappearance of peaks at 1518 cm^{-1} (B2, B1, B10). For B7 and B9, both the curves have a weak peak at 1518 cm^{-1} , and it reveals that the short reaction time (B7, 1 h) and low temperature (B9, $60\text{ }^\circ\text{C}$) result in a small amount of lignin residual. In comparison with the spectra of unbleached (A2) and bleached (B2) cellulose samples, the peak at 1722 cm^{-1} in A2 curve is characteristic of residual hemi-celluloses. In addition, a small shoulder at 1518 cm^{-1} corresponds to the residual lignin. After alkaline peroxide treatment, the spectra of B2 do not show the band at 1722 cm^{-1} and the shoulder at 1518 cm^{-1} disappears. Also, the curve of A4 has a sharper absorbance at 1722 cm^{-1} than B2 does, indicating the adding of catalyst in the formic acid treatment procedure can also help to remove hemi-cellulose. The results reveal that most of the residual lignin and hemi-celluloses can be removed.

Figure 3 shows the FT-IR spectra of isolated acid-insoluble lignin and water-soluble sugars degraded from hemi-cellulose. The peak at 1601 cm^{-1} is originated from the stretching of conjugated carboxide while the absorbance at 1458 cm^{-1} is related to the skeletal vibration of aromatic ring, and the peaks at 1232 and 1121 cm^{-1} are due to the stretching of C–O stretching. In addition, the sharp peak at 1034 cm^{-1} is related to the bending vibration of C–O–C, and all the mentioned peaks correspond to the structure of lignin [15]. For the curve of water-soluble sugars, the absorption at 2822 cm^{-1} is the C–H vibration of alkyl group and the peak from 770 cm^{-1} to 400 cm^{-1} is due to the C–C stretch from the ring of sugars. The absorbance at 1417 cm^{-1} is attributed to the CH_2 bending and the peak at 1361 cm^{-1} is due to the O–H bending while the peak at 1151 cm^{-1} is due to the presence of arabinose residue and the peak at 1039 cm^{-1} is the signal of linkage between –OH and ether group in the sugar units. The sharp peaks of 1151 and 1039 cm^{-1} are characteristics of xylan, and the shoulder at 926 cm^{-1} is the C–H bend of β -D-xylose. SEM has also been widely used to study the structural change of biomass during

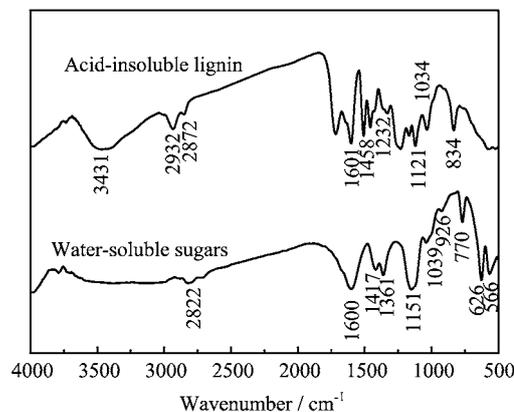


FIG. 3 FT-IR spectra of acid-insoluble lignin and water-soluble sugars.

pretreatment. Figure 4 shows the SEM micrographs of the isolated cellulose samples after different treatments. From Fig.4 (a) and (b), it can be found that the using of HCl as catalyst is helpful to obtain cellulose with high purity. Figure 4 (c) and (d) show a similar result for samples B3 and B5. The results reveal that the capacity of delignification of formic acid is better than the mixed acid (formic acid/acetic acid). Figure 4(a) gives fine fluffy cellulose fibers while the fiber is thick with some aggregates in Fig.4(b), and it is consistent with the residual lignin content of B2 (3.99%) and B3 (5.87%). Figure 4 (e)–(g) show micrographs of cellulose samples that are treated after different times, and it revealed that the longer time for formic acid treatment is helpful for removal of lignin and hemi-celluloses.

The isolated celluloses are the feedstock for conversion to chemicals by a continuous extraction. Figure 5(a) shows the GC chromatogram pure levulinic acid in 1,2-dichloroethane, and the retention time of LA is 10.58 min. Figure 5(b) shows the GC chromatogram of the products after the isolated cellulose was degraded in the continuous extractor, and the retention time at 10.6 min represents the formation of LA. Figure 6 shows a typical ^1H NMR spectrum of the product, and the peak at 2.16 ppm is assigned to the protons of methyl (CH_3), and the peaks at 2.52 ppm are the signal of methylene adjacent to carboxylic acid carbon (–COOH) while protons of another methylene shows signals at 2.82 ppm [7]. The peak at 4.71 ppm is the signal of solvent D_2O . The results reveal that the main product is LA, and it is in high yield.

Mascal *et al.* reported that the major product is 5-(chloromethyl)furfural (CMF) using microcrystalline cellulose as feedstock by a similar process. Their operated temperature is $65\text{ }^\circ\text{C}$ and the extracting agent (1,2-dichloroethane) is replaced every 6 h [10]. The temperature is near the boiling point of the azeotrope of 1,2-dichloroethane and water ($71.9\text{ }^\circ\text{C}$), and it is not easy to control. In this work the reaction temperature is $45\text{ }^\circ\text{C}$ and replacement of 1, 2-dichloroethane. How-

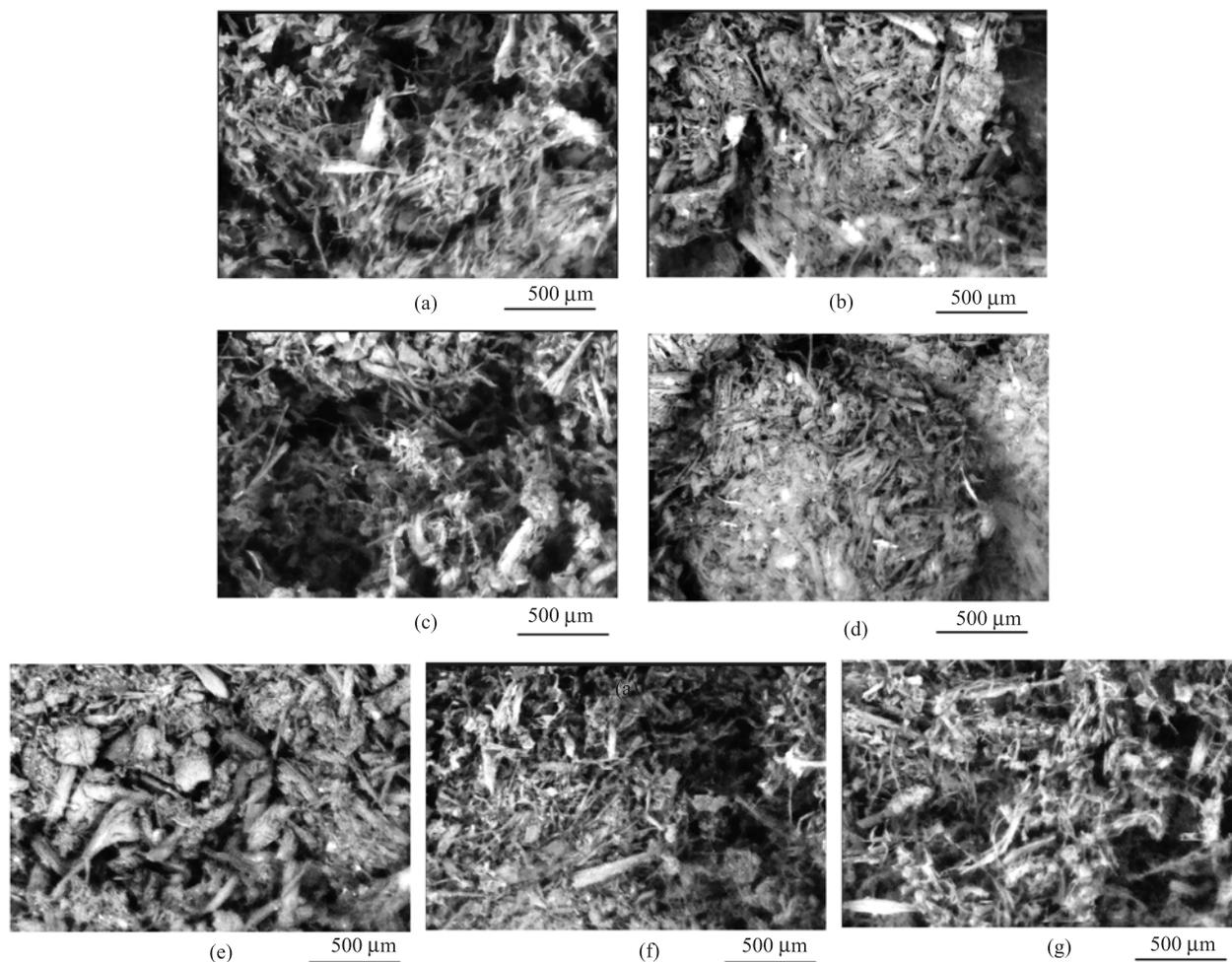


FIG. 4 SEM photograph of cellulose samples of wheat straw after extraction of lignin and hemicelluloses. (a) B2, (b) B4, (c) B3, (d) B5, (e) B6, (f) B7, (g) B8.

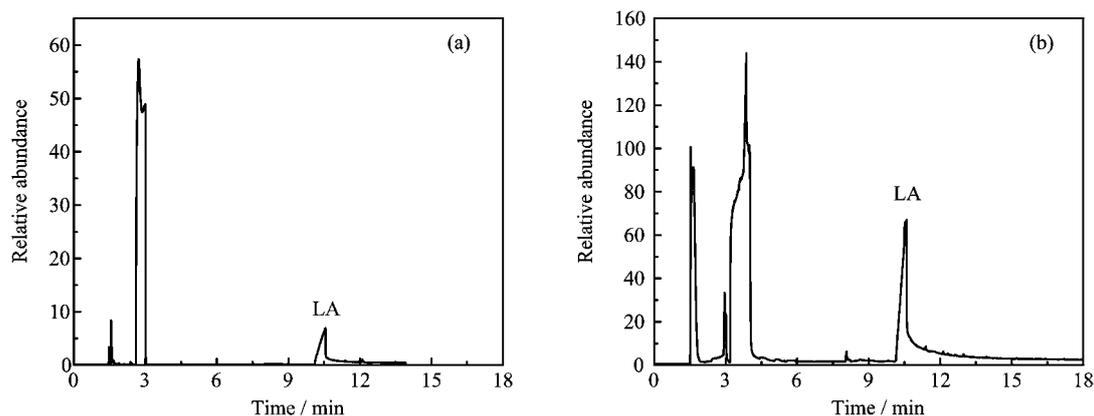


FIG. 5 GC chromatogram of (a) pure levulinic acid in 1,2-dichloroethane and (b) the products obtained by continuous extraction of pretreated biomass.

ever, the major product is LA but CMF.

Girisuta *et al.* has proved that the conversion of cellulose to LA is a complex multi-step process [8]. In brief, the chains of cellulose were broken down to glu-

cose at first. Then, the glucose decomposed to HMF, and finally HMF hydrolyzed to LA and formic acid. As the reaction system we used has a lot of water carried by concentrated hydrochloric acid, and it decomposes

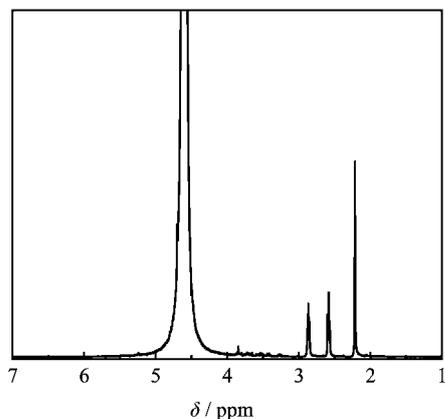


FIG. 6 Representative ^1H NMR of levulinic acid produced from cellulose extracted from wheat straw, solvent D_2O .

HMF and result in the formation of LA. The LA yields of various pretreated straw and microcrystalline cellulose are 13.82%B2, 20.06%A6, 15.27%B6, 30.66%B11, 18.38%B13, and 34%microcrystalline cellulose, which reveals that the residual lignin content has no significant relevance to the yield of LA and the content of cellulose seems to play a vital role. Though the lignin content of B11 is much higher than B2, the former gives the highest yield of LA. The maximum yield of LA is 30.66% based on wheat straw for sample B11.

IV. CONCLUSION

Pretreatment of wheat straw was carried out by organosolvent delignification. The results reveal that formic acid can remove most of the lignin in the presence of HCl as catalyst, and hemi-cellulose can also be removed after bleaching. After pretreatment, high pure celluloses were obtained and they work as feedstock for chemical conversion. Using a continuous extraction process, the isolated cellulose can be degraded into LA by hydrolysis at $45\text{ }^\circ\text{C}$ with 1,2-dichloroethane as the organic solvent with a higher density than that of water.

The process was operated at atmosphere pressure and low temperature, and it is easy to scale up for industrial application. The maximum yield of LA is 30.66% based on wheat straw.

V. ACKNOWLEDGMENTS

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